

USSR Academy of Sciences

International Committee for Solvent Extraction
Chemistry and Technology

ISEC '88

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**Moscow, USSR
July 18-24, 1988**

**Conference Papers
Volume IV**

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Vernadsky Institute of
Geochemistry and Analytical
Chemistry of the USSR
Academy of Sciences, 1988

**ANALYTICAL
CHEMISTRY**

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Efficiency of liquid-liquid extraction as a method of separation and preconcentration - selectivity and extraction percentage - is determined by the selection of the extractant and the extraction system as a whole.

In principle there can not be universal, i.e. multipurpose extractants or systems. Therefore discussing the properties of extractants, it is reasonable to consider them taking into account what type of compounds they extract. The extractable compounds can be divided into two large groups: neutral species (coordinatively unsolvated compounds, metal chelates and coordinatively solvated or mixed compounds) and ion pairs (coordinatively unsolvated ion pairs, mineral and complex metal-containing acids) [1]. Besides, different compounds for some reason not included into the above groups may form a separate one.

Metal chelates have been well studied and widely used. Chelate-forming extractants containing a mobile proton are commonly used in analytical chemistry and technology.

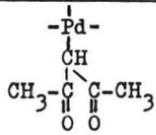
The following notions were formulated just due to the generalization of the experimental data obtained in the study of this class of extractants. These were: the functional group (FG) as a group of heteroatoms responsible for the analytical effect of the reaction, and electron-active group (EAG) or substituent affecting the FG properties. It is worth emphasizing that up to now the notion of the extraction reagent assumes the possibility to distinguish independent FG and EAG in the extractant organic matrix. The study of the extraction behavior of metals in systems with chelate-forming agents has made it possible for the first time to formulate the theoretical dependencies of the extraction constants on the parameters of metal under extraction, extractant and solvent. This in its turn provoked the discussion of the extraction power (EP) of the extractants.

Among the offered extractants we shall discuss the following ones. The reagents $[(\text{PhO})_2\text{PX}]_2\text{NH}$ ($\text{X}=\text{O}, \text{S}$) are shown in [2] to act as effective chelate-forming extractants permitting the rare-earth and actinide elements or Ag^+ , Hg^{2+} and Au^{3+} to be extracted depending on the nature of the donor atoms.

Sodium diethyldithiocarbamate is one of the most widely used reagents for heavy metal preconcentration. A recently offered extractant called tris-dithiocarbamic acid is of interest. It allows the uranium to be preconcentrated in the analysis of sea water [3].

FG of many analytical chelate-forming reagents are known to have analogues among technological extractants. There now exist some examples of the reverse motion of ideas and extractants. 4-Methyl-N-

Table 1. Donor atoms and functional groups of monodentate neutral extractants

O	S	N	P
-O-	-S-	$R_n H_{3-n} N$ ($1 \leq n \leq 3$)	Ph \ Ph-P /\ Ph
$>C=O$	$>C=S$	R- 	C
$\geq P=O$	$\geq P=S$	R- 	
$>S=O$	$O=S<$	RHN- 	
$\geq N=O$	$>N-C \begin{matrix} \diagup S \\ \diagdown SR \end{matrix}$		
$\geq As=O$	$>N-C=S$ O		
$>N-C=O$			
$>N \diagdown$			
$>N-P=O$			
$>N \diagup$			

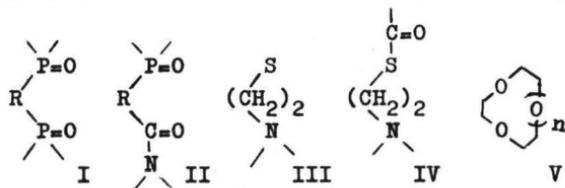
8-hydroxyquinolinylnbenzene-sulphonamide, being a low molecular methyl analogue of the technological extractant LIX-84 has been offered and studied as an extraction-photometric reagent for copper [4]. A number of other attractive chelate-forming reagents was offered in recent years.

Another large class of the extracted neutral compounds consists of coordinatively solvated mixed compounds. These are electron donor-acceptor ones with a neutral complex of extracted metal as electron-acceptor molecule, and on organic base (extractant) as electron-donor molecule. Therefore the theory of the extraction of this type of compounds is based to a great extent on that of the electron donor-acceptor complex formation. Extraction by use of neutral extractants have rather long been developing mainly for monodentate oxygen-containing extractants, ethers and ketones above all (Table 1).

It was in studying monodentate extractants that the EP theory of the related extractants has been developed. This field of solvent extraction has been developing by studying the extractants with new heteroatoms as donor atoms and through FG complication.

The examples of neutral extractants containing almost all heteroatoms of interest are presently available. The FG themselves have been complicating alongside. We would like now to concentrate on the following possible conclusions. First, for complex FG containing several heteroatoms there may be cases where various atoms act as donor ones. Second, one can hardly single out the two separate groups, i.e. FG and EAG. Thus, the possibility of application of the developed approaches to predict the behavior of elements in extraction systems with such extractants becomes hardly discussible. Finally, the avai-

lability of the extractants with complex different FG lead to the synthesis, study and use of polydentate reagents practically designed only from FG. The open chain extractants were followed by cyclic ones and then by the reagents containing both open and cyclic fragments (neutral and acidic). Above all these are organophosphorus reagents containing phosphoryl (I) and carbamoyl groups (II), amidosulphides (III), amidoketosulphides (IV), cyclic polyethers (V). Many of these extractants have been used to solve definite problems.



Among macrocyclic reagents containing other heteroatoms besides oxygen we can mention dibenzo-15-crown-5 analogues containing various combinations of oxygen, nitrogen and sulfur as donor atoms [5]. The study of this group of reagents allowed the methods of silver determination to be developed. The selectivity of these methods is higher than that of the methods based on the use of dialkyl sulphides.

Presently, those specialized in the organic synthesis can synthesize reagents with random number of FG. Here the most acute problem arises concerning the development of the extractant E^p theory, allowing the selectivity relative to any element selected at random to be predicted. Up to now the reagents used in the extraction of any one type of compounds were discussed. The so-called "different compounds", not included into the above mentioned groups due to whatever reasons, should be considered. Among reagents for such compounds organotin extractants R₂SN(NO₃)₂ [6], for instance, are rather interesting. These reagents possess a unique extraction power in the relation to multi-charged phosphate, arsenate and other oxo-anions. These extractants are of interest from the theoretical point of view as well. Formal description of the extraction with such reagents is completely analogous to that applied to conventional anion-exchange extraction processes. On the other hand, the extracted anion enters the inner coordination sphere of the tin atom. And the extractable compounds are essentially the coordinatively solvated ones.

Another example concerns the possibility of the use of crown-ethers (L) to extract metal halide anions in the form of complexes of ion pairs (Kat⁺)_m MX_{n+m}^{m-} where Kat⁺ denotes HL⁺ or ML⁺ (M=alkali metal, X=halide or some other anion). In this case the crown ethers seem to act as solvating agent, the alkali metal - crown ether complex presenting the cation part of the ion pair [7].

The compounds discussed here together with the majority separated by liquid-liquid extraction are usually extracted in a two-phase sys-

tem of water - water-immiscible organic solvent. Yet the possibilities of the extraction as a method of separation and preconcentration of substances in analytical chemistry and not only there, may be extended due to the so-called non-traditional systems.

Systems with water-soluble organic solvents or without any organic solvents will be attributed to such ones. With these systems it is possible to extract various hydrated compounds using, e.g., water-soluble organic reagents; to extract substances in absence of any organic solvent; to obtain water-soluble electroconductive extracts; to increase the extraction rate; to achieve high enrichment factors and to solve some other problems not always solvable through the development of new reagents.

The application of two-phase systems of water - water-soluble organic solvent (WOS) is conditioned by the method of subsequent determination of elements in the extract. Japanese chemists [8] used systems with acetonitrile or propylene carbonate and chlorides or sulfates to extract ion pairs, including anionic halide, thiocyanate and chelate complexes, in order to develop extraction-polarographic methods. The obtained extractants are electroconductive and may be directly used in polarography. Such systems with acetone guarantee a high sensitivity of the flame atomic absorption analysis. WOS containing considerable amounts of water or as they are sometimes referred to as "hydrophylic extractants" were used to extract water-soluble organic and high molecular substances such as albumins, amino acids and other highly hydrated substances [9].

The WOS-based systems may also be used in so-called "homogenous extraction" [10]. In this technique an extractable compound is formed in a homogenous phase on the addition of WOS (for instance, propylencarbonate) to the water solution of metals for faster equilibrium attainment. Then a salting-out agent is added or the preheated solution is cooled to cause phase separation. This technique permits to shorten the time for the equilibrium attainment from several hours to several minutes against the traditional extraction system. The extraction of Fe(III) with thenoyltrifluoroacetone is just the case.

As all of us are specialized in liquid extraction, we work in such a field where the majority of problems is solved by means of organic solvents. One cannot but admit, however, that organic solvents have some unfavourable properties in terms of their practical application. Many solvents are flammable or explosive, toxic, volatile. The latter drawback may be partially eliminated by using fusible extractants.

Two-phase aqueous systems free of organic solvent are now known to exist. Two-phase aqueous polymer systems, applied in biochemistry for the extraction of proteins, cells and other biological substances [11], rank among them. Distributions occur between immiscible solutions of two polymers or between a polymer solution and an inorganic

salt solution, i.e. among phases providing similar conditions for hydration. This makes it possible to extract substances which concentrate in the aqueous phase when traditional organo-aqueous systems are applied. Besides the hydration properties, the polymeric phase possesses another essential feature. That is the value of its relative hydrophobicity - the value of free energy of hypothetical $-\text{CH}_2$ group transfer from the given system to n-octanol. Polymeric phases according to their hydrophobicity rank between water and organic solvents.

The study of the two-phase systems based on water-soluble polymers allowed them to be applied in extraction of inorganic compounds as well, water-soluble organic reagent of different classes being involved [12]. Such reagents can form complexes with metal cations which are transferred from aqueous solution of an inorganic salt (sulfate, carbonate, phosphate, etc.) to aqueous poly(ethylene glycol) (PEG) solution with high distribution coefficients. The number of polar and dissociated groups in the reagent molecules and coordinative unsaturation of complexes showed no marked negative influence on the extraction of metal complexes.

PEG itself containing donor oxygen atoms may serve as an effective extractant for complexes of metals with inorganic ligands, for instance, halide or thiocyanate ions. Thus, the distribution coefficient of copper(II) extracted from sulfate-thiocyanate solution with 40% PEG is 10-fold higher than with tributyl phosphate and 10^4 -fold higher than with diisopropyl ether from the same aqueous solution. It is of interest that anionic dicharged cupric complex, containing two water molecules is extracted by PEG. The extraction of such a complex in a traditional system would be hindered.

Another type of two-phase aqueous systems was offered recently [13]. Phase separation occurring in ternary systems of water-pyrazolone derivative - organic acid is due to chemical interaction between two solid organic substances dissolved in water, for instance, antipyrine (Ant) and monochloroacetic acid (MCAA). The heavy phase separated from the aqueous solution is the solution of Ant monochloroacetate with a high concentration of MCAA. The excess of both Ant and the acid in this phase provides conditions for the extraction of metal complexes.

One of interesting methods of extraction and enrichment of hydrated metal complexes is based on the use of ternary systems with two aqueous phases [14]. Such systems include water, ether, mineral acid and its salt. Hydrated and solvated mineral acid is the main component of the third phase. Due to a high percentage of water in this phase the equilibrium between two aqueous phases with nearly the same composition is provided. This determines the same character of hydration and the identity of forms of metal complexes in the mentioned phases. Methods of the extraction of halide complexes of platinum me-

tals including tricharged anions into the third phase have been developed. The extraction of $[\text{IrBr}_6]^{3-}$ complex not extracted in traditional systems may just serve as an example.

Recently interesting studies devoted to three-phase systems with two organic phases were made. These investigations were carried out at Kiev and Perm Universities (USSR). Such systems allow the effective extraction of different metals to be carried out in a number of cases. Their use has made it possible to achieve extremely high enrichment factors due to a great difference between the volumes of water phase and the second organic phase.

The extraction in the above mentioned two- and three-phase systems goes well together with subsequent determination techniques, thus making them interesting both from the theoretical and practical viewpoint.

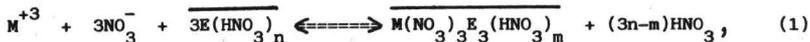
Finally, it is desirable to answer the question discussed at ISEC-80 in Liège: what is better - to search for new extractants and extraction systems or try to obtain more complete and reliable information about the available systems. It seems that both are necessary. Moreover, we believe that either of the directions will be in progress so far as the liquid-liquid extraction will help solving practical problems.

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In previous work [1,2] a supported liquid membrane (SLM 1) consisting of a
 0.25 M CMPO and 0.75 M TBP solution in decalin (CMPO stands for octyl(phenyl)-
 N,N-diisobutylcarbamoylmethylphosphine oxide,the neutral bifunctional organo-
 phosphorus extractant developed at Argonne National Laboratory for the TRUEX
 process [3],and TBP stands for tributylphosphate) has been used for removing
 actinides from synthetic liquid nuclear wastes,concentrating them in a suitable
 strip solution. The selective transport of actinides through the described
 membrane takes place because the carrier CMPO reacts with tri-,tetra- and
 hexavalent actinides in HNO_3 solutions. The extraction and stripping equilibria
 can be represented for a trivalent cation as [3] :



where E represents CMPO and the bar indicates membrane species.

The driving force for the uphill transport of the actinides is generated
 by the concentration difference of nitrate ions in the feed and strip solu-
 tions. As eq.(1) shows, HNO_3 is also transported to some extent through the
 membrane. Its accumulation into the strip solution eventually stops the acti-
 nide transport. To obviate this problem in ref. [2] a second supported liquid
 membrane (SLM 2) was used in series with the first one. It contained the car-
 rier Primene JM-T (a primary aliphatic amine) which removed only HNO_3 from
 the strip solution,neutralizing it in a third aqueous compartment containing
 an excess of NaOH. In this way the actinide transport could proceed to com-
 pletion. The same flat-sheet double liquid membrane system,schematically
 shown in Fig.1,has been used in this work,where the transport of selected ac-
 tinides from HNO_3 solutions or acidified urine samples has been studied with
 the objective of demonstrating the applicability of the SLM technique to the
 separation of actinides from bioassay samples.

Work performed under the auspices of the Office of Basic Energy Sciences,
 Division of Chemical Sciences,U.S.Department of Energy,under contract number
 W-31-109-ENG-38.

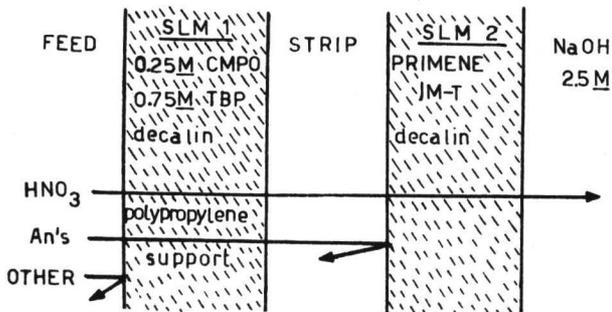


Fig.1. Schematic description of the double SLM system used to remove actinides from dilute solutions such as nuclear waste solutions or bioassay samples

In a first series of experiments the transport of HNO_3 through the double SLM system was investigated in order to measure the influence of the HNO_3 concentration in the feed and of the Primene JM-T concentration in the SLM 2 membrane on the capability of the system to maintain good stripping conditions for long times ($[\text{HNO}_3]_{\text{strip}} < 0.05 \text{ M}$ for about 24 hours). It was found in this way that, by using water as strip solution, the HNO_3 concentration in the feed solution had not to exceed 2 M, and that of the Primene JM-T in SLM 2 had to be in the range 0.75-1 M. For higher concentrations of HNO_3 in the feed solution, and for Primene JM-T concentrations above or below the indicated range, the removal of HNO_3 from the strip solution was not efficient enough to allow a fast and quantitative recovery of actinides in the intermediate compartment (strip solution).

In another series of experiments different strip solutions were tested. Good results were obtained with the following strip solutions: a) 1 M formic acid + 0.05 M hydroxylammonium formate (HAF), b) the same as before + 0.05 M oxalic acid, c) 2 M ammonium chloride + 0.05 M oxalic acid (an ammonium chloride-oxalate solution is often used for actinides electrodeposition [4]).

The results obtained for americium transport through the double SLM system with the above mentioned strip solutions are reported in Fig.2. In all cases Am(III) was effectively removed from the feed with 98-99 % removal reached after about six hours. The permeability coefficient of Am(III), calculated from the straight lines of Fig.2, was in the range $(1.0-1.3) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, in good agreement with literature values [1].

The transport of uranyl ions through the same membrane system was investigated in similar experiments. Also in this case a 99 % metal separation from

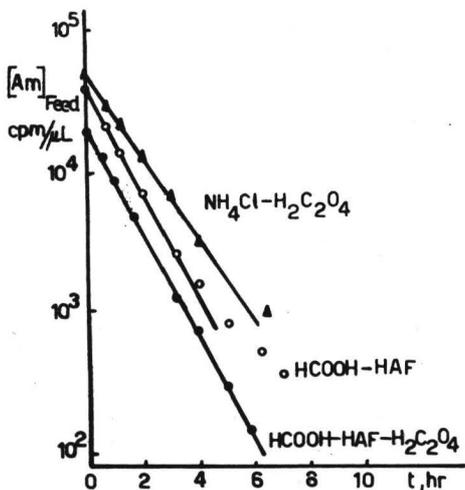


Fig. 2. Am(III) feed activity vs t(hr) for various strip solutions. Feed=2 M HNO₃; SLM 2=1 M Primene JM-T; membranes area=1.71 cm²; volume of feed and NaOH solutions=4 cm³; volume of strip solution = 10 cm³; stirring speed of feed, strip and NaOH solution = 200 rpm

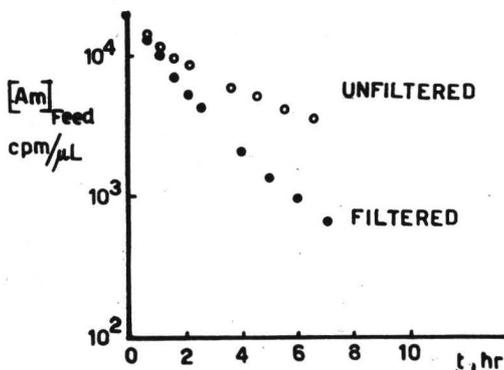


Fig. 3. Am(III) feed activity vs t(hr) for unfiltered and filtered acidified (2 M HNO₃) urine as feed solution. Strip solution = 1 M HCOOH + 0.05 M HAF + 0.05 M H₂C₂O₄. All other conditions as in Fig. 2

the feed solution was achieved in six hours. Some of the initial U(VI) (5-20%), however, was found at the end of the experiment in the NaOH compartment. This fact is probably due to the formation in the strip solution of anionic formate and oxalate complexes capable of reacting with the liquid anion exchanger Primene JM-T.

Fig. 3 shows the results of Am(III) transport experiments performed by using acidified urine as feed solution. This solution was prepared by adding concentrated nitric acid to raw urine up to a HNO₃ concentration of 2 M. The acidified urine solution was then digested at room temperature for some hours before use in a double liquid membrane experiment. It was spiked with ²⁴¹Am just before the experiment was started.

The data obtained with unfiltered urine show a much slower and partial transport, indicating a membrane "fouling" by the organic material still present in the feed solution. Much better results were obtained by prefiltering acid digested urine on a small column filled with porous beads of polyester resin[5]. In this case, as shown in

Fig.3,a 96 % recovery of the initial Am(III) activity was achieved in about 7 hours with a ratio of membrane area to feed volume of 0.43 cm^{-1} and a permeability value of Am(III) equal to $9.6 \times 10^{-4} \text{ cmxs}^{-1}$. In the same experiment a practically quantitative recovery of Am(III) (>99.9 %) in the strip solution was reached after 24 hours (not shown in the figure).

A much faster separation process is expected by using hollow fiber modules with a much larger area/volume ratio.

More experimental work is needed to fully assess the applicability of supported liquid membrane systems to the separation of actinides from biological samples. The areas requiring more investigation are:

- 1) the use of hollow fibers with a high membrane area to feed volume ratio and a high feed volume to strip volume ratio.
- 2) the research on more powerful stripping agents capable of stripping the actinide elements from the CMPO containing membrane even in the presence of relatively high HNO_3 concentrations. In this case the use of a second SLM could be avoided and the whole experimental system would be simpler. Also, the risk of losing a fraction of the actinides as anionic complexes in the NaOH compartment would be eliminated.

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In recent years membranes have been widely used in studies of ion transport. The development of these systems can be traced back to experiments by Nerst and Riesenfeld (1902) [1]. Now we have several methods to utilize liquid membranes for separation processes. An emulsion type consisting of water-oil-water emulsion [2]; a supported type consisting of an oily phase held by capillary forces within the pores of microporous membranes [3]; a liquid film extraction [4] where the feed and stripping solution flow down along vertical solid porous supports and between the supports there is a liquid membrane.

A theory of the process has been developed for various models of simple and activated permeation processes and different engineering condition [5-7]. This paper describes liquid emulsion extraction for preconcentration of metals. We have treated membrane extraction as an analogy of solvent extraction.

Considering a chemical equilibrium in three phases systems we can obtain a formula similar to solvent extraction in batch condition [8].

$$R_{MX} = \frac{(p-1)D_I r_I}{1 + pD_I r_I}, \quad (1)$$

$$p = 1 + \frac{1}{D_{II} r_{II}}, \quad (2)$$

$r_I = V_M/V_I$; $r_{II} = V_M/V_{II}$;
 V_I - feed volume; V_{II} - stripping volume;
 V_M - membrane volume;
 D_I - distribution ratio for outer boundary;
 D_{II} - distribution ratio for inner boundary;
 p - pertraction factor, i.e. ratio of the amount of metal in emulsion to that

in organic phase. R_{MX} should be considered as the maximum efficiency parameter. From the practical point of view it is difficult to reach the theoretical value because of emulsion breaking, feed emulsification, strippant permeation, mutual transport of matrix etc. Due to this, chemical potential difference between the feed and strippant phase diminishes and the permeation efficiency decreases too. A large pertraction factor p enables to use carriers with low solubility in membrane, with low D_I or too expensive but selective reagent in small amounts. For large volume samples we have performed emulsion membrane extraction in dynamic conditions [9]. We contacted the feed volume (V_I) with a fixed amount of emulsion continuously in an apparatus with working volume smaller than the feed ($V < V_I$). It was no solute concentration at the beginning of preconcentration and it has been assumed that the system is in equilibrium in the working part of the column. Changes of the emulsion volume were neglected. Then the yield of the differential preconcentration ensuing from a general equation is:

$$dV_I(c_F - c) = dc(V + V_{II} \frac{D_I}{D_{II}} + V_M D_I) \quad (3) \quad c_F, c - \text{concentration of solute in feeding or raffinate, resp.},$$

at $t=0$, $c=0$ $V_I=0$. After integration

$r = V_M/V$ is the working phase ratio in the apparatus

$$R_{MX} = \frac{V_M D_I}{V_I} (p-1) \left(1 - e^{-\frac{V_I/V}{1+pD_I r}}\right) \quad (4)$$

Application of membrane extraction as a preconcentration method is

connected with high value of the pertraction factor because :

$$\frac{c_{II}}{c_I} = (p-1) V_{II} \frac{c_M}{c_I} = (p-1) D_I r_{II} \quad (5)$$

or

$$\frac{c_{II}}{c_{IO}} = \frac{(p-1) D_I r_{II}}{p D_I r_{II} + 1} \frac{V_I}{V_{II}} \quad (6)$$

High value of the preconcentration factor which can be equal to V_I/V_{II} in limiting case, is preference of membrane extraction even at low D which is in the case of low extractant concentration reached in both batch and dynamic conditions.

Separation factor of two metals is from the membrane extraction point of view :

$$S_{MX} = \frac{(c_{II}/c_I)}{(c'_{II}/c'_I)} = \frac{D_I}{D'_I} \frac{(p-1)}{(p-1)} \quad (7)$$

Kinetic factor for three phases systems with the same composition and monotype metal series can be used to reach $S_{MX} = 1$.

APPLICATIONS

A modified turbine type impeller with stabilisation of rotation has been used for preparation of emulsions [10]. A pertraction column apparatus for flow through preconcentration is constructed [11].

URANIUM

KELEX 100 and DEHPA were used for effective separation of uranium from slightly acidic solution [12,13,14]. As a most perspective carrier in n-alkane membrane with inner (stripping) solution 1-2.5M H_3PO_4 or H_2SO_4 DEHPA was chosen. This system was used for preconcentration of uranium from 20-50l in flow through column apparatus. The preconcentration factor was higher than 350 and recovery was of 98%.

CERIUM

A preconcentration factor of 100 was reached with membrane containing TOPO carrier and in high nitrate concentration. Citrate and EDTA as inner solution were used. The concentration of Ce^{3+} in outer solution was 10^{-6} - 10^{-4} mol/l (fig.1).

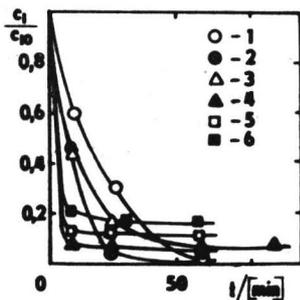


Fig.1

Membrane extraction of cerium. Membrane: 0.01M TOPO in n-dodecane, 4% SPAN 80, outer solution: $1 \cdot 10^{-4}$ M Ce^{3+} (1,2,3), 2M $NaNO_3$ (1,2,3,4,5,6), $1 \cdot 10^{-5}$ M Ce^{3+} (4), $1 \cdot 10^{-6}$ M Ce^{3+} (5), ^{141}Ce only (6), inner solution: 0.01M EDTA, 1M $NaNO_3$ (1), 1M Na_3Cit (2,3,4,5,6), 0.01M EDTA (3), $1 \cdot 10^{-4}$ M EDTA (5,6), $r_I = 0.01$, $r_{II} = 1.0$

COBALT, MANGANESE

Batch pertraction of Co and Mn with aromatic beta-hydroxyoxime (LIX 64N, LIX 65, ABF) industrial extractants was studied. Kinetic and hydrodynamic characteristics of emulsion with minimum of retention of Co in the membrane were optimised. For Co it can be reached a preconcentration factor of 100-170 in batch and 300 in flow through pertraction with high recovery using SPAN 80 detergent. We did

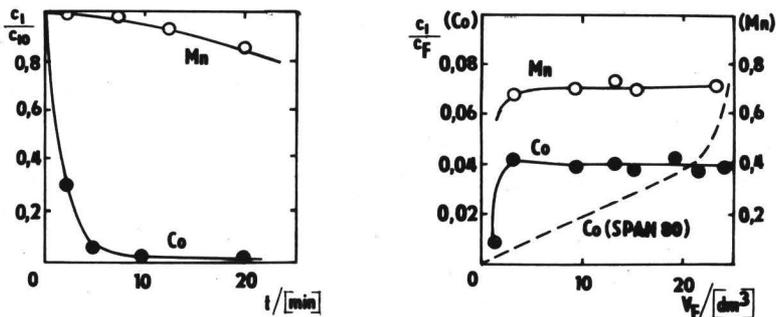


Fig.2

Membrane extraction of cobalt and manganese. Membrane: 1% LIX 64N in n-dodekane, 3% ECA 4360, outer solution: borate buffer pH 7.9, 1.10^{-5} M Co^{2+} , 1.10^{-5} M Mn^{2+} , 0.1M NaNO_3 , inner solution: 0.1M H_2SO_4 , $r_I = 0.1$, $r_{II} = 1.0$

Fig.3

Flow membrane extraction of cobalt and manganese. Membrane: 1% LIX 64N in n-dodekane, 3% ECA 4360, outer solution: borate buffer pH 7.9, 1.10^{-5} M Co^{2+} , 1.10^{-5} M Mn^{2+} , 0.1M NaNO_3 , inner solution: 0.1M HCl , $r_I = 0.1$, $r_{II} = 1.0$, $v_F = 6 \text{ dm}^3\text{h}^{-1}$, emulsion 0.2 dm^3 , recovery (inner solution): 98% Co, 28% Mn

not succeeded in separation of cobalt and manganese because SPAN 80 served as carrier for Co (48%) and for Mn (30%) as well [15,16]. Polyamine ECA 4360 causes slower transport and enables us to enhance the separation factor of Co/Mn (fig.2). Polyamine influence has been shown in the flow through pertraction too. The recovery of Mn drops from 94% to 27% but that of Co rests on the value of 95% (fig.3).

STRONTIUM, CALCIUM

Emulsion membrane extraction of Sr with crown and picric acid as carriers shows that preconcentration of Sr and its separation from Ca can be compared with the ratio of $D_{\text{ISr}}/D_{\text{ICa}}$ for toluene membrane and 18C6 crown at appropriate concentration. Transport of Sr is caused by picric anion gradient in solution I and II which are controlled by HCl in the inner solution (0.5M) [17]. The influence of Ca on the recovery and the transport rate of strontium is shown in figs.4 and 5. Ca is practically not pertracted and this can be used for separation of Sr from highly concentrated (-0.2M) Ca solution with high recovery. Presence of Ca in isolated inner solution is caused by secondary emulgation during pertraction. In this way the separation factor is lower but it can be improved by changing of detergent

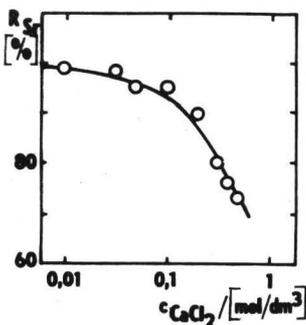


Fig. 4

Recovery of strontium in membrane extraction. Membrane: toluene, 4% SPAN 80, outer solution: $1 \cdot 10^{-5}$ M Sr^{2+} , xM CaCl_2 , $4.5 \cdot 10^{-3}$ M picric acid, $5 \cdot 10^{-5}$ M 18C6, inner solution: 0.5M HCl, $r_I = 0.1$, $r_{II} = 1.0$, pertraction time 10 min

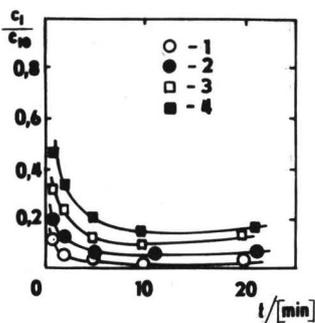


Fig. 5

Membrane extraction of strontium. Conditions see fig.4, concentration of CaCl_2 in outer solution 0.07 (1), 0.15 (2), 0.3 (3), $0.6 \text{ mol} \cdot \text{dm}^{-3}$ (4)

(polyamine instead of SPAN 80), by using the appropriate membrane solution (chlorinated hydrocarbon instead of toluene) and by changing of the ratio V_{II}/V_I . Toluene emulsion stabilised by SPAN 80 is generally not suitable for a long term pertraction because of loss of its hydrodynamic properties - it turns to paste. Application of polyamine ECA 4360 is good from the point of secondary emulgation. It decreases the K_E value from 1.6-1.8 to 1.0-1.1 ($0.1-0.2 \text{M Ca}^{2+}$ in outer solution) and keeps the emulsion in liquid form. The tenside effect on the pertraction of Sr is shown in fig.6. The pertraction of Sr and Ca with toluene (fig.7) and tri-

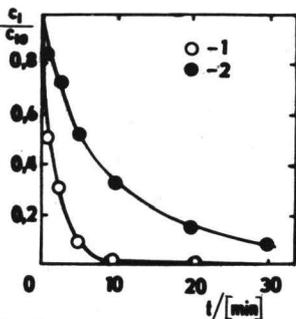


Fig. 6

Membrane extraction of strontium. Membrane: toluene, 4% ECA 4360, outer solution: $1 \cdot 10^{-4}$ M SrCl_2 , $4.5 \cdot 10^{-3}$ M picric acid, $5 \cdot 10^{-5}$ M 18C6, $0.15 \text{M Ca}(\text{NO}_3)_2$ (2), the same as (2) but without Ca^{2+} (1), inner sol. 0.15M HCl, $r_I = 0.1$, $r_{II} = 1.0$

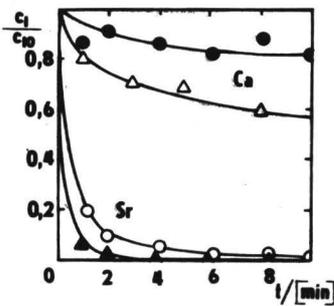


Fig. 7

Membrane extraction of strontium and calcium. Membrane: toluene, 4% ECA 4360, outer solution: $1 \cdot 10^{-5}$ M SrCl_2 , $1 \cdot 10^{-5}$ M CaCl_2 , $5 \cdot 10^{-3}$ M picric acid $5 \cdot 10^{-5}$ M 18C6 (), $5 \cdot 10^{-4}$ M 18C6 (), inner solution: 0.5M HCl, $r_I = 0.1$, $r_{II} = 1.0$

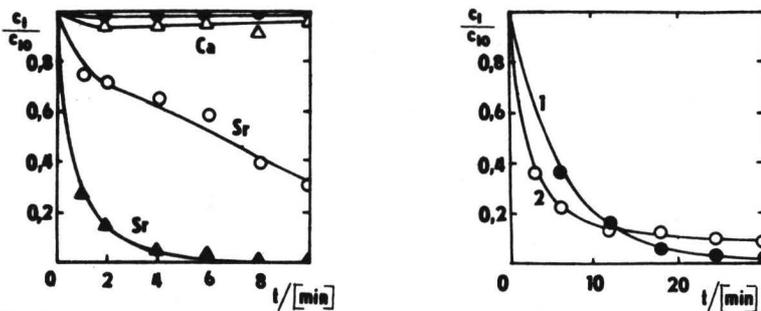


Fig.8

Membrane extraction of strontium and calcium. Membrane: 1,2,4-trichlorobenzene, 4% ECA 4360. Conditions see fig.7

Fig.9

Membrane extraction of strontium. Membrane: 1,2,4-trichlorobenzene, 4% ECA 4360 (1), 4% SPAN 80 (2), outer solution: $1 \cdot 10^{-5}$ M SrCl_2 , $5 \cdot 10^{-3}$ M picric acid, $1 \cdot 10^{-4}$ M 18C6, inner solution: 0.5M HCl, $r_I=0.02$, $r_{II}=1.0$

chlorobenzene (fig.8) membrane is shown. Trichlorobenzene emulsion stabilized by polyamine is suitable for 50fold preconcentration of strontium (fig.9).

PERTECHNETATE

The liquid membrane extraction with Aliquat 336 as a carrier has been studied [18]. The recovery of pertechnetate in the inner solution in experiment with liquid membrane was estimated from the results of solvent extraction according to formula (1). A good agreement between the calculated and experimental results has confirmed the three phase distribution model.

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1. Introduction. This paper proposes a new titration technique for the determination of surfactants. The "Amphimetry" is a distribution titration of ion pairs continuously carried out in emulsions. Dichloroethane ("DCE") is used as organic solvent for all titrations. For indication it is necessary to add an ion pair forming redox indicator to the solution. The redox potential of the free indicator in the aqueous phase is monitored by a platinum electrode and shows a significant change at the endpoint. Reference electrode is a conventional Ag/AgCl/LiCl(EtOH)-electrode or a special all-solid-state reference electrode.

The titration procedure differs for anionic, cationic and nonionic surfactants. The ionic surfactants are titrated directly by a bulky counter ion. The indicator must be of the same charge but less extractable than the analyte. The nonionics are determined by displacement titration of the associate formed by K^+ , nonionic and an anionic surfactant. The cationic indicator which must be better extractable than the associate of potassium and the nonionic.

2. Titration of Anionic Surfactants. [1] Anionic surfactants are titrated in a water/DCE-emulsion with a standardized solution of the cationic surfactant Hyamine 1622[®] at a pH of 8. MnO_4^- or $HCrO_4^-$ can be used as indicators. To avoid an indicator-error the ions are added in the form of their ion associates with the titrant. After addition to the test solution the titrant changes in a first step to the aqueous phase and an equivalent amount of anionic is extracted, cf. figure 1. During titration of the well-stirred solution the ion associate of anionic surfactant and cationic titrant is formed and extracted into DCE. At the endpoint also the indicator is extracted. The indication curve (figure 2) is made up by the redox potential of the free indicator in the aqueous phase and an adsorption potential of the cationic titrant.

The calibration graphs show linearity from 0.5 μmol to 400 μmol per 40 ml emulsion. The standard deviation is $s=0.9\%$ at 10 μmol ($n=7$). The following concentra-

1. Addition of Indicator:



2. Titration:



3. Endpoint:



Fig. 1. Titration procedure for anionics. I=Indicator, T=Titrant, A=Anionic, o=organic, w=aqueous phase

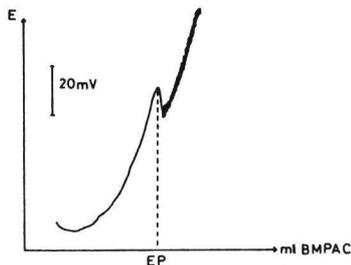


Fig. 2. Titration of 10 μmol of Bis-(2-ethylhexyl)-sulfosuccinate (= Aerosol OT[®])
Indicator: Permanganate

tions (mg/l) of salts do not interfere with the determination [1,2]: NaNO_3 (150), NaH_2PO_4 (1500), NH_4Cl (350), K_2SO_4 (700), NaCl (350), MgCl_2 (350), CaCl_2 (350), FeSO_4 (70), nonionics (50-100). Humic acid shows a strong interference even at very low concentrations.

3. Titration of Cationic Surfactants. [3] Figure 3 shows the titration procedure for cationic surfactants, which is - besides the opposite charges - analogous to that for the anionics. The cationic complexes of Fe^{2+} with 1,10-Phenanthroline, 2,2'-Bipyridyl or 2,4,6-Tri-(2-pyridyl)-s-triazine can be used as indicators. A typical titration curve is shown in figure 4. The linear range of the calibration graph and the standard deviation are the same as for anionic surfactants. Even large amounts of salts do not interfere with the determination (concentrations in mg/l): NaH_2PO_4 (2000), K_2SO_4 (2000), CaCl_2 (2000), MgCl_2 (1200), FeCl_3 (500).

1. Addition of Indicator:



2. Titration:



3. Endpoint:



Fig. 3. Titration procedure for cationics. I=Indicator, T=Titrant, A=Cationic, o=organic, w=aqueous phase

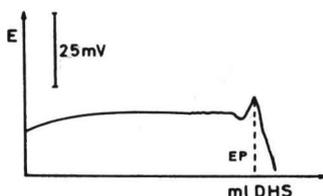


Fig. 4. Titration of 10 μmol of Hyamine 1622

Indicator: Fe-phenanthroline

Even if the cationic surfactants are in a lipophilic matrix they can be determined amphimetrically without preceding isolation. As an example for those problems the titration of a diesel oil additive is examined.

4. Titration of Nonionic Surfactants. [4] Nonionic surfactants ("NIOs") containing ethylene oxide groups can trap cations like K^+ or Ba^{2+} and behave as quasi-cationic. It is possible to extract the associate of K^+ , NIO and an anionic surfactant into an organic solvent and determine the NIO in the organic phase by means of an amphimetrical displacement titration. Figure 5 shows the procedure, figure 6 a typical titration curve. The indicator must be cationic and better extractable than the associate containing the NIO so that it is displaced later than the former.

The calibration functions are linear in the range from 0.5 mg to 20 mg NIO in the organic phase after pre-extraction. The standard deviation is $s=1.1\%$ ($n=6$) for a content of 5 mg Triton X 305. Concentrations up to 1500 mg/l of the following salts do not interfere with the determination: NaH_2PO_4 , CaCl_2 , MgCl_2 , FeCl_3 or NaNO_3 . Humic acid shows a strong interference.

The slope of the calibration function depends on the average number of ethylene oxide groups in the NIO, cf. figure 7. This indicates that one potassium cation is trapped by an average number of 20 ethylene oxide groups. Two ways for the quantification are possible: individual calibration functions for each nonionc (with respect to the individual slopes) or a general calibration function for one standard substance.

1. Pre-Extraction of Nonionics:



Separate organic phase

2. Displacement Titration:



3. Endpoint (Displacement of Indicator):



Fig. 5. Titration procedure for nonionics. I=Indicator, T=Titrant, A=Anionic. o=organic, w=aqueous phase

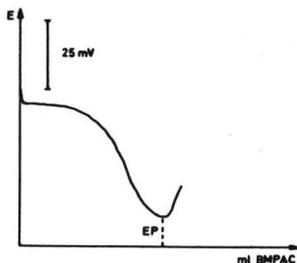


Fig. 6. Titration of 5 mg of BRIJ 56^o (9 EO-groups) Indicator: Fe-phenanthroline

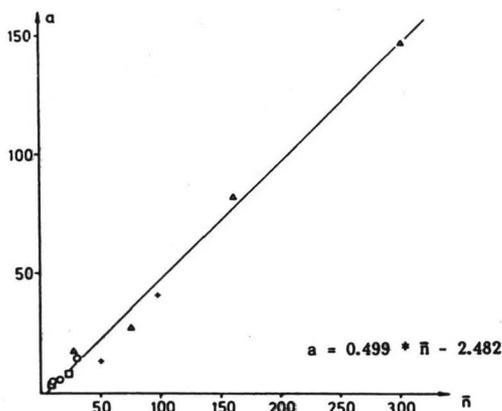
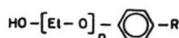
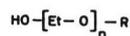


Fig. 7. Plot of the slopes of the individual calibration functions for several different nonionics vs. average number of ethylene oxide groups

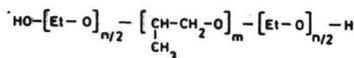
○ Triton



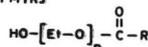
□ BRIJ



△ Pluronic



+MYRJ



5. Conclusions. The electrochemically indicated amphimetry is a simple, fast, inexpensive, sensitive and precise method for the determination of ionic and nonionic surfactants. The detection limit is worse than that of the extraction photometric methods so that the surfactants must be enriched from water or waste water samples before determination. As the titration is carried out continuously the amphimetry can be run on automated titration systems. This is an advantage over the extraction photometric methods.

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Extraction of metal-halide complexes with basic dyes is widely used in extraction-photometric and extraction-fluorometric methods. These methods display high selectivity and low detection limit. However, the theory of extraction of ion associates (IA), formed by metal-halide complexes with basic dyes is not sufficiently developed.

We have found some characteristics of dyes' extraction ability as a function of their basicity, size, charge, substituent nature and structure of the molecule as a whole.

In order to figure out the influence of dye nature on its' extraction properties we have carried out systematical study of extraction of halogen complexes of Cd, Hg, Ga, In, Tl, Pb and Sb with different triphenyl- and triarylmethane, rhodamine, cyanine, styrene, thiazene and some other dyes.

It is found that the size of the dye molecule does not affect their extraction properties. Thus, refractometric radii of brilliant green, BG (3.64 Å), and crystalviolet, CV (3.66 Å) and also malachite green, MG (3.46 Å) and fuchsin, FN (3.36 Å) does not differ significantly, as the extraction ability of BG is much more higher than of CV and that of MG is higher than of FN: ion associates formed by metal-halide complexes and FN does not extracted at all with solvents of low polarity.

The general basicity of the dyes also does not determine their extraction properties. Thus, total basicity increases in the raw MG-BG-MV-CV, but extraction of Ga, In and Sb decreases in the sequence BG-MG-CV-MV.

For the dyes of the same type and class in most cases there is a correlation between total positive charge on association stage and the extraction efficiency. The charge magnitude on the boundary groups carrying the maximal positive charge increases in a sequence KV (3.80) - MG (3.92) - EF (4.40) - BG (4.68) and in the same sequence increases their extraction ability for Sb, Cd and In.

The behaviour of the rhodamine dyes was found to be the similar.

The hydrophilicity-lipophilicity balance of the dyes influence extraction properties markedly. Dyes having hydrophilic groups ($-NH_2$, $>NH$, $-N=N-$, OH^- , $COOH^-$, etc) strongly interacting with water molecules could faintly extract metal-halide complexes in solvents of low polarity.

A very faint extraction power of fuchsin compared to other tri-phenylmethane dyes (TPMD) with benzene as a solvent could be explained by very high hydrophilicity of FN which molecule has three NH_2 - groups and strongly interacts with water molecules. The similar relationship has been found for triarylmethane and thiazene dyes. With the increase of hydrophilicity in the raws victoria blue 4P-victoria blue B-basic blue K and methylene blue-azur II-azur I-thionene extraction efficiency falls down. The same influence has hydrophilic COOH -group for rhodamine dyes; their extraction power raises in the raw rhodamine C-rhodamine GG-butylrhodamine.

It is shown for astrafloxine derivatives R-CH=CH-CH=R as an example that the substitution of methyl group, attached to ternary nitrogen, for oxyethyl one leads to the decrease of extraction of HgI_3^- , HgBr_3^- and HgCl_3^- from 99.98 and 78% to 40,20 and 2% accordingly.

Most of halogen complexes (HgX_3^- , InX_4^- , GaCl_4^- , etc.) are poorly extracted with solvents of low polarity but the extraction is increased to a great extent when using solvent mixtures containing electron-donor solvents (ketones, ethers, etc.) because of H-bonds forming ($>\text{NH}\dots\text{O}<$; $-\text{COOH}\dots\text{O}<$; $-\text{OH}\dots\text{O}<$) and solvation of the dyes.

We have also investigated the influence of stereochemical factors on the extraction efficiency of basic dyes. The extraction of halogen complexes of Hg, Cd, In and Tl with hinoline dyes of different structure has been studied. It is found that the dyes which are o-substituted to nitrogen atom carrying positive charge and taking part in association process with halogen complex has extraction ability less than m- and p-substituted ones which has no stereochemical interference.

The extraction efficiency of the dyes increases with the increase in electrophilicity of radicals in amino-groups. Since, dyes having p-diethylaminophenyl group extract metal-halide complexes better than analogous ones with p-dimethylaminophenyl group. The similar results were obtained for triphenylmethane, rhodamine, cyanine- $(\text{R}_1-\text{CH}=\text{CH}-\text{R}_2)$, hinoline- $(\text{R}_1-\text{CH}_2=\text{N}-\text{R}_2)$ and azo-dyes $(\text{R}_1-\text{N}=\text{N}-\text{R}_2)$.

An increase of total charge of the dyes decreases extraction efficiency sharply. Replacement of one charge dye cation by two charge one leads to drastic decrease in the distribution coefficient of ion associate. Two charge reagents-methyl green (Met.G) and iodine green (IG) and their complexes with Sb, Hg, Tl are weakly extracted with benzene and its derivatives; for quantitative extraction the use of more polar solvents such as chloroform, dichloroethane and mixture of benzene and nitrobenzene is necessary.

Two charge cations Met.G and IG does not extract "coordinationally saturated" metal-halide complexes as those of cadmium and lead.

There are two characteristic cases for the extraction process with two charge cyanine dyes:

a) dye molecule has nitrogen atoms carrying positive charges and divided by common conjunction chain $>\overset{+}{N}=C-(CH)_n-\overset{+}{N}<$;

b) these atoms are isolated by hydrocarbon group $>\overset{+}{N}-CH_2-(CH_2)_n-\overset{+}{N}<$. In the first case extraction of metal-halide complexes is not observed practically, in the second case extraction proceeds as effectively as with the analogous one charge cyanine dyes.

The general rule is shown for the extraction of metal-halide complexes with cyanine dyes of $R_1-CH=(CH_n)-CH=R_2$ structure. Extraction of $InCl_4^-$, $HgBr_3^-$, $GaCl_4^-$, $FeCl_4^-$, $CuCl_2^-$ increases with the enlargement of hydrocarbon chain.

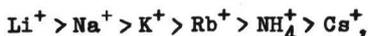
The extraction efficiency of dyes with halogen complexes of metals which cations could be treated as "soft" acids (according to Pyrson) raises with the increase in the acidocomplex stability from chloride to iodide. Thus for IA halogen complexes of Tl(III) with 2-[1/5 dimethylaminothienyl-2/-vinyl-2]-1,3,3-trimethyl-3N-indol (DTVTI) the extent of extraction falls in the raw TlI_4^- - $TlBr_4^-$ - $TlCl_4^-$ (see Table).

Extraction of halogen complexes of Tl(III) with DTVTI

Complex	$\lg K_{TlX_4^-}$	λ_{max} $R^+TlX_4^-$	$R_{Tl}, \%$
$R^+TlI_4^-$	31.8	580	99.8
$R^+TlBr_4^-$	23.9	575	79.1
$R^+TlCl_4^-$	18.3	570	62.5

A bathochrome shift of absorbance maxima of IA extracts appears to be raised from different polarization of dye chromophore system in the field of Tl(III) halogenide complexes.

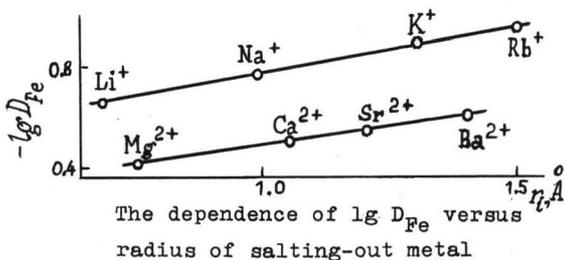
Some metals (Ga, In, Fe(III)) being "hard" Pyrson's acids was found to be easily extracted as IA with basic dyes from salting-out solutions such as alkali and alkali earth chlorides and NH_4Cl or $AlCl_3$. Normally $GaCl_4^-$, $InCl_4^-$ and $FeCl_4^-$ complexes with basic dyes couldn't be extracted by solvents of low polarity from the solutions of low acid content. If other conditions being equal the salting-out agents could be arranged in the sequences:



The distribution coefficients of metals are in linear correlation with salting-out cation radii. Such a dependence is shown on Fig. for the extraction system Fe(III)-MeCl(MeCl₂)-astrazone purple 2C-toluene.

The steady increase in the extraction of IA is observed depending on the charge of salting-out cation in the raw $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ which is in accordance with the increase of cation hydration extend. LiCl displays the highest salting-out effect compared to other metal chlorides. These effect obeys Sechenov's law for the extraction of chloride complexes of Ga, In and Fe(III) with different basic dyes (triphenylmethane, cyanine and azo-dyes).

The influence of water structure on the extraction of IA should be mentioned. For example, if one change ordinary water in the system Fe^{3+} -LiCl-H₂O-ethylviolet-toluene for D₂O or for the water treated with magnetic



field the extraction of FeIA increases by 5-10%. The same effect is observed when adding some hundredth percent of polyethyleneglicol (PEG-5000) or polyacrylamide which macromolecules distort water structure in some way. The increase in the extraction of IA when changing ordinary water seems to be explained by modification of water structure and decrease of its' activity. For the same reason the solubility of IA in water phase is decreased.

In the extraction process of metal-chloride complexes with basic dyes in the presence of salting-out agents the most effective solvents are aromatic hydrocarbons and some acetic esters ($DK < 6$). These solvents are convenient because they practically do not extract metal-chloride complexes in the absence of dyes and extract dye chlorides not significantly.

Their extraction with aromatic hydrocarbons decreases with the decrease of Hildebrand solubility parameter in the raw benzene > toluene > ethylbenzene > propylbenzene > butylbenzene. The linear correlation is observed between $\lg D_{Me}$ and alkyl chain length in benzene derivatives. The extraction efficiency of IA decreases also with the increase of substitution extent in benzene ring in the raw benzene > toluene > o,p,m-xylol > mesetylen. A quantitative characteristic of SA extraction efficiency in dependence of solvent basicity and molecular mass has been found.

EXTRACTION AS A SOURCE OF ADDITIONAL INFORMATION
WHEN CONCENTRATIONS IN MULTICOMPONENT SYSTEMS ARE
SIMULTANEOUSLY DETERMINED

9-6

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Information from measurement of analytical signals when they act upon each other under certain assumption [1] may be given by the following equation

$$P_{inf} = n\bar{R}I_d \bar{S} \ln r_u' r_1^{-1} \quad (1)$$

when \bar{R} - signals permitting factor, their selectivity, dash above - a sign of value constancy within signal measurement interval from r_u to r_1 ; \bar{S} - the number of graduations on n signals intensity I , which is concerned with the interval of measurement results similarity, Δ : $S = I/\Delta$

When different methods of analysis are applied extraction influence upon analytical signal has to do with an increase of its intensity in the process of extractional concentration, i.e. with an increase of S graduations number.

Extractional concentration is usually combined with group or individual separation, i.e. with decrease of the number of compounds defined in extracts obtained. As seen from equation (1) at high level analytical signals intensity measurement standardization overlapping at interval r_u-r_1 , decrease of their number in information growth from each of them and hence in similarity improvement of concentration definition results.

In most method of analysis with broad non-selective signals it's difficult to use equation (1) for strict apriori comparison of results because of permittance factors value uncertainty.

The choice and comparison of optimum information concerning components concentration from additive overlapping signals measurement in the method is advisable to do by minimization of errors in the results of concentration determination with the help of certain means and criteria [2]. Error minimization - is the choice of information when all factors influencing it are included: the number of overlapping signals, their permittance and intensity. However it's convenient to use equation (1) for causal relationship of error minimization results with information from signals measurement.

So, simultaneous photometric N_d and S_m determination as being extracted into butylacetate of heteroligand complexes with pyridineazorezorcine (PAR) and tetraphenylborate (TPB) after initial measurement optimization results in statistically uncertain results (see Table 1, N 1).

Fig.1 shows the absence of information about concentration of each simultaneously defined components in signals measured. N_d and S_m complexes lightabsorbance spectra are of mender difference in ν_{max} , i.e. permitting factors $R = 0$ and hence $P = 0$. These non-informative signals may be modified with the keep of extraction in order to obtain their better permittance.

LrPAR TPB complexes extraction at various pH may be measured on lightabsorbance of extracts. A quotient of lightabsorbance division upon lanthanide general concentration induced into a system may be expressed as graduated coefficient provided that extraction in a system is constant when concentrations are measured in the range of their determination. Such coefficient spectra for Nd and Sm complexes extracts depending on pH are given in Fig.1, validity of such treatment of analysis graduation with excess of complexing reagents in a system is shown in[3]. From Fig.1 it follows that maxima in extraction spectra \mathcal{E} -pH are shifted, i.e. signal permitting factor is considerable and equations system for Nd and Sm simultaneous determination, which is composed using initial measurement optimization criteria 2, gives satisfactory results (Table 1, N 2) as compared to a previous variant of analysis.

Table 1. Results of simultaneous (Nd and Sm) determination with PAR and TPB $C_m \cdot 10^5 \text{ mol/l}$ - concentrations defined. It's given: $C_{Nd} = 1,56 \cdot 10^{-5} \text{ mol/l}$ $C_{Sm} = 1,47 \cdot 10^{-5} \text{ mol/l}$, $S_c \cdot 10^5 \text{ mol/l}$ - standard error at $n = 6$

N	pH	λ , nm	C_{Nd}	S_{Nd}	C_{Sm}	S_{Sm}
1	6,8	5000-550	1,7	2,2	1,4	1,1
2	6,3; 6,6; 6,8	510-550	1,5	0,14	1,5	0,09

In method molecular absorbance spectroscopy some additional information about concentrations of components defined simultaneously may be obtained when they are extracted into various solvents, i.e. at the expense of solvatochromatics effects[4]. Change of medium may influence absorbance spectra of each component great-

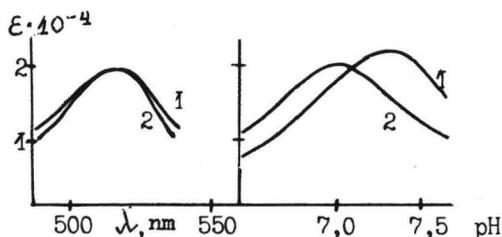


Fig.1. Extraction (\mathcal{E} -pH) and absorbance (\mathcal{E} - λ) spectra for Nd(1), Sm(2) with PAR and TPB complexes

ly and in several ways. Linear equation system of Buger's law may be composed by choosing optimum positions from spectra \mathcal{E} - λ and \mathcal{E} -solvent for simultaneous photometric concentrations determination. Log wave bands of absorbance spectra of Mn(11) and Zn with PAN in CCl_4 and $\text{CH}_3\text{COOC}_5\text{H}_{11}$ extraction complexes show considerable solvatochromatics effects (see Fig.2). The results of simultaneous determination of Mn and Zn concentration obtained by equation system resolution which are composed on additive lightabsorbance measurement in optimum positions in summary spectrum of each extract (N 1,2) and in the number of positions from absorbance spectra in two extracts (N 3) are given in Table 2. In the last case standard deviations in the results of concentrations determination are much less, since equation system there is more information about

Table 2. Result of simultaneous determination of Mn and Zn with PAN
 $C_M \cdot 10^5 \text{ mol/l}$, $S_C \cdot 10^6 \text{ mol/l}$. Are given: $C_{Zn} = 1,17 \cdot 10^{-5} \text{ mol/l}$,
 $C_{Mn} = 0,92 \cdot 10^{-5} \text{ mol/l}$, $n = 6$

N	SOLVENT, λ , nm	C_{Mn}	S_{Mn}	C_{Zn}	S_{Zn}
1	CCl_4 ; 545; 550; 555; 570, 575	0,91	0,12	1,18	0,09
2	$C_7H_{14}O_4$; 530,550,555,565,570	0,92	0,10	1,17	0,10
3	CCl_3 ; 550,560. $C_7H_{14}O_2$; 550, 565, 570	0,92	0,08	1,17	0,07

concentrations of each component because of using a greater number of signals, the number of components determined being equal.

Cases of using solvatochromatics effect for growth of multicomponent extraction photometric analysis results similarity may have a wide application since their realization does not increase duration of determination: necessary repeated extraction by one solvent in changed for extraction in several solvents.

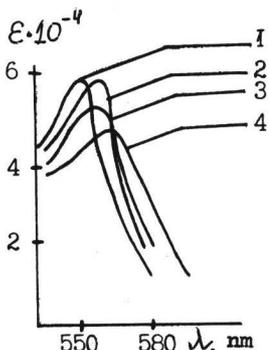


Fig. 2. Absorbance spectra of complexes Zn(1,2) and Mn(3,4) with PAN in CCl_4 and $CH_3COOC_5H_{11}$ (1,3)

Much additional information may be obtained using interligand exchange in metal chelate extracts. Numerous variants of exchange realization combined give an opportunity to use all factors of information growth about concentrations of signal components - R, S and n according to equation (1).

So, similarity of Cu, Fe and Ni simultaneous determination results in waste water on measurement of summary lightabsorbance of these metals pyridinazonaphtolats extracts in $CHCl_3$ is much worse their results obtained by procedure modified by induring oxiquinoline into extract (Table 3). Oxiquinoline in metathetical reactions only with cooper pyridinazonaphtolate yields cooper oxinate in extract not absorbing light in the range of spectrum, which is used when signal is measured. The results of the determination on Cu lightabsorbance extract difference before and after oxine introduction are of less standard deviation, as results of Fe and Ni simultaneous determination on lightabsorbance of complexes with PAN which were not changed after oxine addition. When waste waters are analysed the task of choosing analytical reagent for Cd and Zn determination is for instance, what is better for determining these elements: PAN or ditizone? Prediction, as in [2], relative standard deviation S_r , of these elements simultaneous determination with PAN is about 10% (for the middle of determined concentrations fange), for ditizone - is about 5%. When Mn is present extraction of only Cd and Zn

with PAN is impossible: Mn is also extracted[5], and Sr prediction when Cd, Mn and Zn with PAN are determined simultaneously fails: Sr=30% Extractions of Cd and Zn complexes with ditizone in CHCl_3 also interfere Mn. In this case interligand exchange in extracts allows

Table 3. Results of simultaneous determination of Cu, Fe and Cu with PAN with (N2) and without use (1) of interligand exchange, $C \cdot 10^5 \text{ mol/l}$; $S_c \cdot 10^5 \text{ mol/l}$ - standard derivation, $n = 4$.

N	C_{Fe}	S_{Fe}	C_{Cu}	S_{Cu}	C_{Zn}	S_{Zn}
1	1,18	0,02	0,44	0,03	0,82	0,03
2	1,17	0,02	0,42	0,01	0,84	0,01

realization of the following scheme of analysis which provides determination of all components with certain validity Cd and Zn with ditizone being included. Extraction and concentration of Cu, Cd, Fe, Mn and Zn with PAN in CHCl_3 complexes at pH 10 → measurement of extract light-absorbance, A_1 → reextraction Cd, Mn and Zn in buffer solution with pH=4 → measurement of extract light absorbance A_2 → oxiquinoline introduction into extract and Cu, Fe and Ni determination as mentioned above → pH growth of reextract up to 11 and Cd, Mn and Zn extraction with oxine solution in CHCl_3 → introduction of ditizone into a solution subjected to the metathetical reaction with oxinates only Cd and Zn measurement extract light absorbance and calculations → concentrations resolution of Cd and Zn in ($A_1 - A_2$) with partial graduation coefficient for their pyridinazonephthalates and Mn concentration calculation.

The above example shows that interligand exchange in extracts combined with simultaneous concentrations determination may be used as a simple means of information growth about concentrations of components determined. Neutral chelates extraction into non-polar organic solvents may give essential information when complexing in solvents is studied, to use more exact when metrological unity of equilibrium constants determination results is provided. It has to do which possibility to use the neutral chelate state in organic phase as a standard one since when salt composition of water phase is changed.

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The most of the separating methods are based on the formation of a new phase in whose volume or on surface analyte is concentrated. Only extraction allows to obtain an equilibrium between several different in their nature and practically easily separated liquid phases. This ensures the principal possibility to distribute each of analytes in a separate phase.

Traditionally the extraction was considered as a process of interaction of an analyte with just an organic compound, i.e. solvent. Now a concept is getting confirmed that a process of extraction by the phase, i.e. a complex extractant with properties different from a solvent, takes place.

In multi-phase extraction systems the new phases being formed are always intermediate in their properties between the aqueous and the organic phases have different extraction ability.

The most widely spread and studied type of multi-phase extraction systems is the three-phase systems (TPS). There are more than 200 publications on TPS in literature but in most of them the formation of the third phase (3P) is considered as a drawback. In most of papers no difference is made between TPS of different types.

The lack of systematic arrangement of TPS made difficult to describe them and to find out the most prospective ones for their practical use.

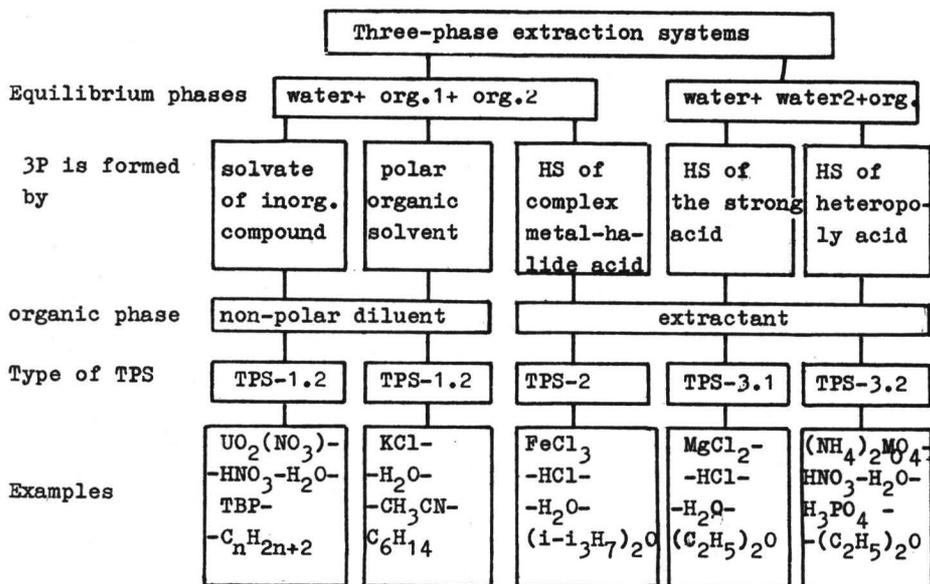
We have suggested the following classification of TPS on the basis of the nature of equilibrium phases (Table 1).

TPS-1.1 are formed while extraction from acid solutions by mixtures of amines or TBP with diluents takes place. The 3P of this type of TPS was used as an extractant for effective extraction and concentration of micro-elements for the first time [1].

TPS-1.2 are formed by lamination of an aqueous solutions of the polar organic solvent in the presence of inorganic salt and non-polar diluent. For the first time in analytical chemistry such system was used for simultaneous quantitative separation of three elements by extraction each of them into one of the equilibrium phases [2]. It could be assumed that the existence of significant number of polar solvents combined with different complex forming agents produces the 3P with essentially different properties and makes these systems useful for realization of multi-phase separation methods.

TPS-2 are the first ones which were practically used. In the most studied system $\text{FeCl}_3\text{-HCl-H}_2\text{O-DIPE}$ the 3P is formed by lamination of organic phase into ether phase and phase of hydrate-solvate (HS) of HFeCl_4 . Genesis, composition and properties of the 3P confirm that it

Table 1. Classification of TPS



is the second organic phase in its nature. Extraction ability of the 3P depends on free HCl content in it. For example, extraction of copper ($D \leq 0,3$) could result in its significant loss. But it is possible to optimize the conditions of extraction to make TPS-2 effective for group separation of micro-elements by "casting of the matrix" and makes method compatible with a lot of methods of final determination because the separated impurities are left in the aqueous phase, thus re-extraction is not necessary.

The most unusual type of TPS was discovered and studied by us [3]. TPS-3 are formed in systems $MeX_n \cdot Hx \cdot H_2O \cdot R_2O$ as a result of lamination of the aqueous phase at high acid and salt concentrations (Fig.1). Here $X = Cl^-, Br^-, ClO_4^-$; $R_2O = DEE, DPE, DIPE$. The 3P is produced by HS of HX with various ratio water/ether. The contents of the 3P are determined mainly by the nature of the acid and less influenced by cation of the salt. Thus for all chloride systems investigated $(H_2O + DEE) / (HCl + MeCl_n) = 5.5 (S=0,2)$. The confirmation of high water and acid content with considerable concentration of ether in the 3P (table 2) makes it unique extractant comprising two equilibrium aqueous phases with similar conditions of hydration and complex formation, being unusual for conventional extraction. The 3P has intermediate values of dielectric constant between aqueous and organic phases. This determines the same primary hydration (solvation) of ions and identity of complex anions' forms in the aqueous and the 3P. The distribution is mainly influenced by the proportion of charge and radius of ion at this conditions. The investigation of distribution of more than twenty complex ions proved

that in empirical equation $C_{3P} = K \cdot C_{init}^m$, for dependence of micro-components' concentration in the 3P on their initial concentration in solution parameters K and m are influenced by the charge and radius of complex ion (Fig.2).

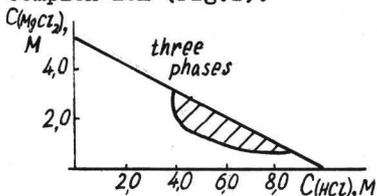


Fig.1. Phase diagram of TPS-3

Table 2. The composition of the 3P

TPS	Content., mol. %			
	H ₂ O	ether	HCl	salt
TPS-2	17-35	50-80	4-12	3-4
TPS-3	65-37	10-15	17-20	0.2-0.5

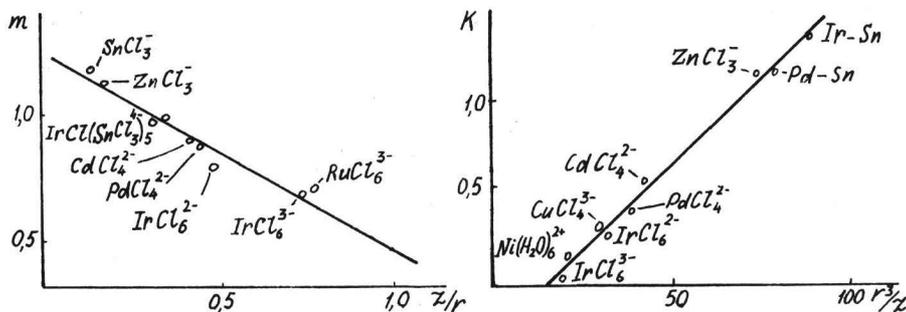


Fig.2. Dependency of parameters m & K on radius r & charge Z of ions

The large size of ion provides effective extraction even for high-charge ions (table 3).

The third phase of TPS-3 was used for extraction of platinum metals [4]. Being fast and simple, the procedures have good metrological characteristics.

Table 3. Extraction of platinum metals by the 3P of TPS

Complex	D
$[\text{OsBr}_6]^{2-}$	60
$[\text{PtCl}_2(\text{SnCl}_3)_2]^{2-}$	100
$[\text{IrCl}(\text{SnCl}_3)_5]^{3-}$	> 300
$[\text{OsCl}(\text{SnCl}_3)_5]^{4-}$	260
$[\text{RuCl}_2(\text{SnCl}_3)_4]^{3-}$	> 150
$[\text{PdCl}_2(\text{SnCl}_3)_2]^{2-}$	> 200

The use of the 3P as a high-effective extractant has advantage of easy re-extraction of extracted components.

To vary the extractive ability of the 3P it is necessary to change its contents by using different R_2O and / or anions. It is possible to predict new TPS-3 on the basis of discovered criteria using data on equilibria in $\text{MeX}_n\text{-H}_2\text{O}$ and $\text{HX-H}_2\text{O-R}_2\text{O}$ systems. To form TPS-3 it is necessary that: (1) an organic solvent (ether) should be dissolved sufficiently in the aqueous phase of the three-component system.

in the range of complete hydration of the acid (Fig.3); (2) for one mol of MeCl_n equivalents should be $h < 6$ mol of water in saturated solution (12 mol for perchlorates) (table 4).

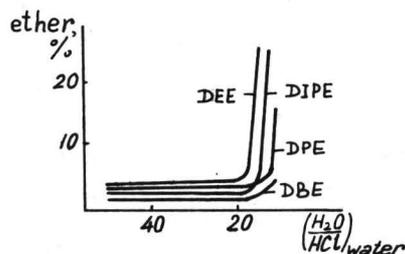


Fig. 3. Solubility of ether in HCl acid

Table 4. Solubility of salts and the TPS-3 formation

Salt	h	TPS	Salt	h	TPS
NH_4Cl	8.0	-	AlCl_3	5.4	+
NH_4Br	7.2	-	CrCl_3	10.4	-
NH_4I	4.7	+	CoCl_2	6.8	-
NaCl	9.0	-	NiCl_2	5.6	+
NaBr	6.3	+	NaI	4.7	+

Prospects for use of TPS are based on the two aspects of their novelty: - realization of multi-phase extraction method different from always two-phase conventional extraction methods; - intermediate properties of the 3P as unusual extractant. It should be mentioned that this unusual extractant could be also used for the two-phase extraction equilibrium.

The requirements to method of separation and concentration has been changed because of development of modern analytical methods. Very often now there is no need in quantitative separating of interfering components. It is sufficient to diminish their contents to 100-1000-fold excess over the concentration of an analyte. While using high-selective methods of final determination it is reasonably to perform group concentration of analytes. Thus non-selective extractant should be put in practice. TPS of all types could be effectively used to solve these problems. On the other hand, TPS-1.2 and TPS-3 could provide high-selective separation especially by application of non-traditional water-soluble reagents.

The results of investigation and practical application of TPS prove the possibility to enrich analytical practice by non-traditional extractants and extraction methods. Further investigations of TPS will contribute essentially extensive application of extraction in analytical chemistry.

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The new techniques proposed give wide possibilities for the extraction separation and concentration of organic and non-organic substances in three-phase systems and the selective extraction-photometric determination of elements in two-phase systems.

Three-phase systems. The new type of three-phase extraction systems (TES), viz., an aqueous solution of mineral acid salts, a polar and a non-polar solvent, has proved to be effective for the concentration and the separation of non-organic as well as organic substances present in various environmental [1]. The possibility was shown and the conditions were established for the cation extraction of Zn, Cd, V, Cr, Al, Ni, Co, Cu, Fe, Mg and rare earths in TES by means of pelargonic, capric and lauric acids in combination with allyl-, pentyl-, decyl- or benzylamine. The obtained experimental data on the extraction distribution of metals in TES led to the following conclusions concerning the possibility of the separation of elements by means of a single three-phase extraction.

1. Metals, which form oxygen-containing anions (e.g., vanadium, chromium, manganese, bismuth, molybdenum, tungsten etc.) are practically retained completely into the aqueous phase in the alkaline medium.
2. Metals, which form stable amine complexes (e.g., copper, nickel, cobalt, zinc, cadmium etc.), are quantitatively extracted into the middle phase under the same conditions.
3. Metals, which do not give compounds mentioned (e.g., iron, aluminium and rare earths), are extracted quantitatively into the upper phase.

The techniques were elaborated for the separation of triad metals, e.g., iron-copper-vanadium, iron-copper-chromium, iron-nickel-chromium etc., by means of a single three-phase extraction.

The study was performed on the extraction behaviour over 100 organic compounds of different classes: non-ionic, cationic and anionic surfactants, dyes, mineral oils, one-, two- and three-atom phenols, amines, monocarboxylic acids, fats and aromatic hydrocarbons. New techniques were worked out for the single extraction separation of three groups of organic substances - high molecular weight amines, surfactants and three-atom phenols; mineral oils or fats, one-atom phenols and low molecular weight amines; aromatic hydrocarbons, surfactants, dyes etc. We proposed a new technique for the concentration of metals or organic substances which allows not only concentrate but at the sa-

me time separate these substances transferring them into different organic phases of the three-phase system. New techniques were elaborated for separating and determining the mixture of 4-5 organic substances - two dyes, trioctylamine, fat and oil - by means of performing two parallel three-phase extractions over pH ranges 0-4 and 9-13. The table presents experimental data on the extraction behaviour of organic substances in TES: 3 M aqueous solution of sodium chloride - acetonitrile - hexane.

The distribution of organic substances between the three phases of the system: 3 M aqueous solution NaCl - CH_3CN - C_6H_{14}

Phases	Substances	pH _{ex}
Phase III (hexane)	Amines ($>C_{10}$)	8 - 14
	Mineral oils	0 - 14
	Fats (vegetable, animal)	0 - 14
	Lubricant materials (cable lubricants etc.)	0 - 14
	Monocarboxylic acids ($>C_{15}$)	0 - 6
	Aromatic hydrocarbons (benzene, tolyene, xylene)	0 - 14
Phase II (acetonitrile)	One-atom phenols (phenol, crezols, 1-naphthol)	0 - 9
	Surfactants (anionic, cationic, non-ionic)	0 - 14
	Amines (C_5-C_{10})	10 - 14
	Dyes (acid green anthraquinone N-2C, acid bright green anthraquinone N-4G, direct black 2C, crystal violet)	3 - 12
	Bengal pink B	0 - 6
Phase I (3M NaCl)	Amines (C_1-C_4)	0 - 8
	Three-atom phenols	8 - 14
	Soaps	8 - 14
	Monocarboxylic acids (C_1-C_3)	0 - 14
	Dyes (calcion, xylenol orange, direct black 2C, readily cleaned red, arsenazo 1, acid scarlet 2G, acid chromium dark blue)	3 - 12
	Chromazurol S	9 - 13

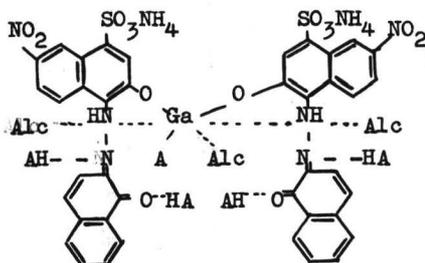
This table shows the possibility of separating quite different combinations of three organic compounds in a single extraction.

The calculations made for the interaction energies of substances with aqueous and organic phases allowed us to explain and predict the reasons of compound distribution into different phases of the three-phase extraction system.

Two-phase systems. In order to increase selectivity, sensitivity contrast of the reactions between metallochrome reagents and metals

in their extraction-photometric determination we proposed to use mixed extractants, composed of chloroform, concurrent acid reagents, monocarboxylic acids in particular and neutral solvating organic compounds, e.g., alcohols. A study has been made of the extraction of complexes of gallium, indium, aluminium and other metals with Pyrocatechol Violet (PCV), Eriochrome Black T (EBT), Bromopyrogallol Red (BPR) and other metallochrome reagents into the mixtures of chloroform, capronic (propionic) acid and n-butyl (n-amyl) alcohol.

Monocarboxylic acids and alcohols provide the extraction of hydrophilic coloured complexes into the organic phase by means of solvation of these compounds. Monocarboxylic acid anions influence concurrently the complexation between metals and dyes and thus promote the extraction selectivity of coloured compounds. The composition of complexes extracted into the organic phase can be shown on the example of gallium compound with ECB and capronic acid by the given formula.



The expression for extraction constant of gallium complex with PCV into the mixture of chloroform, capronic (HR) and propionic (HA) acids is as follows:

$$K_{\text{ex}} = \frac{[\text{Ga}(\text{NH}_4\text{H}_2\text{Ind})\text{RA} \cdot 6\text{HR}]_o [\text{H}^+]^3_w}{[\text{Ga}^{3+}]_w [\text{NH}_4^+]_w [\text{H}_2\text{Ind}^-]_w [\text{HA}]_o [\text{HR}]_o^7}$$

The concentration of coloured complex of gallium in organic phase was estimated by use of optical density of the extract, taking into account the degree of extraction of metal into organic phase. The concentration of H^+ was determined experimentally. The concentration of free gallium ions in aqueous phase was calculated taking into account the hydrolysis and the interaction with propionic and capronic acids by the equation:

$$[\text{Ga}^{3+}]_w = \frac{C_{\text{Ga}(w)}}{a + b\beta_1 + b^2\beta_2 + b^3\beta_3 + d\beta_1' + D^2\beta_2' + d^3\beta_3' + \beta_{\text{Ind}}[\text{H}_3\text{Ind}^-]^2}$$

where $C_{\text{Ga}(w)}$ - is overall gallium concentration in aqueous phase after the extraction;

$$a = \frac{10^{-2\text{pH}} + K_h' 10^{-\text{pH}} + K_h'' K_h''}{10^{-2\text{pH}}}$$

where K_h' and K_h'' - are first and second hydrolysis constants of gallium; $b(d)$ - is a coefficient, presenting the concentration of anions of propionic (capronic) acid in aqueous phase $\text{A}^-(\text{R}^-)$, calculated by use of the distribution constant P , dimerization constant K_d and dissoci-

ation constant K_{HA} (K_{HR}) by the equation:

$$b = [A^-]_w = - \frac{K_{HA} D_{HA}}{4 P_{HA} 10^{-pH} K_{D(HA)}} + \sqrt{\left(\frac{K_{HA} D_{HA}}{4 P_{HA} 10^{-pH} K_{D(HA)}} \right)^2 + \frac{C_{HA} K_{HA}^2}{2 K_{D(HA)} P_{HA}^2 10^{-2pH}}}$$

where

$$D_{HA} = \frac{K_{HA} + [H^+] + P_{HA} [H^+]}{[H^+] P_{HA}};$$

β_n and β'_n - are stability constants of gallium complexes with propionic and capronic acids respectively, β_{Ind} - is stability constant of gallium complex with PCV, $[H_3Ind^-]$ - is equilibrium concentration of PCV in aqueous phase:

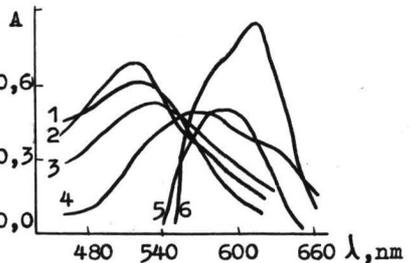
$$[H_3Ind^-] = \frac{(C_{PCV} - [Ga(NH_4H_2Ind)RA \cdot 6HR]_o) [H^+]_w}{(K_2 + [H^+]_w) (D + 1)},$$

where C_{PCV} - overall concentration of PCV, K_2 - dissociation constant of the phenol group of PCV substituted by metal, D - distribution coefficient of PCV. The concentration of monomeric form of propionic (capronic) acid in organic phase was calculated by the equation:

$$[HA]_o = - \frac{D_{HA}}{4 K_{D(HA)}} + \sqrt{\left(\frac{D_{HA}}{4 K_{D(HA)}} \right)^2 + \frac{C_{HA}}{2 K_{D(HA)}}}$$

The calculation was made with the computer M-6000 using programm in FORTRAN. The value $K_{ex} = (1,4 \pm 0,3) \cdot 10^4$ was found for this system.

The use of the mixed extractants promotes the optimisation of spectrophotometric characteristics of coloured complexes of metals. Fig. shows that in the case of gallium complex with ECB there is a counter-directed shift of absorption spectral lines of extracts of dye and complex compared with those in aqueous solutions. It provides the increase in reaction contrast from 30 to 90 nm. At the same time it increases the absorption intensity[2].



The absorption spectra of ECB(1-3) and its complexes with Ga(4-6) in aqueous solutions (3,4), chloroform solutions of HR(1,5) and mixed extractants(2,6)

The use of mixed extractants made it possible to elaborate exclusively selective, sensitive and contrast methods for gallium and indium determining.

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The determination of traces in insoluble lead compounds after their transformation to $Pb(DDTC)_2$ and extraction of the DDTC-complexes of Cd,Co,Cu,Fe,Ni,Zn thus formed offers another way for separation and preconcentration [1].These three phase extraction technique could solve some difficult analytical problems connected with the trace analysis in various pure substances.The possibilities for quantitative separation of traces of metal dithiocarbamates from a dithiocarbamate as residue are not investigated [2,3]. The precipitation of the macrocomponent as dithiocarbamate at simultaneous extraction of the dithiocarbamate complexes of the trace elements in small organic phase were applied to analysis of pure TeO_2 , $NiSO_4$ and $CoSO_4$.

Table 1. Three phase extraction for trace analysis in TeO_2

Element	2g TeO_2 dissolved in NaOH				1g TeO_2 transformed to $Te(DDTC)_4$		
	Recovery(%)			b/b_0^x	Recovery(%)		b/b_0^x
	pH 9	pH 10	pH 12	pH 10	pH 6,5	pH 10	pH 10
Co	98±2	98±3	90±3	0,99	98±2	98±2	0,99
Cu	99±1	99±1	94±4	0,99	96±2	98±2	0,97
Fe	97±2	96±3	3±1	0,96	90±4	95±3	0,88
Ni	98±3	98±2	85±3	0,99	94±2	98±2	0,90
Pb	98±3	98±2	-	0,98	68±5	94±3	0,92

The dependence of the three phase extraction on pH for trace analysis of TeO_2 (Table 1) indicates that the best results are achieved at pH 10.The TeO_2 samples were dissolved in NaOH and then the pH-value adjusted with HCl(1:1).Quantitative concentration of the trace impurities as dithiocarbamate complexes in the organic phase by direct transformation of the TeO_2 to $Te(DDTC)_4$ in presence of borax buffer(pH 10) is possible only for 1g sample.The standard addition method must be applied for calibration.For 2g sample the transformation from one solid phase(TeO_2) to another ($Te(DDTC)_4$) is not complete.

The three phase extraction technique permits the determination of traces in 1g $NiSO_4$ (Table 2).

Table 2. Three phase extraction for trace analysis in NiSO₄

Element	Recovery(%)					b/b ₀ ^x
	V _o /V _w					
	1:1	1:2	1:3	1:4	1:5	
Cd	82±5	90±3	>99	>99	>99	0,99
Co	90±4	98±2	>99	>99	>99	0,99
Cu	-	-	-	>99	>99	0,99
Fe	-	-	-	>99	>99	0,98
Pb	80±4	90±4	98±2	>99	>99	0,97
Zn	80±6	88±5	92±4	>99	>99	0,97

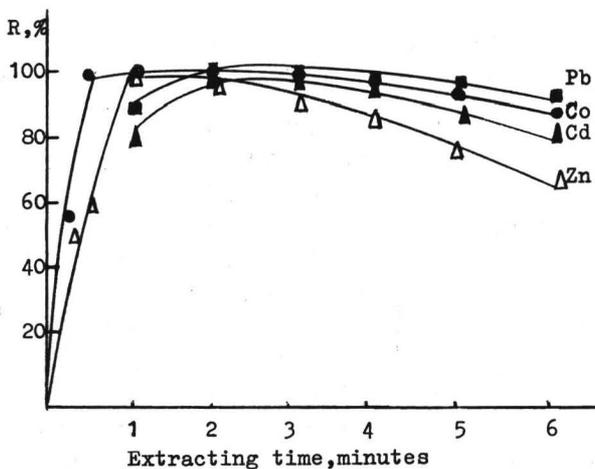
^xb - slope of the calibration curve after ethree phase extraction from matrix.
b₀- slope of the calibration curve after extraction from water standard solutions.

Table 3. Statistical characteristic of the three phase extraction procedure

Element	Concentration μg/g	TeO ₂		NiSO ₄	
		S _r (%)	DL ^x (μg/g)	S _r (%)	DL ^x (μg/g)
Cd	0,8	6	0,08	5	0,1
Co	1,6	4	0,2	3	0,3
Cu	0,8	3	0,05	2	0,07
Fe	1,6	5	0,3	4	0,5
Ni	1,6	4	0,2	-	-
Pb	1,6	4	0,3	4	0,5
Zn	0,8	6	0,08	5	0,1

^xDL - detection limit

The data represented on Fig. show the effect of extracting time on trace recovery in the extraction from NiSO₄ after dissolving one gramm of the sample in 10 ml H₂O and precipitating the macrocomponent as Ni(DDTC)₂. Lower recoveries of the trace elements in the organic phase at higher extraction time are presumably due to their adsorption on the solid phase during the extraction step.



Effect of extracting time on trace recovery

The three phase extraction is not appropriate for analysis of cobalt compounds. The cobalt diethyl dithiocarbamate residue does not permit the formation and separation of three phases and the atomic absorption measurement of the organic phase is impossible.

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Versatility, simplicity and great methodical flexibility of extraction in comparison with ion exchange accounted for widespread use of the extraction chromatography in 60's and 70's. However the nearly complete instrumentation, especially after the appearance of ion chromatography blocked the further development. The main disadvantage of the extraction chromatography - the unstability of the stationary phase on an inert support creates results in some serious difficulties in using the extraction chromatography columns in HPLC.

That is why the extraction chromatography now moves in the following directions:

- 1) the use of bond highly effective sorbents with a further fixation of a stationary phase on their surface together with up to date chromatographic equipment, e.g. ion-pair chromatography;
- 2) the use of solid phase polymeric materials with an extractant in the sorbent matrix (solid extractants);
- 3) the use for semipreparative separations of a drop counter flux chromatography as a kind of "column less" chromatography;
- 4) a modification of the classic extraction chromatography with the aim of enhancing the selectivity of separation, the proper choice of stabilization conditions for the stationary phase on a support and the automation of both the separation process and determination.

The selectivity of separation process can be enhanced by a combination of several separation mechanisms, as has been shown in [1-3]. We investigated chromatographic ion behaviour under simultaneous extraction and electromigration. The process was carried out by applying to the extraction chromatography column a DC voltage of various magnitude and polarity. If the direction of ion electromigration in the electric field coincides with the direction of the eluent flux, the potential is considered to be positive (i.e. accelerating). The change of polarity is considered to be equivalent to a "negative" potential (i.e. decelerating potential). An outlay of the used equipment based on a typical liquid chromatography is given in Fig.1.

The main units are: 1 - a DC power supply; 2 - a special chromatography column with an electrode compartment and cooling; 3 - a feeding pump; 4 - a photometric detector; 5 - a recorder.

The behaviour of Ag(I), Cu(II) and Ce(III) ions has been studied in systems HDEHP - aqueous acidic solutions. The potential gradient va-

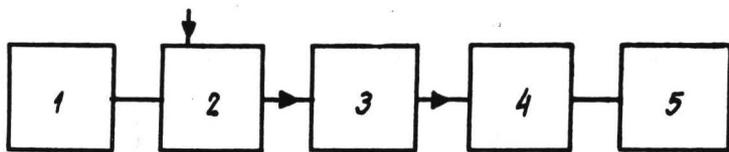


Fig.1. A diagram of an experimental set up with an automatic registration for the use potentials applied to the column

ried in the range of 10 - 30 v/cm. For comparison the chromatograms were obtained without no potential applied to the column and also the ions' migration in the electric field for no movement of the unstationary phase. Fig.2 gives the elution curves of Ag(I) ions with no potential and with a potential of different polarity. The eluent flux may kept constant at 0.2 ml/min·cm².

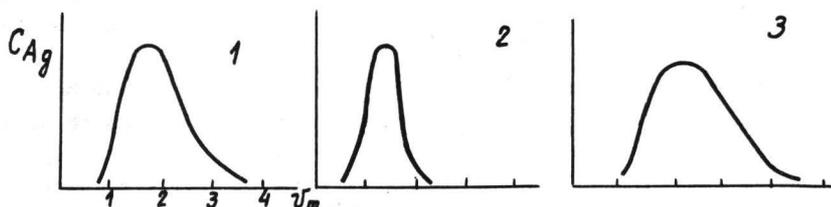


Fig.2. Elution curves of Ag(I) ions: 1 - no potential applied; 2 - accelerating potential applied; 3 - decelerating potential applied

In Table 1 data are given on chromatographic behaviour of Ag(I), Cu(II) and Ce(III) ions in case accelerating (+) and decelerating (-) potential applied to the column.

Table 1. Maxima of the chromatographic peak values (V_{mr}) and half-height widths ($W_{0.5}$) in units of free column as a function of experimental conditions

Voltage gradient, v/cm	Chromatographic parameters of the ions					
	Ag(I)		Cu(II)		Ce(III)	
	V_{mr}	$W_{0.5}$	V_{mr}	$W_{0.5}$	V_{mr}	$W_{0.5}$
0	2.0±0.2	1.4±0.1	2.8±0.3	1.5±0.1	2.5±0.2	2.9±0.3
+10	1.5±0.2	0.9±0.1	2.2±0.3	1.0±0.1	2.0±0.2	1.0±0.1
+20	1.3±0.2	0.6±0.1	1.5±0.2	0.7±0.1	-	-
-10	2.3±0.2	2.3±0.1	2.9±0.3	2.2±0.1	2.5±0.2	4.7±0.3
-20	3.5±0.3	3.4±0.2	3.2±0.3	2.6±0.1	-	-

All of the ions on application of the positive potentials are eluted earlier and the chromatographic peaks shorten. If the sign is reversed the picture is inverted, but the effect of the ion charge is difficult to evaluate. The results show that with an applied poten-

tial one can get the double effect: the change of selectivity because of the field influence upon the capacity factor and the increase in efficiency because of the peak width change.

On the base of the obtained results separation of V(IV) and V(V) and also Ce(III) and Pr(III) has been carried out in the system HDEHP - mineral acid under of acidity which is in "normal" chromatographic condition excludes the separation [4].

The used extractant - HDEHP has a low rate of mass transition for therefore one can expect an greater rate of mass transition and influence for the other systems with more faster kinetics.

An important characteristic of the stationary phase in the extraction chromatography is the stability of the phase on a support. The loss of the extractant into eluent may cause a change of the detector response because the extractant in the solution under certain conditional markedly shifts lowers the extinction of coloured complexes of some ion metals, as been shown in [5].

Two ways to overcome the drawbacks are possible: first - removal of dissolved extractants from the solution; second - the search of synergetic combinations of extraction systems with a higher stability of the phase on a support.

Experimentally it was found that upon passing the eluate through a layer "dry" inert support (e.g. teflon) excludes the extractant from the solution and excludes the associated systematic errors. That is why the experimental set up included an auxiliary column with the inert support put in after the separation column. TBP - HCL sistem for the separation of an ion mixture of Fe(III), Ni(II) and Mo(VI), chosen as a model sistem. The monitoring of elements contents was carried out using known photometric methods of Fe(III), Ni(II) and Mo(VI) determination. Under these conditions the analyses were made with and without the auxiliary column for the removal of the extractant. The results are given in Table 2.

Table 2. The results of quantitative determination of metals by extraction-chromato-photometric method

Metal	Taken, ppm	Determind metal, ppm					
		extractant not removed			extractant removed		
		$\bar{X}, n=10$	$\Delta X_m, \%$	$S_r, \%$	$\bar{X}, n=10$	$\Delta X_m, \%$	$S_r, \%$
Fe(III)	100	80	20,0	20.5	101	1.0	4.0
Ni(II)	20	20	-	4.2	20	-	3.1
Mo(VI)	30	22	26.7	13.6	29	3.3	4.5

Another way the increase of selectivity and efficiency can be obtained by the use of senergetic combinations of extractants. We have studied in detailla a system of two β -diketones: HDBM and HAA, which substantially betterthan others in kinetic parameters, thus providing high extraction of metalls under large flux rates [6]. Besides the sysem is higly stable on the support.

The synergetic effect here is shown on the example of extraction study of Ni, Co, Cu and U. Thecorressponding curves are given in Fig. 3. The composition of the formed complexes has been determined and

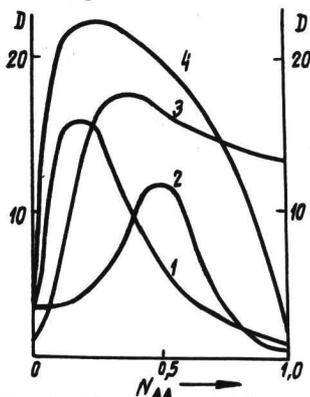


Fig.3. The curves of synergetic extraction metalls in the system HDBM-HAA- CHCl_3
1- U; 2- Co; 3- Cu; 4- Ni

the extraction constants has been evaluated. From the temperatyre dependence of the constants the thermodynamic characteristics of the proper synergetic extraction reaction have been evaluated. The analysis of the result makes it possible to suggest a mechanism of formation of synergetic adduct upon extraction of the ions.

Presented material shows that the possibilities of extraction chromatography are far from exhausted. In 86-87s the new models of liquid chromatographies tecniques with the inert fluid flow line were appeared. Their gidravlic line were made from titan or polimer materials for the biotechnology (LC 410 BIO - Perkin-Elmer, Bio LCC - Dionex, etc.). It can be relied upon succceccful using them in inorganic chromatography analysis with the strong acids or the complex reagents used as mobile phase.

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Several sulphur and nitrogen containing ligands have been already utilized for the selective separation of precious metals. However, chelating solid and liquid extractants of this type coordinate platinum metals very strongly, so that the release will be incomplete and the ligand may decompose. Evidence is given that the binding of anionic chlorocomplexes of metals predominantly via an anion-exchange mechanism makes the reversion of the extraction easier.

Some time ago we observed such effects by comparing two different types of functionalized polymers with incorporated sulfur bonded dithizone (P-D) or dehydrodithizone (P-TD) as functional groups [1,2].

Obviously, the properties of the anion-exchanger "P-TD" were more profitable in comparison to the chelating resin P-D. Although the sorbent P-TD removed gold, osmium and the primary platinum group metals effectively and reversibly, some special problems remained. For example it was difficult to adsorb and to elute Ir(IV) completely from the resin. Furthermore, the desorption yields of the primary platinum group metals were also affected by co-extracted iridium. Therefore we were keenly interested in the extraction behaviour of liquid analogues of P-TD resin. For this purpose various substituted derivatives of dehydrodithizone were prepared as demonstrated in Figure 1.

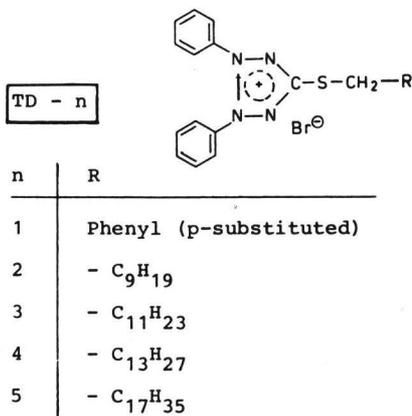


Fig.1. Formulaes and symbols of tetrazolium salts

These pale yellow, crystalline compounds are soluble in alcohols, halogenated alkanes and aromatics.

In order to investigate their basic properties, extraction procedures were carried out with $5 \cdot 10^{-3}$ molar solutions of the appropriate extractant, dissolved in chloroform. Equal volumes of a tenfold molar excess of the anion exchanger and aqueous metal salt solutions were shaken together for the appropriate time and then analyzed.

The aryl-substituted compound T-D1 extracts some metal ions in their most common higher oxidation states very easily. Au(III), Os(IV) and Ir(IV) are separated from the aqueous phase to more than 90 % as soon as they are shaken, while the extraction yield of Pt(IV) is remarkable lower and in the case of Fe(III) negligible. However, it is noteworthy that Pd(II)- and Pt(II)- are precipitated immediately in the organic phase by the aryl-substituted extractants.

In contrast to this behaviour, the alkyl-derivatives form ion-pairs with chloro-complex anions of PGM's without precipitation. As demonstrated by Fig.2 individual solutions of gold and precious metals can be treated successfully with TD-2 in the whole range of hydrochloric acid concentration. The results obtained leads to the following order of extractability. Au(III) > Os(IV) > Ir(IV) > Pt(IV) >> Pd(II).

As expected, the extractability of iridium drops down nearly completely after reduction to the trivalent state. However, the analogues behaviour of the Pt(II) species is somehow surprising, as in common ion-exchange systems chlorocomplexes of both Pt(IV) and Pt(II) are effectively extracted.

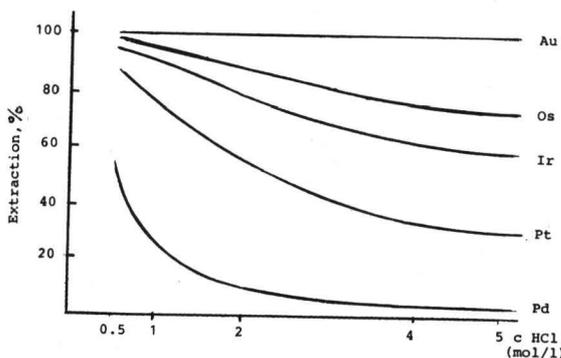


Fig.2. Effect of hydrochloric acid concentration on the extraction of individual metal ions by TD-2

Similar extraction yields, obtained for the decyl-derivative TD-2, resulted also by use of the other long-chain alkyl compounds. However, the tetradecyl - and octadecyl - derivatives exhibited an increasing tendency to form emulsions during the extraction step, so that further work was restricted to TD-2.

For a final investigation of the basic extraction properties of this tetrazolium salt mixtures of gold, platinum group metals and base metals in their common higher oxidation states were applied at increasing hydrochloric acid molarities. The data obtained are presented in a diagram (Fig.3).

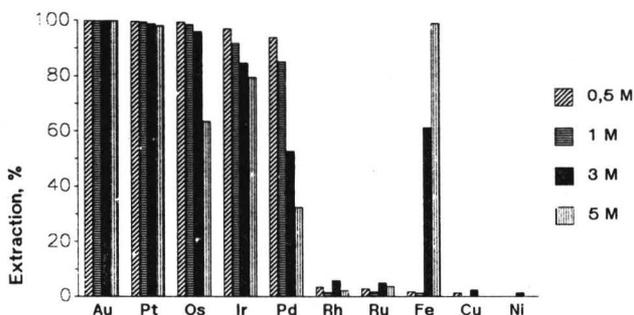


Fig.3. Simultaneous Extraction of precious und base Metals at different HCl-concentrations (shaking time 1h)

The result of this study meets our expectation from the results presented before. Thus Rh and Ru as well as Cu and Ni are extracted only negligible in every case, whereas the increasing concentration of hydrochloric acid furthers the formation of extractable chloro complexes of Fe(III). However, it is noteworthy that the base metal extracted can be removed simply by action of dilute hydrochloric acid.

The ability of a metal loaded extractant to be stripped is a very important property. In the case of the palladium-loaded tetrazolium salts, dilute perchloric acid acts satisfactorily as stripping medium.

A solution of thiourea is also effectiv in contrast to the thiocyanate ligands. The choice of a stripping agent depends on the actual separation problem as the presence of coextracted metal ions influences the stripping characteristics of the individual metals strongly.

For example, admixed Ir(IV) leads to coprecipitation of Pd and Pt during the thiourea procedure. Only gold is stripped completely and osmium remains unattached in the organic phase.

Repeating this experiment with a different feed solution (Fig.4) which did not contain Ir results, however, a quantitative release of Pt and Pd together with Au into the aqueous solution.

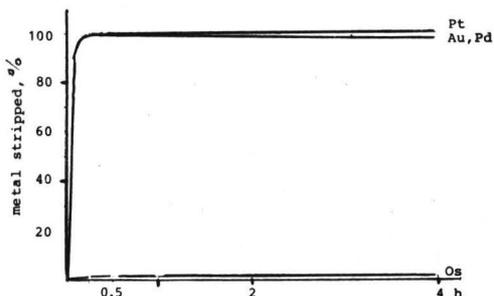


Fig.4. Simultaneous stripping of metal ions from TD-2 with thiourea (Ir not present) -extractant freshly loaded-

It is interesting to note that a three days storage of the loaded TD-2 causes a retarded release of Pt from the organic phase by action of thiourea.

This effect observed may be a hint at a more complicated mechanism of extraction, involving not only simple ion-pair formation.

Nevertheless, the class of sulphur containing tetrazolium salts is still under investigation and additional experiments may verify some advantageous properties.

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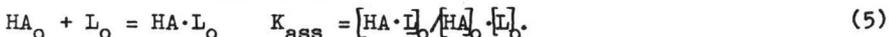
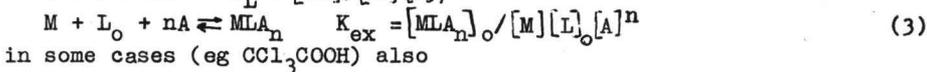
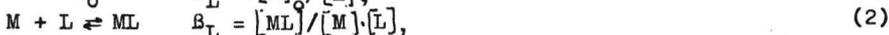
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Numerous papers report on metal ion extraction with crown compounds and different counter-ions, mostly picrates (eg the recent review [1]). In previous publications we have studied the influence of organic dye anion and the nature of diluent on metal extraction with dibenzo-18-crown-6, 18-crown-6 and 15-crown-5 (eg [2, 3]). This communication deals with the new results in the study of ternary complexes: metal ion - crown compound - organic anion and with the analytical use of such complexes.

There are three classes of ternary complex compounds in the organic phase: 1. contact ion pairs $M(\text{crown})^+ \text{Anion}^-$, 2. solvent separated ion pairs (outer-sphere complexes), 3. dissociated ions in solution. Classes 1, 2 and 3 can be distinguished from extraction equilibria data: the reactions in these cases are described by different equations. When the metal concentration in the organic phase was higher than 10^{-5} mol/dm³, we never observed dissociation in CHCl₃. For all phenolate ions the contact and solvent separated ion pairs have different UV spectra: the difference becomes more significant in derivated spectra. For example, in the spectrum of the second derivation of T118C6⁺ C₆H₂(SO₃CF₃)₃O⁻ there are two bands at 346 nm (contact ion pair) and at 361 nm (solvent separated ion pair). A structure, in which one anion is directly coordinated by metal ion while another is separated, was proposed for several $M(\text{crown})^{2+}$ ions.

Extraction equilibria are described by the equations:



In (1)-(5) L denotes crown compound, A counter-ion and the subscript "o" organic phase. Thermodynamic extraction constants were calculated from concentration constants using Davies equation for activity coefficients in the aqueous phase.

In contrast to well known extraction of picrates, the use of new counter-ion carboxylates and trifluorsulfonylphenolates makes possible extraction from strong acidic media.

Crown ethers as well as acyclic polyethers improve the extraction of lead carboxylates. The synergetic effect increases for halogen-carboxylic acids. The extraction of carboxylates with crown ethers was also effected for a number of alkali and alkaline earth metals, silver and thallium (Table 1).

Table 1. Extraction constants of M 18C6 (CCl₃COO)_n complexes at 290 K. Concentration constants for 1 M LiCCl₃COO

M ⁿ⁺	lgK _{ex} (conc.)	lgK _{ex} (therm.)	
Ag ⁺	1.23 ± 0.05	1.8	P _{HA} = 0.07
Tl ⁺	2.54 ± 0.03	3.0	
Na ⁺	0.34 ± 0.02	0.9	K _{ass} = 80
K ⁺	2.31 ± 0.01	2.9	
Rb ⁺	1.53 ± 0.03	2.0	[∞] Cs(18C6) ₂ CCl ₃ COO
Cs ⁺	1.54 ± 0.03 [∞]	2.4 [∞]	
Ca ²⁺	0.94 ± 0.02	2.2	
Sr ²⁺	2.98 ± 0.01	4.2	
Ba ²⁺	2.40 ± 0.02	3.6	
Pb ²⁺		8.02	
Bi ³⁺		6.8	

We have not found any communication on Bi(III) extraction by crown ethers in cationic form. The reason of this may be the formation of Bi(OH)₃ hydroxide in slightly acidic media. The extraction system 18-crown-6 - CCl₃COOH gives us the possibility to complete Bi extraction from strong acidic media (pH 1-2) into CHCl₃ or CH₂Cl₂. The formation of unstable complexes BiCCl₃COO²⁺ (β = 10) in aqueous phase and Bi18C6 (CCl₃COO)₃ in organic phase has been found.

The substitution of NO₂ group in picric acid molecule by SO₂CF₃ group increases the dissociation constant of phenole molecule (for C₆H₂(CF₃SO₂)₃OH, pK_a = -2.6) and the extraction constants of corresponding complexes (Table 2).

Table 2. Extraction constants of MLA_n complexes (lgK_{ex})

A \ ML:	CsPEG-1500	TlPEG-1500	PbPEG-1500	Cs18C6	Tl18C6	Pb18C6
C ₆ H ₂ (NO ₂) ₃ O	2	4.1	8.4	4.4	6.3	11.7
C ₆ H ₂ (SO ₂ CF ₃) ₃ O	6.3	7.6	11.5	7.8	9.8	13

Acyclic polyethylene glycoles (PEG) are another class of extractants for metal ion extraction. The highest K_{ex} values were obtained for PEG-1000 and PEG-1500 (the number of CH_2CH_2O groups is 23 and 35)

The best extraction was observed for Tl^+ and Pb^{2+} (Table 3). The

Table 3. Thermodynamic extraction constants of MLA_2 complexes at 290 K (A = 1-picrate, 2-methanyl yellow)

L	Ca^{2+}		Sr^{2+}		Ba^{2+}		Pb^{2+}	
	1	2	1	2	1	2	1	2
PEG-400		6.4		7.4			7.7	9.4
PEG-600	5.1	6.5	6.35	7.6	7.8	9.2	8.25	9.7
PEG-1025							6.4	
PEG-1000			6.65		7.95		8.35	
PEG-1500		6.7	6.7	7.7			8.35	9.8
PEG-3000							8.0	
PEG-4000							8.0	8.5
DB18C6		5	4.9	6.2			6.6	8.0
18C6	6.04		9.7	10.4	9.7	10.7	11.8	13.2
DB24C8	3.06		3.98		6.85		6.31	

substitution of OH groups in PEG by quinoline increases the extraction constants of lead complexes, but in contrast to PEG such a compound extracts 3d metal ions. The extraction constants of polypropylene glycol complexes are comparatively small.

The values of K_{ex} for acyclic polyethers depend on diluent much stronger than those for macrocyclic crown ethers. The parameters E_T or $BP^{\#}$ permit one to predict the best diluents: $CHCl_3$, CH_2Cl_2 , $C_6H_5NO_2$. But in this group of solvents we have not found any correlation between E_T , $BP^{\#}$ and lgK_{ex} (Table 4).

Table 4. Extraction constants of $PbPEG-1500 A_2$ complexes in different solvents (lgK_{ex})

Solvent	$BP^{\#}$	E_T	Methanyl yellow	Picrate
$CHCl_3$	4.5	39.1	9.8	8.35
CH_2Cl_2	4.0	41.1		8.9
$C_2H_4Cl_2$	3.5	41.9	8.5	7.7
$C_6H_5NO_2$	4.3		ca 9.7	
C_6H_5Cl	2.4	37.5	< 6	< 5

The ΔH values for $\text{PbPEG-1500(picrate)}_2$ and $\text{PbPEG-3000(picrate)}_2$ are nearly the same: -21.1 ± 1.0 and -20.8 ± 0.5 kcal/mol, while for $\text{SrPEG-1500(picrate)}_2$ $\Delta H = -18 \pm 1$ kcal/mol.

The extraction constants depend not only on the cavity size of crown ether molecule. The complete description of extraction process needs an account of all ligand groups in coordination spheres. The correspondence between the geometric and electronic structures of metal ion and its ligand attachment in ternary complex is a reason of perfect extraction instead of "macrocyclic effect", which cannot be used for podands. It is clear that the role of counter-ion and solvent in extractability and selectivity may be significant and they may change the extraction properties of metal-crown ether system.

A model based on analogy between filter and crown-ether molecule in a two-phase organic solvent-water system is proposed for potassium channel selective filter. The selectivity of K^+ channel can be quantitatively described by this model.

A selective photometric method for potassium determination using tropeoline OOO-II and 18-crown-6 is proposed for a number of polyionic solutions for injections containing Ca, Na, CO_3^{2-} etc. For the highest selectivity of photometric sodium determination with 15-crown-5 was obtained using toluene and xylene as diluents.

A number of photometric and atomic-absorption methods for lead(II) determination in water, food, alloys have been developed. Lead can be extracted from slight acidic solutions into CHCl_3 with 18-crown-6 using Methanyl Yellow as counter-ion ($\xi = 5 \times 10^4$). We can determine lead after extraction with 18-crown-6 and CCl_3COOH directly in organic phase with PAR or after reextraction with sulfoarsazen. All these methods were used for lead determination in different alloys (0.01-1 % Pb). Bismuth can be separated by extraction in CHCl_3 with 18-crown-6 and CCl_3COOH from Co, Cu, Zn, Cd, Fe, Al etc. Photometric and atomic-absorption methods for Bi determination after extraction are proposed.

A number of photometric extraction methods for determining crown ether (> 0.1 ppm) and acyclic polyethylene oxides (> 1 ppm) in various solvents have been developed. The distribution constants of crown compounds in several systems with some diluents and different ionic background in aqueous phase were determined by these methods.

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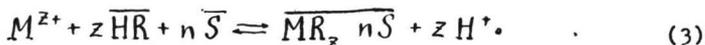
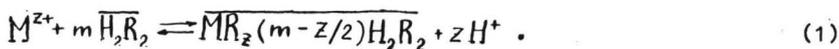
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Carbonic acids (CA) of various types - fatty monobasic, dicarbo-
nic (such as sebacynic), aromatic, fatty-aromatic, α -oxyfatty-
aromatic and their halogenderivatives are effective for extraction
of some metals, including $Cu, Co, Ni, Mn, Cd, Zn, Hg, Bi, Sn, Al, Ge, Be, Fe$ and many others. In comparison
with extragents, appertained to another classes CA distinguish one
self by accesibility, low toxic properties, low solubility in the
water (for caprylic - C_8 , and pelargonic acids - C_9 , it has va-
lue less then 0,2 and 0,1 gramme (litre respectively), good abili-
ty for regeneration (ability to act in the exclusive circles),
high distrubtion coefficients for carboxylated complexes of metals
(CCM), wide possibilities for variation of CA initial concentrati-
ons in the dussolvents and values of pH under extraction. These
properties advance CA as perspective analytical reagents for iso-
lation, concentration and determination of some groups and separate
metals from various materials and media.

CCM forming in the heterogeneous extraction systems, have vari-
ous chemical composition (normal carboxylates, "oversolvated" car-
boxylates, variousmetal and variousligand mixed and polymeric car-
boxylates), extraction constants values K_{ex} which beeing dependent
on basic properties of metal cations, ionic strength, pH, concen-
trations conditions and polarity of organic phase

We have investigated many CCM's for their subsequent using in
the chemical analysis [1-6]. For example some of them are pre-
sented in the Table 1, where symbols HR and H_2R_2 designate main-
ly monomeric or dimeric state of CA molecules of proper monobasic
acids in the dissolvent respectively [1-6].

Under using of undiluted liquid CA or their concentrated solu-
tions in the dissolvents mixed cation-exchange-solvate mechanism
of extraction takes place, and interaction may be expressed by one
of three common shemes:



Here M^{Z+} symbol of Z-charged cation and line over symbol means
that it belongs to organic phase.

Table 1. Some characteristics of CCM, forming under extraction by benzilic (diphenyloxyacetic), caprylic (C₈) and pelargonic (C₉) acids solutions.

Ion	Composition of aq. phase	Composition of org. phase	CCM composition	lg K _{ex}
Cu ²⁺	0.25M NaClO ₄	benzilic acid, (HR) heptanol	CuR ₂	-3.80±0.15
Ni ²⁺	0.25M NaClO ₄	benzilic acid, (HR) heptanol	NiR ₂	-6.40±0.25
Mn ²⁺	0.25M NaClO ₄	caprylic acid (H ₂ R ₂)-CCl ₄	MnR ₂ ·3H ₂ R ₂	-11.22±0.11
Pb ²⁺	0.5 M NaCl + 0.05 M MgSO ₄	pelargonic acid (H ₂ R ₂)-CCl ₄	Na ₂ PbR ₄ ·4H ₂ R ₂	-13.20±0.21
Zn ²⁺	0.5 M NaCl + 0.05M MgSO ₄	pelargonic acid (H ₂ R ₂)-CCl ₄	ZnR ₂ 2H ₂ R ₂	-5.65±0.25

Information about stoichiometry and K_{ex} values allow to choose conditions of the quantitative isolation of metals from aqueous phase. Thus, values of pH_{0.99}, corresponding extraction degree E=99% under proper ratio between arganic and aqueous phase volumes $\tau = \sqrt{V}$ and at proper CA concentration may be computed as (scheme 1):

$$pH_{0.99} = \frac{1}{Z} \left(2 + \lg \tau - \lg K_{ex} - m \lg [H_2R_2] + \lg \gamma_M \right) \quad (4)$$

Here γ_M^i - so called "side reaction" coefficient [7], which takes into account the whole complex formation processes of M^{Z+} ion in the aqueous phase, whose value is inverse regarding the part of noncomplexed ion - $\alpha_{M^{Z+}}$ from total analytical concentration C_M in the aqueous phase.

According obtained information about K_{ex} and literary data for γ_M^i values, we have developed some methodes for group separation of heavy and rare metals (Fe, Pb, Zn, Cd, Mn, Co, Ni, Sn) from nature waters, including sea waters. With using of nondiluted liquid fatty acids, such as caprylic and pelargonic we have reached degree of concentration $\tau = 100$ at guaranteed efficiency of extraction E ≥ 99% by single extraction, with matrex components (ions of Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, HCO₃⁻)

remaining in the aqueous phase. This fact provide for elaboration of some straight electrothermic methodes AAS determination of Pb , Zn , Cd , Mn , Sn directly at the organic phase, free from matrex effect and influence effects, due to other components. Detection limit (DL) for all mentioned methodes does'nt exeed 0,1 mcG/l, it's absolute value beeing near 0,1 nanoG. Relative standard deviation (S_r) for initial solutions, containing 1-10 mcG/l variates in the range 0,07-0,15.

Another way of utilli ation of CCM for chemical analysis purposes we have reall ed by extraction of "various-ligand" mixed complexes, containing exept anions and solvating molecules of CA, some hydrophobic chromophoric ligands (O -phenantraline= Ph , pyridilazonaphtol= $HPAN$, morine= HMO , α -nitrozo- β -naphtol= HNN) On this base we have developed some selective and sensitive combined methodes of extraction-photometric determination of Fe , Cu , Co , Ge in the nature waters. Some characteristics of dyed mixed CCM's are presented in the Table 2.

Table 2. Some characteristics of dyed various-ligand CCM's

Metal	Extragent	Cromoph. ligand	Chem. compos. of CCM	τ	$pH_{0.99}$	λ_{max} (nm)	$\epsilon_{max} \times 10^4$
Fe	5M pelar-gonic acid,	$3 \cdot 10^{-5}M$ Ph	$Fe(Ph)_3R_2 \cdot 6H_2R_2$	50	4.3	512	1.1
Cu	5M pelar-gonic acid	$10^{-3}M$ HPAN	$CuPANR \cdot H_2R_2$	25	3.2-4.6	550	2.5
Co	3M pelar-gonic acid	$5 \cdot 10^{-4}M$ HNN	$Co(NN)_2R$	10	4.0	415	2.1

These methodes are characteri ed with concentration DL, not exeeding 1,5 mcG/l; S_r beeing in the range 0,05-0,1 for initial concentrations of elements $\sim 3-10$ mcG/l.

Exhaustive extraction of CCM's with guaranteed $E \geq 99\%$ affords an opportunity for preparation of the standard solutions of metals in the nonaqueous media, which have chemical composition closely imitating composition of crude oils, oil products and other non-aqueous liquids. Such solutions have great significance for developing of quantitative spectroscopic methodes. By double extraction from standard aqueous solutions at proper pH values and fol-

lowing dilution of extracts with appropriate nonaqueous liquids w we were able to prepare the whole range of nonaqueous standards, some examples of which are presented in the Table 3.

Table 3. Examples of nonaqueous standard solutions of metals, obtained by extraction with CA

metal	$\bar{C}_M, \text{mC/l}$	Extragent composition	pH _{0.99}	Composition of CCM
Cu ²⁺	0.100	2M caproic ac. -heptanol	4.8-5.5	CuR ₂ ·2HR
Cu ²⁺	5.00	undiluted pelarg. ac.	4.2-5.5	Cu ₂ R ₄ ·2HR
Fe ³⁺	2.00	2M heptanoic ac. -heptanol	3.5-4.3	NaFeR ₄
Pb ²⁺	0.03	2M pelargonic ac. - CCl ₄	4.2-5.0	Na ₂ PbR ₄ ·4H ₂ R ₂
Mn ²⁺	0.50	undiluted caprylic ac.	5.5-6.0	MnR ₄ ·3H ₂ R ₂

Thus, it is possible to obtain nonaqueous solutions, containing 10^{-5} - 10^{-2} % of different metals in the various organic matre^x (hydrocarbons aromatic compounds higher alcohols and so on), which are stable at keeping and homogenous in cimposition. The stability of such samples and reproducibility of their analytical properties (with coefficient of variation less, than 3% under testing during one year) have been proven by continious control.

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The coloured liquid ion exchangers are characterized by simplicity of their production, selectivity and the low limit of detection of some ions and biologically active organic substances. The solvent which presents the second phase is reusable without removal from the reaction zone. Optical density of the solvent is measured both in water and organic phases depending on the substance which is being defined. The reagents widely available and cheap such as crystal violet, brilliant green, xylene orange and other compounds are used for liquid ion exchangers production. Getting mixed with complex ions these coloured substances produce compounds being little dissolved in water. These solid associates in the form of residue can be preserved for a long time. They achieve the colour of that dye stuff in which they are in this solution depending on the latter acidity. Thus from 6-9 M solution of hydrochloric acid produced by crystal violet (CVCl) and chlorstibation (A^-) is separated in the form of an orange residue $\mathcal{L}V$. The associate orange colour is conditioned by two charge form of crystal violet being formed at the high acidity of the solution. To get a coloured liquid ion exchanger 30-50 ml of water are poured into the separating funnel, 0,05 g of solid ion associate is put in, 30 ml of toluene or some other solvent are added. Being mixed the solvent gets the violet colour as a result of transition of two charge form of the dye stuff into one charge form. Then it is filtered through the dry paper and dissolved with the solvent to the necessary optic density which is not changed if preserved in a dark place. It should be noted that the dry solid associate without water is not dissolved in toluene. The associate may undergo the exchange reactions as well as acidity-reduction ones producing crystal violet without application of any organic solvents; the optic density of water solution permits to judge about the concentration of the substance which is being defined. The latter is introduced into one of the phases depending on its solubility. The choice of the phase for measuring the optic density depends on the existence of some other coloured substances; in case of the absence of those mentioned above the optic density measurement can be carried out in any of the phases. When the water phase is either dyed or turbid the optic density measurement is carried out in the organic phase.

The coloured ion exchangers may undergo the reactions of exchange and acidity-reduction. In the exchange reactions cation of the

organic dye stuff is able to be substituted for colourless cations or coloured organic cations of various nature. The substitution degree depends on the nature of organic cation, its structure, basicity, hydrophobity, resistance and solubility of the compounds which are being formed. These and other factors define selectivity of pointing out various organic cations with the help of coloured liquid ion exchangers.

The acidity-reduction reaction of coloured liquid ion exchangers with various substances has been studied by the author of the paper together with Dekhtyarenko L.I. and Yankovskaya E.V. The detection limit depends on the substance nature.

Table 1. The organic substances detection limit in the reaction with CVA

The substance which is being defined	Detection limit mkg/ml
cysteine	0,16
glutathione	0,25
pyrocatechol	0,06
hydroquinone	0,15
resorcinol	0,54

As far as sensitivity is concerned the new method has some advantages comparing with those already existing. Thus while defining cysteine with CVA the detection limit is one order of magnitude below (lower) than by the

modified nitroferricyanide and phenantroline methods and much lower than by ninhydrin method. Sergeev et al. have studied the selective extraction-photometry defining some phenols, amines, aminoacids and heterocyclic with nitrogen compounds by means of CVA [2].

Coloured liquid ion exchangers are produced as a result of the interaction of colourless organic cations and coloured complex compounds of the type $\text{Fe}(\text{SCN})_4^-$, $\text{Co}(\text{SCN})_4^{2-}$ and the like as well. When $(\text{R}_3\text{NH})_2\text{Co}(\text{SCN})_4$ compounds with phosphate ions are added to associate solution the decrease of optic density of solution is observed. Sulphates, chlorides, fluorides also affect the colour associate $(\text{R}_3\text{NH})_2\text{Co}(\text{SCN})_4$ but to the lesser degree than the phosphates.

The coloured liquid ion exchangers have been studied on the basis of the associates with alkylammonium cation and intra-complex compound of cation of the metal with xylene orange [3]. Carrying out these reactions in the solutions of bicarbonate in presence of alkylamines salts allows to reduce the limit of detection of metals ions and to increase reaction contrastivity due to reextraction of surplus amount of xylene orange when exchanging it to bi-

karbonate-ions. The coloured associates resistance depends on the nature of colourless organic cation. More resistant coloured associates react to the presence of mineral salts such as chlorides and sulphates of sodium to a lesser degree (Table 2).

Table 2. Dependence of optical density of associates produced by yttrium (III) and xylene orange with organic cations $[\text{KHCO}_3] = 0,2 \text{ mol}$

0,1 M chloride salt of reagent in the mixture CCl_4 + propanole	Optical density	
	in salts absence	in salts presence
cetylpyridine	0,99	0,38
alkyltrimethylammonium ($\text{C}_{10}-\text{C}_{16}$)	0,90	0,08
trialkylbensilammonium (C_7-C_9)	0,97	0,05
dodecylammonium	0,98	0,90
the primary alkylamines fraction ($\text{C}_{10}-\text{C}_{12}$)	0,97	0,90
dimethyldodecylammonium	0,96	0,63
dimethylalkylammonium ($\text{C}_{14}-\text{C}_{16}$)	0,99	0,92

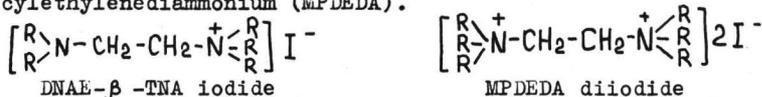
The coloured associates undergo the reactions of exchange and acidity-reduction with ions and organic compounds at different phases: liquid ones not mixing, the solid phase - water, as well as in the micellar solutions where the micelles act as microphase.

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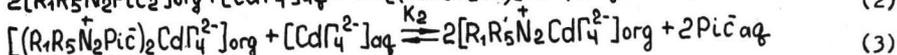
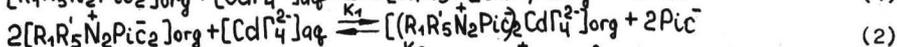
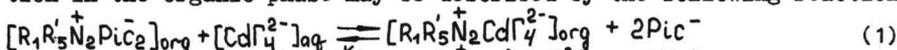
It is known that bibasic extragents of anions, namely, dialkyl tin salts [1], bis-quaternary phosphonium salts [2], exhibit pronounced bivalent anion affinity. We have investigated as metal extragents the salts of dinonylaminoethyl- β -trinylammonium (DNAE- β -TNA) and methyl pentadecylethylenediammonium (MPDEDA).



The above compounds have been synthesized by stepwise alkylation of ethylenediamine and purified in the octane-dimethylformamide extraction system. Extraction of cadmium bromide and iodide complexes by MPDEDA picrate in toluene and its binary mixtures with chloroform, amylacetate and octane by the intermediate exchange method has been investigated. For comparison with monofunctional QAS, cadmium extraction by trinyloctadecylammonium (TNODA) has been studied under similar condition.

The chemical analysis of extracts, the analysis of bilogarithmic dependences of cadmium distribution coefficients on a reverse coefficient of picric acid distribution as well as the comparison of the dependences of side reactions coefficients, calculated from tabular instability constants of cadmium iodides and bromides complexes, and tentative exchange constants on concentration of iodide and bromide ions have revealed that mono-QAS and bis-QAS extract cadmium as a bivalent particle $Cd\Gamma_4^{2-}$.

In this case equilibria for MPDEDA in the absence of self-association in the organic phase may be described by the following reactions:



Analysis of a great bulk of data (about 100 experimental points) at concentrations ranged from 10^{-3} to 10^{-5} for bis-QAS and from 10^{-2} to 10^{-5} m/l for cadmium has shown that with an anionexchanger being filled with cadmium up to 50%, the extraction equilibrium is described by Eq.(2), in the case of cadmium exceeding 50% Eq.(3) is employed, while Eq.(1) is not applicable. For cadmium percentage being less 50%, the value of K_1 (Table 1) is estimated. Constant values of K_1 are indicative of the extraction process described by Eqs.(2,3). From these data it follows that the tentative exchange constants both for iodide and

CdI_4^{2-} -anions with decreasing a toluene content in the mixture that makes their anion-exchanger affinity different. Chloroform, amylacetate added to toluene affects only slightly the extractibility of cadmium halogenide complexes by MPDEDA salts.

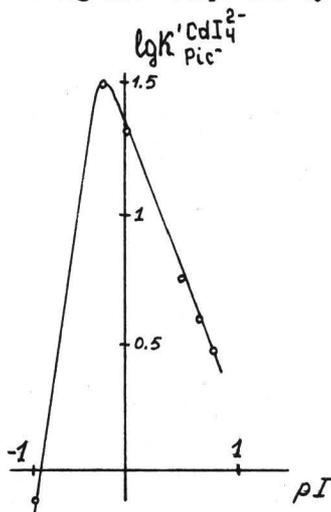


Fig.1. The bilogarithmic dependence of tentative K'_{exch} on iodide ion concentration for MPDEDA in toluene

Dinonylaminoethyl- β -trinonylammonium iodide is an intermediate substance in the MPDEDA synthesis. A specific feature of DNAE- β -TNA, as compared to monofunctional QAS, is their high solubility in inert aliphatic hydrocarbons as well as possibility to control the number of ionogenic sites in an extractant molecule by pH variation.

The extraction of halogenide complexes of mercury (II) from alkali media by DNAE- β -TNA salts has been examined by the intermediate exchange method. A study has also been made of the extraction by TNODA salts.

In both cases the extraction halogenide complexes of mercury (II) proceeds as the anion exchange reaction:

$$RR_3N^+ \cdot An^- + HgI_3^- \xrightleftharpoons{K'_{exch}} RR_3N^+ \cdot HgI_3^- + An^-$$

where $R - C_9H_{19}$,

$R' - C_{18}H_{37}$ for TNODA and $R' - (C_9H_{19})_2N$ for DNAE- β -TNA.

The nature of substituents at the tetrasubstituted nitrogen atom only slightly influences the extractibility of halogenide complexes mercury (II) by TNODA and DNAE- β -TNA salts, with polar solvents (alcohol, chloroform, toluene) being used. However, stronger branching in the DNAE- β -TNA molecule and a greater size of its radical initiate an abrupt increase of their solubility in inert aliphatic hydrocarbons as compared to monofunctional QAS to yield a pronounced analytical effect. Table 2 summarises the values of $K'_{exch} \frac{HgI_3^-}{Cl^-}$ obtained for

Table 2. $K'_{exch} \frac{HgI_3^-}{Cl^-}$ values obtained for the salts of TNODA in toluene and DNAE- β -TNA in decane

Anion	TNODA		DNAE- β -TNA	
	toluene	decane	toluene	decane
$HgCl_3^-$	$1.2 \cdot 10^5$	practically	$5.0 \cdot 10^5$	$1.0 \cdot 10^6$
$HgBr_3^-$	$3.2 \cdot 10^7$	undissolved	$9.8 \cdot 10^7$	$3.4 \cdot 10^8$
HgI_3^-	$9.8 \cdot 10^9$		$1.0 \cdot 10^{10}$	$1.8 \cdot 10^{12}$

the salts of TNODA and DNAE- β -TNA in toluene and decane. A use of decane solutions of DNAE- β -TNA salts instead of toluene solutions of TNODA salts causes a pronounced increase of the extractibility of the mercury (II) halogenide complexes that may be due to decreased expenditures of energy in resolution during the exchange process. But the expenditures of energy decrease with strengthening of the hydrophobic nature of HgI_3^- -ion that gives rise to different anion-exchanger affinities (Table 2).

The extractibility of halogenide complexes of mercury (II) is essentially affected by the nature and concentration of a ligand. Fig. 2 depicts a bilogarithmic dependence of tentative exchange constants of $K'_{exch} \frac{HgI_3^-}{Cl^-}$ on concentration of iodide ions. Similar dependences with maxima at chloride and bromide ions concentrations equal to 10^{-1} and $2 \cdot 10^{-2}$ m/l respectively, have been obtained in the case of extracted chloride and bromide complexes of mercury (II). Maxima on the curves are attributed to the fact that at these ligand concentrations mercury (II) is in the form of HgI_3^- -anions which exhibits the highest extractant affinity. A maximum shift towards highest ligand concentrations in the series $I^- < Br^- < Cl^-$ is due to weakening of the strength of extracted HgI_3^- -complexes in this series.

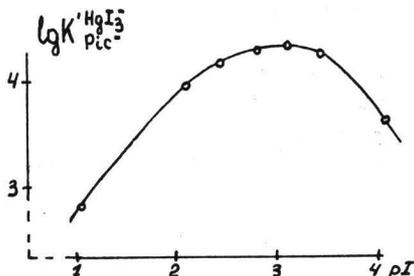


Fig. 2. The bilogarithmic dependence of tentative $K'_{exch} \frac{HgI_3^-}{Cl^-}$ on iodide ion concentration for DNAE- β -TNA in decane

The obtained data are correlated well with tabular K_{inst} values of the corresponding halogenide complexes of mercury (II). An increase in the $K'_{exch} \frac{HgI_3^-}{Cl^-}$ value, with transition from chloride to iodide complexes of mercury (II) is explained by increasing the size and strengthening hydrophobic nature of a metal complex anion, as a ligand size increases.

Thus, application of new bifunctional ammonium extragents, i.e. MPDEDA and DNAE- β -TNA improve essentially the selectivity of extraction of halogenide complexes of mercury and cadmium that may be employed for developing the highly effective methods of extraction, concentrating and determination of the given metals. It may be presumed that the synthesized extragents will possess the raised affinity to other bivalent anions. The authors possess data which are indicative of elevated affinity of SO_4^{2-} and WO_4^{2-} -ions to bis-QAS.

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IN ANALYTICAL CHEMISTRY

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Dialkyldithiophosphoric acids $(RO)_2PSH$ are widely used as reagents for the solvent extraction of inorganic metal salts. The values, characterizing the process of extraction (constants of extraction, partition constants and stability constants of complexes) give a possibility to use these reagents for the separation and concentration of many metal ions. For example di-2-ethylhexyldithiophosphoric acid D2EHDPH has been applied for the separation of Bi(III), Cu(II), Tl(I), Ag(I), As(III) [1,2].

However this is not a good selective reagent since it forms very stable complexes with many metal ions that are extracted from aqueous solutions under equal conditions. Therefore the procedure of separation of metal ions by D2EHDPH is too complex. So separate the metals more suitable to apply derivatives of dialkyldithiophosphoric acids with a small hydrocarbon chain, for example DEDPTH of DBDTPH.

The comparative extraction of Hg(II) by DEDTPH and DBDTPH has been studied using radiometric method. Carbon tetrachloride was used as organic solvent. The results of the extraction of Hg(II) as a function of hydrochloric and sulfuric acids concentration indicate that DEDTPH is much more effective extractant for Hg(II). This reagent quantitatively extracts Hg(II) in more wide region of concentration of HCl and H_2SO_4 (Table). The different behavior in distribution of Hg(II) dialkyldithiophosphates in the range from 0 to 7 is probably explained by different stability of these complexes and the formation of negatively charged complexes $HgL_n^{(2-n)}$, where L - anion of dialkyldithiophosphate. It has been established that the molar ratio Me:L in the extractable species is 1:2 when both extractants are used.

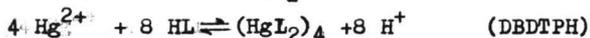
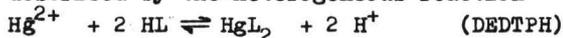
The extraction conditions of Hg(II), Cd(II) and Zn(II)

The metal ion (II)	DEDTPH	DBDTPH
Hg	8 M H_2SO_4 - pH 7 5 M HCl - pH 7	6 M H_2SO_4 - pH 2 3 M HCl - pH 2 3,0 - 0,3 M HCl [3]
Cd	pH 2 - 6	pH 1 - 7
Zn	no extract	pH 2 - 4 0,01 - 0,12 M HCl [3]

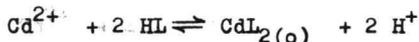
The distribution ratio of Hg(II) was measured as a function of Hg(II) concentration in aqueous phase at constant concentration of reagents and HCl or H₂SO₄. The effect of Hg(II) concentration was investigated by varying the concentration of metal from 1.10⁻⁷ to 2.10⁻⁵ mol/l. The distribution coefficients of Hg(II) using as extractant are dependent on the concentration of Hg(II) from 8 M H₂SO₄ (6 M HCl) to pH 7. When Hg(II) is extracted by DBDTPH from hydrochloric and sulphuric acid solutions (6,0-1,0) the distribution ratio increases and is constant if the metal is extracted from the aqueous phase in the pH region from 0 to 4. Probably the extractable compound associates in organic phase.

The degree of association of Hg(II) dibutyldithiophosphate in organic phase has been determined using measurement of distribution ratio as function of Hg(II) concentration in aqueous phase. The slope of the dependence $\log D_{\text{Hg}(o)} - \log C_{\text{Hg}(o)}$ is about 4 corresponding to the complex (HgL₂)₄ when Hg(II) is extracted by DBDTPH from sulphuric acid (6,0 - 0,5 N). The association of Hg(II) dibutyldithiophosphate starts when the Hg(II) concentration in aqueous phase is 1.10⁻⁶ mol/l. The association of Hg(II) complexes in organic phase in the range pH from 0 to 4 or by DEDTPH from 8 M H₂SO₄ to pH 7.

In region of high acidities the extraction of Hg(II) may formally be described by the heterogeneous reaction



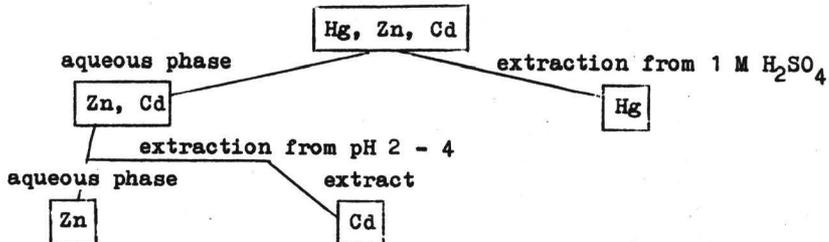
The distribution of Cd(II) by the reagents under investigation is a function of the hydrogen ions and reagents concentration. For the quantitative extraction of Cd(II) a large excess of reagents is required. The complexation of Cd(II) with DEDTPH and DBDTPH has been studied using the distribution method. The results of the investigation are given in the table. In parenthesis the data for DEDTPH are given: $\log K_{\text{ex}} = 5,3$ (4,1), $\log \lambda_2 \beta_2 = 10,6$ (5,3), $\log \beta_1 = 3,62$, $\log \beta_2 = 9,7$. In the pH range of 0 - 4 the dibutyldithiophosphate of cadmium is extracted corresponding to the equation :



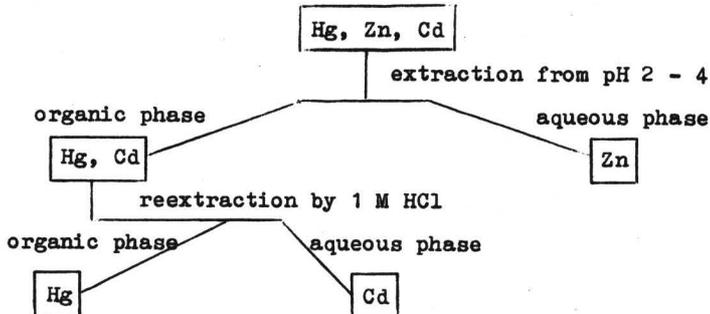
The data for the extraction of Zn(II) by the DBDTPH correspond to those report by [4]. These authors give (the present results are given within brackets) : $\log K_{\text{ex}} = 1,67$ (1,90), $\log \lambda_2 \beta_2 = 6,05$ (6,10), $\log \lambda_2 = 5,37$ (4,03), $\log \beta_2 = 2,27$ (2,38).

On the basis of the experimental data two methods of the separation of Hg(II), Cd(II) and Zn(II) by DEDTPH were developed (Figure).

Method 1



Method 2



Methods of the separation of Hg(II), Zn(II) and Cd(II)
by diethyldithiophosphoric acid

The method of the separation of Hg(II) from Cd(II) and Zn(II) was examined radiometrically. The results are satisfactory, s_r does not exceed 0,01 .

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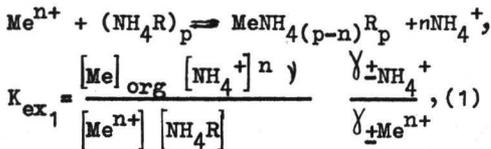
To decrease the detection limit of flame photometry and atomic absorption determination of Li, Rb, Cs in calcium chloride brines and products of their treatment one should separate the general interference components Ca and Sr, e.g. by extraction.

An extractant and a diluent for the given systems are chosen such that high distribution ratios (D) for Ca and Sr are obtained at the lowest D's for Li, Rb and Cs.

The study of extraction of alkali and alkaline earth elements by di-(2-ethylhexyl) phosphoric (DEHP) and di-(2-ethylhexyl) dithiophosphoric (DEHDTP) acids as well as by ammonium salts showed that the use of ammonium di-(2-ethylhexyl)dithiophosphate (NH_4R) with tributyl phosphate (TBP) provides the best separation of Ca, Sr and Mg from solutions [1,2]. Fig.1 shows the maximum extraction of alkaline earth metals at $\text{pH} > 5$ obtained by neutralization of the aqueous phase with ammonium hydrate, the extractant being partially or completely in the organic phase as a univalent cation.

Ammonium salt is strongly associated in saturated hydrocarbons in contrast to polar solvents [1]. Therefore, the extraction of metals as a function of solvent may be described as follows:

For saturated hydrocarbons



where p is a degree of extractant association, γ is a number of reaction centres occupied by one molecule of metal.

For polar solvents (alcohols, TBP)

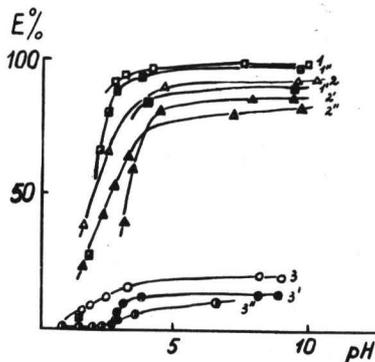
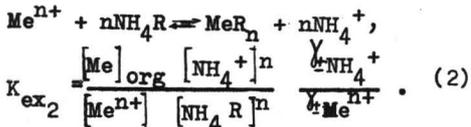


Fig.1. Extraction of Sr(1,1',1''), Ca(2,2',2'') and Li(3,3',3'') in 1 M NH_4Cl with 1 M DEHDTP into octanol (1-3) and heptane (1'-3') as a function of pH. 0.5 M (DEHDTP-TBP) - heptane (1''-3''). C_{Me} , g/l: Ca - 7.4, Sr - 1.0, Li - 0.1

The effective extraction constants (Table 1) have been calculated according to the equation (1) or (2).

Table 1. Effective extraction constants of metals

System	$\log K_{ex_1}, \log K_{ex_2}$					
	Li	Rb	Cs	Mg	Ca	Sr
DEHP-NH ₄ - - heptane	0.07				2.22 ± ± 0.06	1.46 ± ± 0.03
DEHDTP-NH ₄ - - heptane	-0.72 ± ± 0.10	-0.22 ± ± 0.08	0.18 ± ± 0.08	0.4 ± ± 0.05	0.64 ± ± 0.10	0.67 ± ± 0.04
DEHDTP-NH ₄ - - octanol	-0.48 ± ± 0.02					
DEHDTP-NH ₄ - - TBP					1.6 ± ± 0.06	

The extraction of metals by heptane solutions of NH₄R decreases in the sequence Cs > Rb > Li ~ Na ~ K.

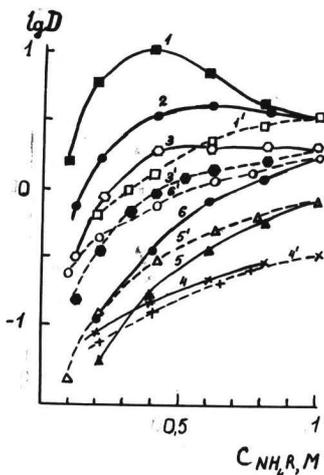


Fig.2. Distribution ratio of Ca(1), Sr(2), Mg(3), Li(4), Rb(5), Cs(6) as a function of the DEHDTP-NH₄ concentration in the mixture with TBP in heptane (the broken lines are the same but in the absence of TBP). The total concentration of NH₄R and TBP is equal to 1 M

The use of ammonium salts has some advantages as compared to the acidic form. Salts are, as a rule, more stable, require no pH regulation, provide good lamination and practically do not change phase volume. The cation exchange of NH₄⁺ for alkaline earth elements with a further NH₄Cl sublimation allows the salt background of a brine to be decreased by 95-97% in one stage of extraction.

Neutral additives of TBP result in a higher capacity of extractant in relation to Me²⁺, slightly increase Li extraction and sharply suppress Rb and Cs extraction. Fig.2 shows the influence of extractant composition (mixture DEHDTP-NH₄-TBP) upon extraction of metals.

Factors of synergism $S = \log \frac{D_{mix}}{D_1 + D_2}$ versus the nature of extracted metals and NH₄R:TBP ratio are given in Table 2.

Table 2. Factors of synergism

S = log D _{mix} - log D ₁ , D ₂ → 0				
NH ₄ R:TBP	1:4	2:3	3:2	4:1
Me ⁿ⁺				
Ca ²⁺	0.98	0.89	0.51	0.18
Li ⁺	0.05	0.06	0.04	0
Rb ⁺	-0.38	-0.24	-0.13	-0.05
Cs ⁺	-0.57	-0.30	-0.15	-0.05

Synergetic effect has the maximum for the extractant composition NH₄R:TBP = 1:4. The absolute value S decreases in the sequence Ca > Sr > Mg > Li.

The obtained data allowed the optimum conditions to be chosen to separate the CaCl₂ base from Li, Rb, Cs with a further flame photometry determination of Li and atomic absorption detection of Rb and Cs in the aqueous phase.

The 0.5 M mixture of ammonium dialkyl dithiophosphate with TBP has been used for matrix breaking during lithium determination. In the given systems, one can observe the minimum distribution ratios independent on its concentration within 0.1-10 ppm and inversely proportional to the ammonia ion activity in the aqueous phase as well as the maximum separation coefficients β_{Me^{2+}/Li^+} (e.g. log $\beta_{Ca/Li}$ is equal to 1.8, 1.4 and 1.15 for calcium, strontium and magnesium, respectively).

The use of equimolar (0.5 M) NH₄R mixture with TBP in heptane during one stage of extraction at $V_{org}:V_{aq} = 3:1$ allows the contents of Ca (7.6 g/l) and Sr (0.32 g/l) in the Li-bearing brine to be decreased to 0.2 g/l of Ca and 0.02 g/l of Sr which do not prevent from determination of Li. Besides that, in the presence of Ca and Sr the value D_{Li} is constant and equal to 0.19 in a wide concentration interval of Li in the aqueous phase, which indicates the absence of co-extraction in the given systems.

Ammonia does not wash calcium from an organic phase up to 5.4 M content (pH 11.4). A calcium reextraction can be observed at NH₄Cl concentration more than 0.4 M. The optimum conditions for washing the rest of lithium in organic phase are as follows: 0.4 M NH₄Cl and 1 M NH₃, $V_{org}:V_{aq} = 1:2$. The extraction cleaning decreases the detection limit of lithium in calcium chloride brines by an order and provides detection of Li in strontium compounds. Relative standard deviations of lithium determination do not exceed 0.05.

The use of NH_4R mixture (0.5 M) and TBP (2 M) in heptane at $V_{\text{org}}:V_{\text{aq}} = 2:1$ decreases Ca concentration in brine from 8 g/l to 0.4 g/l, D_{Rb} and D_{Cs} being equal to 0.16 and 0.2 and constant as metal concentration being changed from 10^{-4} to 10^{-1} g/l.

The substitution of NH_4Cl for the CaCl_2 base with a further NH_4Cl sublimation allows alkali elements to be concentrated and alkaline earth element effect to be removed.

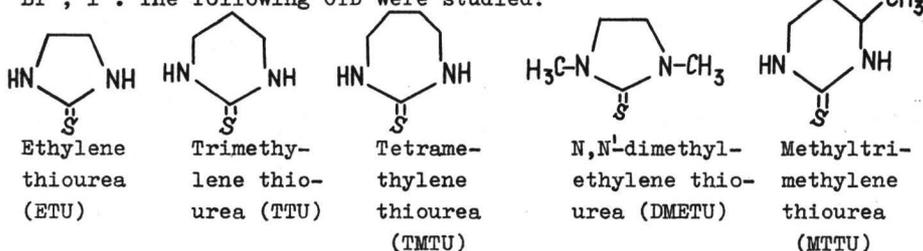
A technique of extraction-atom-absorption determination of Rb and Cs in calcium chloride brines with general salt background equal to 400 g/l for Rb and Cs contents $(0.5 - 3) \cdot 10^{-3}$ g/l with a relative standard deviation less than 0.07 has been developed.

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To develop the selective procedures for the isolation and extraction-photometric determination of the μg quantities of bismuth, the extraction of bismuth complexes with the cyclic thiourea derivatives (CTD) and halogenide ions from the sulphuric acid media was studied. In the presence of the excess of the complexing agents the formation of the extractable complexes Bi-CTD-A^- was observed, where $\text{A}^- = \text{Cl}^-$, Br^- , I^- . The following CTD were studied:

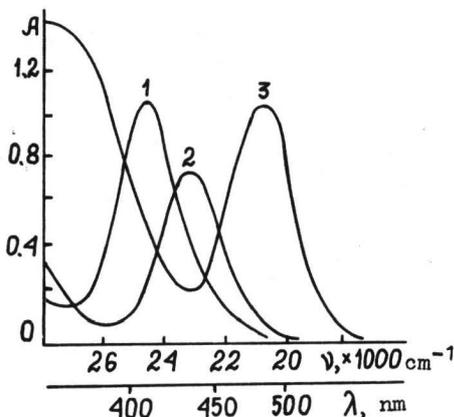


The optimal conditions for the complexation and extraction were found using the method of the experimental design of Box-Wilson.

Under these conditions the spectrophotometric characteristics of the extractable complexes were determined. The data obtained are given in Table 1.

The absorption spectra of the complexes don't practically depend on the CTD nature, but depend considerably on the nature of a monobasic acid anion (Fig.). The determination of the basicity constants of the studied compounds (Table 2) and their distribution coefficients between the aqueous and organic phased (Table 3) allowed to calculate the conditional constants of the bismuth extraction (Table 4),

by chloroform in the presence of the anions. The extraction constants decrease regularly in the series $\text{I}^- > \text{Br}^- > \text{Cl}^-$ which proves the empirically found phenomenon of the preferenti-



The absorption spectra of the bismuth complexes with tetramethylene thiourea extracted by chloroform in the presence of the anions.

Aqueous phase: $1 \cdot 10^{-4} \text{ M Bi}$;
 0.005 M TMTU ; $0,5 \text{ M H}_2\text{SO}_4$;
1. $0,15 \text{ M Cl}^-$; 2. $0,01 \text{ M Br}^-$;
3. $0,001 \text{ M I}^-$; $l = 1 \text{ cm}$

Table 1. Conditions of the Formation and Extraction and Spectrophotometric Characteristics of Bismuth Complexes with Cyclic Thiourea Derivatives

System		[H ₂ SO ₄], M	[CTD],M	[A ⁻],M	λ,nm	ε·10 ⁻⁴	Solvent, extraction,%
CTD	Anion						
ETU	Cl ⁻	3.0-3,5	0,05	0,15	395	-	MIBK, <30%
	Br ⁻	0.25-3,0	0.08	0.08	422	-	MIBK, ≈ 85%
	I ⁻	0.6	0.05	0.004	480	1.0	CHCl ₃ , ≈90%
TTU	Br ⁻	0.5	0.04	0.15	428	1.3	CHCl ₃ , >95%
	I ⁻	1.5-4,0	0.02	0.005	485	1.4	CHCl ₃ , >95%
TMTU	Cl ⁻	0.5	0.03	0.15	405	1.2	CHCl ₃ , >95%
	Br ⁻	0.5	0.006	0.01	430	0.8	CHCl ₃ , >95%
	I ⁻	0.5	0.006	0.001	480	1.1	CHCl ₃ , >95%
DMETU	Br ⁻	3.3	0.05	0.02	430	1.3	toluene, >95%
	I ⁻	1.5-5.0	0.003	0.003	485	0.75	toluene, >95%
	I ⁻	1.5	0.014	0.004	492	0.9	CHCl ₃ , >95%
MTTU	Cl ⁻	1.4	0.03	0.23	403	1.1	CHCl ₃ , >95%
	Br ⁻	1.5	0.02	0.04	430	1.5	CHCl ₃ , >95%
	I ⁻	0.3-3.5	0.01	0.002	482	1.3	CHCl ₃ , >95%

Table 2. The Basicity Constants (K_{BH⁺}) of Some Cyclic Thioureas

$$K_{BH^+} = \frac{[CTD][H^+]}{[CTDH^+]}$$

CTD	ETU	TTU	TMTU	DMETU	MTTU
K _{BH⁺}	117	13.5	5.6	676	8.9

Table 3. Coefficients of CTD Distribution (E) between the Aqueous and Organic Phases (E = C_{org} / C_{aq})

CTD \ Organic phase	Toluene	CCl ₄	1,2-di-chloro-ethane	CHCl ₃	Ethyl acetate	Butyl alcohol -1	MIBK
ETU	0.03	0.0	0.17	0.17	0.30	0.83	0.20
TTU	0.21	0.13	0.21	0.45	0.50	0.80	0.29
TMTU	0.33	0.0	1.72	3.54	1.43	3.12	1.12
DMETU	40	25	320	550	-	48	61
MTTU	0.07	0.05	0.66	1.35	0.40	1.57	0.49

Table 4. Logarithms of the extraction constants ($\lg K_e$) of bismuth complexes with the cyclic thioureas and halogenide-ions with chloroform

$$K_e = C_{\text{com}} \frac{\left(1 + \frac{1 + [H^+]/K_{\text{BH}^+}}{E}\right)^2}{(C_{\text{Bi}} - C_{\text{com}})(C_{\text{A}^-} - 3C_{\text{com}})^3 (C_{\text{CTD}} - 2C_{\text{com}})^2}$$

A ⁻ \ CTD	ETU	TTU	TMTU	TMETU	MTTU
Cl ⁻	7.9*	-	7.6	-	7.5
Br ⁻	8.9*	9.9	12.5	10.2**	10.9
I ⁻	13.1	14.3	14.9	13.5	15.7
I ⁻	-	-	-	15.1**	-

* extraction with MIBK;
 ** extraction with toluene.

al extraction of iodide-thiourea complexes and corresponds to the greater strength of the bismuth iodide complexes.

The maximal values of the extraction constants were obtained for CTD possessing the largest cycle size (seven-membered for TMTU) or the most carbon atoms in the radical at thioamide fragment in the studied series which may be due to the increase of the ligand hydrophoby and, hence, of the bismuth complex. Introducing the methyl groups at the carbon atoms, and, especially, at the nitrogen atoms, results in the increase of the CTD molecule hydrophoby, and in the corresponding increase of the extraction constants values. In case of N,N-dimethyl derivatives of DMETU the ligand hydrophoby increases so, that the complex extraction by the low-polar solvent toluene becomes possible with the high value of the extraction constant.

It should be noted that for the bismuth extraction CTD are the most suitable as well as the solvents where the moderate distribution of CTD between the aqueous and organic phases ($E = 1+50$) is realized. This is due to the fact that the formation of the complex Bi-CTD-A^- takes place in the aqueous phase but its stability in the extract demands the certain excess of the ligand in the organic phase.

The obtained data on the constants of the complexes extraction and their spectrophotometric characteristics allowed to choose the optimal systems for the analytical application: iodide and bromide bismuth complexes with six- and seven-membered CTD.

Table 5. The Results of Bismuth Determination

Object	Bismuth content, %	
	certified	found
Tungsten ore 2039-81	$2.3 \cdot 10^{-2}$	$(2.2 \pm 0.1) \cdot 10^{-2}$
Sulphide ore 793-76	$3.4 \cdot 10^{-3}$	$(3.3 \pm 0.1) \cdot 10^{-3}$
sulphide ore 792-76	$4.5 \cdot 10^{-3}$	$(4.2 \pm 0.1) \cdot 10^{-3}$
Nickel alloy M 44	$(4.2 \pm 0.2) \cdot 10^{-3}$	$(4.26 \pm 0.13) \cdot 10^{-3}$
Standard piece of rare metal metasomatite DBR-1	-	$(4.4 \pm 0.4) \cdot 10^{-3}$
Standard piece of chalcophilic metasomatite DBX-1	-	$(4.6 \pm 0.5) \cdot 10^{-4}$
Standard piece of meymechite DBM-1	-	$(2.2 \pm 0.2) \cdot 10^{-4}$
Standard piece of dunite CDY-1	-	$(1.1 \pm 0.2) \cdot 10^{-4}$
Nb_2O_5	$5 \cdot 10^{-4}$	$(4.8 \pm 0.2) \cdot 10^{-4}$

It was found that the extraction-photometric determination of 2-50 ug of bismuth as the complex $Bi-TMTU-I^-$ in not interefered with 0.5-1.0 g of Ni, Fe, Co, Al, Mn, Zn, Nb, Sb, Sn; 100-200 mg of U, TI, Mo, W, as well as 1 g of ascorbic and tartaric acids, sulphates. Oxidants should be reduced before the extraction.

The extraction-photometric methods for the determination up to $10^{-4}\%$ of bismuth in nickel alloys, tungsten ore, polymetallic ores, niobium pentoxide, rocks, metallic antimony were worked out. The results of bismuth determination in some objects are given in Table 5.

A COMPARATIVE STUDY EXTRACTION OF METAL COMPOUNDS WITH
CHROMOPHORE REAGENTS AND LONG-CHAIN QUATERNARY AMMONIUM
SALTS AND THEIR SOLUBILIZATION WITH MICELLES OF NON-IONIC
SURFACTANTS

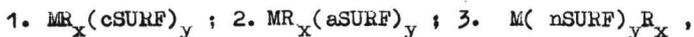
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The usage of the surfactants of different nature as additional components of analytical reactions opens a lot of new possibilities for their utilization. Under such conditions we can see changes in spectrophotometric characteristics, oxidizing potentials of substances and there appears the possibility of changing the concentration conditions of reactions, solubility of products. It allowed wide use of surfactants (SURF) in photometry and extractal separation, in chromatography and a number of other cases [1].

In this paper we have looked through the usage of SURF in extraction, where they are additional components of metal ion reactions with hydrophobic reagents, as well as using of solubilization products of such reactions by micellar forms of SURF. Both methods have big practical importance. They permit straight forward execution of analytical reactions in homogenic and two-phase environments.

One can single out three groups compounds, formed in the metal-chromophore reagents-SURF system:



where cSURF-cationic, aSURF-anionic, nSURF non-ionic SURF.

They interact by association mechanism, mixed ligand complex formation and formation of complex compounds of metal ion with non-ionic SURF molecules [1, 2].

At the extraction of such compounds we usually use just a little quantity of SURF, which does not exceed their threshold of micelles formation in water solutions.

Under such conditions we extract more simple associates of reagents R - SURF, that increases contrast of photometric reactions. For the fulfillment of similar reactions in water solutions we use redundant quantity of SURF. In using charged SURF it is possible the concurrent influence on the central ion and the reduction of painting product output. Besides there can be formed intensively painted associates of reagents, which make worse the photometric conditions. Such influence is especially developed in alkaline environment.

By our experiments we have shown that it is possible to use non-

ionic SURF for solubilization of metal compounds with chromophoric reagents and cSURF. For solubilization one can use non-ionic SURF. Micellar forms of such SURF stabilize the compounds in water solutions, at the same time providing high contrast of reactions. Such effects illustrated Figure 1 (a,b), on the example of molybdenum compounds with bromopyrogallol red (BPR) and cetylpyridine chloride (CP). It is seen from the Fig. 1, that in solutions (pH 6) the execution of reaction is not effective due to the disturbing action of associates reagents painting (Fig.1,a,curve3). Solubilization of compounds with BPR and CP by micelles of non-ionic SURF OP-10 (polyoxoethylated ether) hypsochromically shifts the absorption band reagents associates (Fig.1,b,curve3). Here we have the increase of complex output (Fig.1,b,curve4). This effects are due to the fact that non-ionic SURF suppressed dissociation of hydroxide group of BPR.

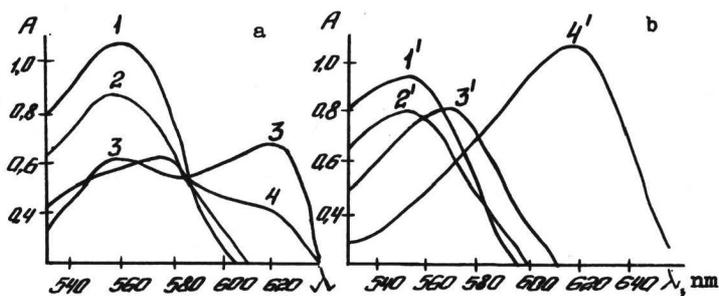


Fig.1. Electron spectrum of reagents and complexes of molybdenum

(in absence- a and in presence- b of OP-10). 1,1'-BPR;

2,2'-Mo-BPR; 3,3'-BPR-CP; 4,4' - Mo- BPR -CP.

$C_{Mo} = C_{BPR} = C_{CP} = 3 \cdot 10^{-5} M$; $C_{OP-10} = 2 \cdot 10^{-4} M$; pH 6

CP joins to the most dissociated sulfo-groups of reagent, that is not in the chain of the conjugate. It increases the contrast of the reaction. Among interesting peculiarities of the reaction one should point out the broadening of optimal conditions of interaction in alkaline field, that is also concerned with the influence of non-ionic SURF. At the extraction of compounds Mo-BPR-CP by chloroform all the spectrophotometric characteristics of the compounds are retained.

(The data are illustrated in Table 1).

It is known from the literature [3], that micelles of SURF or

their premicellar aggregates influence on the central ions, providing their dehydration. Under such conditions the reactional ability of metal ions is increased, also the number of united ligands is increased as well as the compound stability grows.

Such dependence was shown on the example of reaction with bromopyrogallole red and hexyldiantipyrilmethane (HDAM). It is known that the HDAM is a large hydrophobic base. To use reactions with this reagent typically take the extraction by organic solvents. Our experiments indicate, that this reaction could be fulfilled in water phase at solubilization the compound by micelles of OP-10. Under such conditions the reaction passes in more wide range of acidity, the joined groups BFR increases (Table 1). For optimal formation of compounds is considerably less HDAM (4-6 times, instead of 800 times at extraction) It proves the growth of stability bond in compounds.

Table 1. The chemical-analytical characteristics of the complexes

Reactants	Stoichiometry M:R:SURF	pH opt.	λ_{\max} , nm	ϵ_{\max} $\times 10^{-4}$	medium
BPR-CP	1:1	6,5	620	-	aqueous
BPR-CP	1:1	6,5	570	-	micelles OF-10
BPR-CP	1:1	1,5	520	-	extr. CHCl_3
Mo-BFR-CP	1:2:1	1,5-7,0	620	5,9	micelles OF-10
Mo-BFR-CP	1:2:2	1,2-1,8	620	5,3	extr. CHCl_3
Mo-BFR-HDAM	1:2	2,5-3,7	620	4,5	micelles OF-10
Mo-BFR-HDAM	1:1:2	0,3-0,6	620	3,8	extr. CHCl_3
Cd-PAR-OP-10	1:2	10	500	10	micelles OF-10
Cd-PAR-CP	1:2:2	9,2	520	11,8	aqueous; extr.

The studied reaction prevents general chemical interest as it shows the principal possibility of solubilization by micelles of nSURF compounds, including different organic base.

The effects under consideration are typical for the other chromophoric reagents. So, the similar dependence are made for bromophenole blue, phluorones, oxiazo-compounds. As an example in the Table 1 are compared the properties of extraction cadmium compounds with PAR and CP and solubilization products by micellar forms of SURF. The effectiveness of both methods makes the reaction uni-

versale applicable for extractional determination and photometry in water solution [4] .

Thus, the solubilization of metal compounds with chromophoric reagents and organic base by micelles of non-ionic SURF allows to increase the contrast of reaction, as well as stabilized the painting in time. It is similar to the extractional systems.

At the same time the application of nSURF micelles widen the field of interaction in alkaline environments, increases the reaction capability of central ions, promote the formation of more intensively painted and coordinately saturated compounds.

The above mentioned reactions have wide application at separation and determinating of metal or SURF of different nature.

Some of developpe methods we have shoun in the Table 2. They come up to standards methods.

Table 2. The analytical research of the reactions M-R-cSURF-nSURF

Reactants	Object	Determi- nable component	The interval of following Ber's law mkg/ml	Sr
Co-PF.FF-CP-OP-10*	blood serum	Co	0,004-0,006	0,035
Mo-BFR-CP-OP-10	steel,(sol)	Mo(CP)	0,1-0,4 (0,6-3,5)	0,03 (0,04)
Mo-BFR-HDAM-OP-10	steel,(sol)	Mo(OP-10)	0,3-0,8 (10-50)	0,022 (0,04)
Cd-FAR-OP-10	sewage	Cd	0,1-1,0	0,026

* FF.FF- phenylphluorone

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Stripping voltammetry is the most sensitive electroanalytical method for the determination of trace levels of substances which may be preconcentrated onto the working electrode prior to the actual quantitation. A markedly increased selectivity of analysis can be achieved by the employment of effective separation technique. The use of solvent extraction in stripping voltammetry is usually associated with reextraction of metal into aqueous phase or involves mineralization of the organic phase. From the point of view of working steps number reduction a direct determination in non-aqueous medium seems to be prospective.

In our previous study [1] we showed the possibility of electrolytic accumulation of metals on hanging mercury drop electrode (HMDE) after extraction of their diethyldithiocarbamate (DDC) complexes to benzene. Analytical data for cadmium determination in 1:1 benzene-methanol medium and separation of copper as an interfering element from the mixture with cadmium, lead and zinc have been obtained. The aim of this work is to verify the possibility of deposition potential decrease in the presence of mercuric ions which undergo to the metal exchange reaction with the central atom of dithiocarbamate complexes. The question of selectivity of analysis of cadmium, lead, thallium and indium giving overlapping stripping peaks has been also studied.

Experimental. For the extraction NaDDC (cupral) as well as more selective and stable $Zn(DDC)_2$ were used. Experimental conditions are given in Table 1. Polarographic analyser of the PA 2 type with the set of Rotating Disc Electrode (Laboratorní přístroje, Praha) were employed. A HMDE of the Kemula E-69b type (Radiometer, Copenhagen) and mercury film electrode MFE prepared "in situ" by the mercury deposition on a glassy carbon disc were used as indicating electrodes. The reference electrode was calomel electrode with 4 M LiCl and a salt bridge filled with the supporting electrolyte. The auxiliary electrode was platinum electrode.

Results and Discussion. The dependence of cadmium, lead and thallium stripping peak current on deposition potential has been investigated. From the time independent reduction potential values it follows that in the presence as well as in the absence of mercuric ions the DDC complexes are reduced during the deposition step on both

Table 1. Experimental conditions of solvent extraction voltammetric determination

Metal ion	Aqueous phase	Organic phase/agent	Supporting electrolyte/deposition potential
Cd ²⁺	0.05-0.3 M HClO ₄ or pH 5 - 6	benzene/Zn(DDC) ₂ or NaDDC	benzene-methanol 1:1 0.1 M NaClO ₄ /-0.9 V
Pb ²⁺	0.05 - 1 M HClO ₄ or pH 5 - 6	benzene/Zn(DDC) ₂ or NaDDC	benzene-methanol 1:1 0.1 M NaClO ₄ / -0.9 V
Tl ⁺	pH 5 - 6	benzene/NaDDC	benzene-methanol 1:1 0.1 M NaClO ₄ / -0.65 V
In ³⁺	2 M HClO ₄	chloroform/ Zn(DDC) ₂	chloroform-ethanol-water 1:4:1; 0.005 M CH ₃ COONa, 0.006 M HCl, 0.06 M KBr/ -1.1 V

HMDE and MFE. In the case of thallium, however, the difference between the reduction potential of Tl⁺ and TlDDC is due to low complex stability, only small. Addition of HClO₄ lead to the shift of the deposition potential towards the more positive values. This is obviously caused by the release of metal from DDC complex prior to the electrolysis. The condition of the exchange reaction evidently lies in the presence of Hg(II) reactive form. The reaction equilibrium is considerably shifted to the right and the exchange reaction proceeds quickly.

The Hg(II) concentration was maintained in the 10⁻⁴ M region in order to ensure the excess of Hg(II) against the extracted complexes as well as its usual value for the mercury film formation. No significant peak current changes were observed in the range 3x10⁻⁵ to 6x10⁻⁴ M Hg(II) and 5x10⁻³ to 5x10⁻² M HClO₄. At the presence of mercuric salt the electrochemical reversibility of the redox systems increases.

Under the conditions securing metal release from DDC complex the calibration curve was obtained for cadmium. The dependence of peak current on cadmium concentration in the original aqueous solution in the range 10⁻⁷ M is linear. The reproducibility is characterized by the relative standard deviation cca 7 % at the level 1x10⁻⁷ M, the limit of the determination is 1x10⁻⁸ M. It was also tested the possibility to make the extraction as well as the voltammetric measurement in the same vessel.

The difference of the values of stability and extraction constants of the individual DDC complexes [2, 3] gives the assumption of the separation of these also at the great concentration ratio of metals.

The ascertained possibility of determination is summarized in Table 2. The ratio between the metal amount which was determined and that taken for the analysis was always near one. The determination may be realized also on the principle of one vessel.

Table 2. Separation conditions for metal determination in the presence of interfering metal

Molar ratio of metals	Aqueous phase	Agent/ Organic phase	Extraction time
Cd - Tl 1 : 1000	0.3 M HClO ₄	Zn(DDC) ₂ / benzene	3 min
Tl - Cd 1 : 200	pH 5 - 6	NaDDC/ benzene	3 min
In - Cd 1 : 1000	2 M HClO ₄	Zn(DDC) ₂ /chloroform	10 min + Cd reextraction
In - Tl 1 : 1000	2 M HClO ₄	Zn(DDC) ₂ /chloroform	10 min

The obtained results confirm the possibility to use the formation of DDC complexes in the determination of metal traces in more complicated systems by the combined method : solvent extraction stripping voltammetry. The possibility of influencing the extraction selectivity [3] allows to consider the determination of other metals, too. The efficiency of separation is increased by back extraction of interfering metal from the organic to aqueous phase. Potential possibilities of stripping voltammetry allow also the determination at lower concentration level than at the verified one. It is, however, necessary to keep the principles of trace analysis inclusive the work in one vessel. Preliminary separation in the extraction step is here both perspective as well as tedious and risky procedure.

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The applying of commercial X-ray-spectral apparatus for the analysis of technological solutions, ores and concentrates has been limited by low-sensitivity apparatus, difficulties in the concentrating procedure and preparation of radiating patterns. There is the task of determination of bismuth and chalcogens in complicated objects.

Bismuth extraction from the solutions with different anionic composition by low-melting extractants has been studied. Technical monocarboxylic acids (fractions $C_{17}-C_{24}$, stearic acid, 8-hydroxyquinoline, mixture of tributylphosphate (TBP) with paraffin hydrocarbons served as the low-melting extractants.

The optimal conditions of bismuth-ion extraction from halogenide, nitrate and sulphate solution have been found for different reagents. The composition and behaviour of the extracting compounds were established by the methods of IR-spectroscopy, spectrophotometry, X-ray phase analysis. The increase of hydrogen ions concentration lead to change of composition of extracting compounds from $BiX_3 \cdot 3TBP$ to $BiX_4 \cdot 2TBP$.

The extraction constants in the system bismuth - stearic acid - paraffin hydrocarbons - water at $80^\circ C$ have been calculated:

$$K_{ex} = 0,87 \pm 0,12 \text{ (1,0 M stearic acid in paraffin);}$$

$$K_{ex} = 0,85 \pm 0,07 \text{ (0,1 M stearic acid in paraffin).}$$

There was established on the basis of achieved results that the most perspective low-melting extractants for the extraction of bismuth in analytical practice are high carboxylic acids (HCA).

Extraction of chalcogen elements (sulphur(VI), selenium(IV), tellurium(IV) that accompany bismuth in ores and minerals was studied. Extraction of these elements was carried out by the melts of HCA (technical fractions with the number of carbon atoms ≥ 15) from neutral and bromide solutions.

The influence of different factors on the distribution of above-mentioned anions in the system the melt of HCA - water: acidity of aqueous phase, the contact time, the phase volume ratio, the concentration of elements, ionic strength and salt composition of aqueous phase was studied. The optimal conditions of the maximal extraction of sulphur(VI), selenium(IV) and tellurium(IV) in the absence and

in the presence of the chlorides and nitrates of some metals have been found.

There was established, that selenium and tellurium are extracted from acidic chloride and bromide solutions. The maximal extraction was observed in the case of selenium(IV), which has been extracted quantitatively in the wide interval of acidity. The composition of extracted species was proved: $H_2SeCl_6 \cdot 2HR$ (for the 2-4 M HCl). The difference in extractive capacity of Se(IV) and Te(IV) allows to carry out efficient separation of these elements.

The considerable influence of salt composition of the aqueous phase on the extractive capacity of chalcogen elements was established. There was found the dependence between the concentration of different metal cations in aqueous phase and extractive properties of chalcogens.

The series of the influence of different ions on the extraction of the anions with the melts of HCA have been found. The obtained results permit to propose the express methods of determination of chalcogen elements in the solutions with complex salt composition. Some objects such as semiconductor materials, sewage were analysed by proposed methods.

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To eliminate matrix effects in different multielement methods of the determination of microimpurities in Zn, Cd, Hg, Sn and Pb tellurides it is essential that matrix elements should be isolated. To do this, extraction and extraction chromatography can be used to advantage.

The technique of sorption of a number of matrix elements on the column, which has been insufficiently studied, is of great interest from the viewpoint of a single-stage separation of various elements for multielement methods of analysis. An optimal choice of the extraction system enables the method to be unified with respect to a wide range of materials to be analyzed as well as different ways of detection.

Practically all the matrix elements comprising semiconductor tellurides are readily extracted either with tri-n-butylphosphate (TBP) or tri-n-octylamine (TOA) from 3-6 M HCl solutions [1,2]. We have found that a TOA+TBP mixture efficiently extracts the above microcomponents both separately and in different combinations. The mixture was found to exhibit a synergistic action (Fig.1).

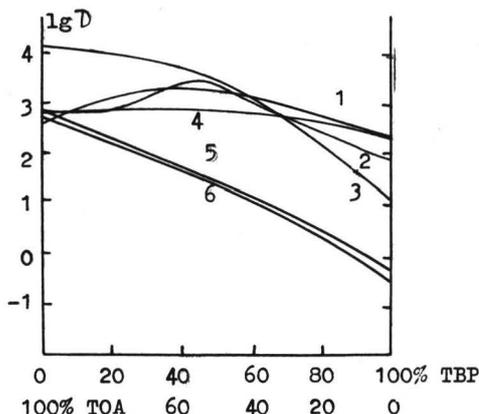


Fig.1. Extraction of microamounts of Zn, Cd, Hg, Sn, Pb and Te with TOA and TBP mixtures. Curve 1 - Te ($C_{Te}=0.2$ M); 2 - Hg(0.2 M); 3 - Cd(0.2 M); 4 - Sn(0.07 M); 5 - Pb (10^{-3} M); 6 - Zn(0.2 M). Curves 1-5 - 3 M HCl; 6 - 0.1 M HCl

Yet, under these conditions many impurities are poorly extracted (Na, Mg, Al, K, Ca, V, Cr, Ni, Mn, Rb, Sr, Y, Cs, Ba, REE, Bi), if at all (the distribution coefficient $< 10^{-2}$) (Fig.2).

Thus, the possibility exists of separating the impurities from the matrix elements. Besides, the latter were found to suppress extraction of impurity elements. By way of example, Fig.3 shows the data on the influence of zinc microamounts on extraction of impurities. However, in extraction separation the relative concentration coefficients (F) are small in spite of low distribution coefficients of impurities and suppression of their extraction by macrocomponents. This indicates that in the cases in question extraction preconcentration cannot afford efficient separation of matrix and impurity elements.

Yet, in neutron activation analysis of the matrices the values of F should not be smaller than 10^8 [3]. Such values can be achieved in extraction chromatographic preconcentration by means of multiple extraction-reextraction cycles.

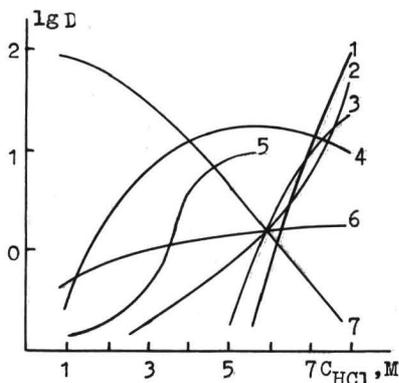


Fig.2. Extraction of Hf (curve 1), Zr(2), Sc(3), Cu(4), Co(5), As(6), Ag(7) with a TBP+TOA mixture (1:1) in accordance with HCl concentration

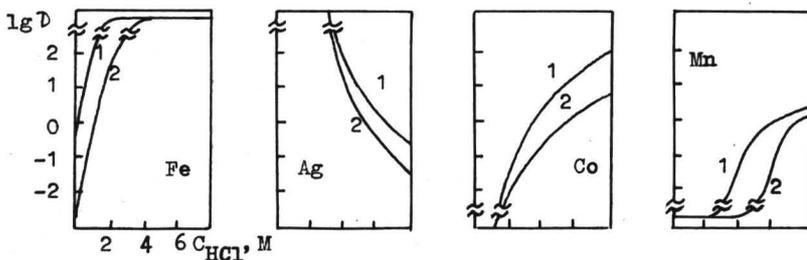


Fig.3. Extraction of microamounts ($\sim 10^{-4}$ M) of elements in the absence (1) and presence (2) of 0.2 M Zn

It has been previously shown [4] that the use of extraction chromatography in the system of TOA+TBP mixture-HCl solutions allows an efficient single-stage separation of the following impurity elements: Na, Mg, Al, K, Ca, Sc, V, Cr, Mn, Co, Ni, Cu, As, Rb, Sr, Y, Zr, Ag, Cs, Ba, REE, Hf and Bi. One of the disadvantages of extraction chrom-

atography lies in a relatively large volume of impurity containing eluate which increases the time of separation and blank test values.

To reduce the volume of the eluate, we have studied the effect of column feed by the matrix elements. The eluate volume was quantitatively shown to decrease with increasing weight of the sample (Fig.4).

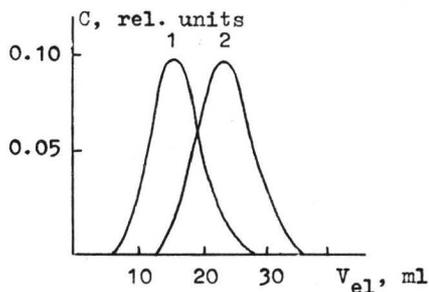


Fig.4. Zinc elution curves. The elution was performed with 9 M HCl from a column filled with 15 g of a PTFE+TBP mixture (H=17 cm; D=1.2cm; $V_o=8$ ml; $V_s=5$ ml) in the presence (curve 1) and absence (curve 2) of 100 mg of Te

To optimize the height of the sorbent layer (and to minimize the eluate volume) at a certain sample weight the distribution of macrocomponents along the column height was studied (Fig.5).

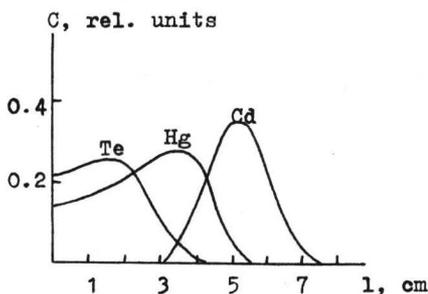


Fig.5. Distribution of the matrix elements along the height of the sorbent layer upon separation of impurities from 100 mg of $Cd_xHg_{1-x}Te$; the column filled with 15 g of PTFE with a TOA+TBP mixture (H=19.5 cm; D=1.05 cm; $V_o=10$ ml; $V_s=5$ ml). Eluent - 3 M HCl

Assuming that the least sorbed matrix element is distributed in the chromatographic column in accordance with the normal law, the sorbent layer height can be calculated for a given value $F_{A/B}$, where A is the least sorbed matrix element and B is the most sorbed impurity. Fig.6 shows the results of the calculation for the case of separating impurities from 100 mg of $Cd_xHg_{1-x}Te$.

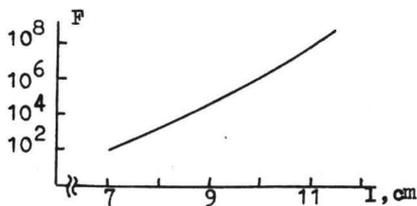
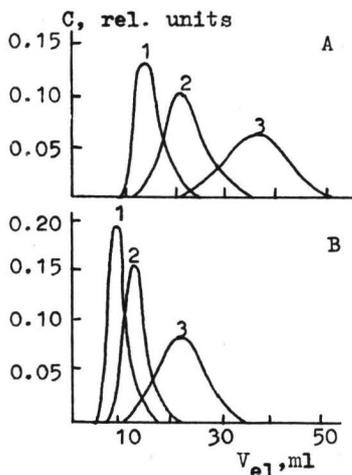


Fig.6. Coefficient of relative concentration of impurities as a function of the sorbent layer height upon separation of impurities from 100 mg of $Cd_xHg_{1-x}Te$. Column with D=1.05 cm. Eluent - 3 M HCl

Fig.7. Elution curves of Na, Cr, La, Hf (curve 1), As (2) and Cu (3); column with a high sorbent layer (A) and an optimal height (B). Eluent - 3 M HCl. Column A: H=19.5 cm; D=1.05 cm; $V_o=10$ ml; $V_s=5$ ml. Column B: H=12 cm; D=1.05 cm; $V_o=7$ ml; $V_s=3.1$ ml



The use of the foregoing approach for optimization of the sorbent layer height is illustrated in Fig.7 by impurity elution curves for an optimal size column (calculations made for $F=10^8$) and a column with a sorbent layer height exceeding its optimal value. From these curves it is evident that optimization enables the eluate volume to be reduced (in this case by 30%).

The investigations performed made it possible to develop a universal technique of single-stage extraction-chromatographic separation of more than 20 impurity elements from all semiconductor tellurides. The technique is suitable for neutron-activation and atomic spectroscopy methods of analysis and affords determination of impurities with detection limits from $10^{-4}\%$ to $10^{-9}\%$.

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Emission spectroscopy [1,2] and atomic absorption spectrometry [3,4] with preliminary separation of the matrix element by solvent extraction have been used for microimpurities determination in high purity platinum. However, the extractant used (trioctylamin and isoamyl alcohol-methylisobutylketone) are not selective with respect to gold, iron, molybdenum, antimony and tin.

In this work solvent extraction of the chloride complexes of Au(III), Fe(III), Sb(V), Sn(IV) and Mo(VI) from diluted hydrochloric acid into methylisobutylketone (MIBK) [5,6] in combination with flame AAS determination of these elements in high purity platinum, is proposed.

The group extraction of $1-40 \text{ mg} \cdot \text{l}^{-1}$ Au, Fe, Mo and Sb, and $20-100 \text{ mg} \cdot \text{l}^{-1}$ Sn, in the presence of $10-100 \text{ g} \cdot \text{l}^{-1}$ Pt from 6 M HCl at $V_w:V_o=3:1, 2:1, 1:1$ and $1:2$, and 300 s phases contact has been investigated. The effect of platinum on the extraction and atomization of each element, under investigation, has been considered [7]. It has been found that, the extraction of microelements is not influenced quantitatively by the matrix element, which is partially extracted ($D=0.05$), but the latter suppresses their AAS determination. This problem has been overcome by completely stripping the platinum from the organic phase by 6 M HCl.

The behaviour of other low extractable microimpurity elements (Al, Ca, Mg, Ni, Cr, Pb, Cu, Mn) attending platinum, have also been studied. A depressing influence of the matrix element on their extraction and more effective stripping in its presence, have been found out.

The mutual interferences of the extracted elements in the flame at different quantitative ratios, have been investigated [7]. Availability of interferences in condensed phase at interferent to analyte ratios of more than 10:1, has been found. These interferences have been very pronounced at ratios of 50:1 and resulted in 25% of modifications of the absorbance signals.

One of the simplest ways to eliminate interfering effects is to use additions with respective action. Considering the extraction mechanism of chloride complexes into MIBK, the influence of long-chain quaternary ammonium salts, has been studied [7]. The latter are not suitable for selective elements extraction, but when added to MIBK, after its separation from the aqueous phase, eliminate completely all the interfering effects. Their protective action has been explained by forming stable ion pairs with oversized alkylammonium cation.

On the basis of these investigations, a simple and reasonably practical procedure has been proposed. After sample decomposition by aqua regia, the analytes have been extracted from 6 M HCl solution of Pt ($100 \text{ g} \cdot \text{l}^{-1}$) into equal volume of MIBK. The aqueous phase has been removed and the platinum which has remained in the organic solution has been stripped twice by the equal volumes of 6 M HCl. A protective agent, trioctylmethylammonium chloride, (1% against V_0) has been added. The calibrating solutions have been treated in the same manner.

The absorbances have been measured at resonance absorption lines in $\text{C}_2\text{H}_2/\text{air}$ flame for Fe, Au and Sb, and in $\text{C}_2\text{H}_2/\text{N}_2\text{O}$ flame for Mo and Sn at $1.6/19 \text{ l} \cdot \text{min}^{-1}$ and $3.6/14 \text{ l} \cdot \text{min}^{-1}$ flow rates, respectively.

Data on accuracy, precision (RSD) and detection limits (DL) are presented in Table.

Characteristics of the method proposed, $t(P=0.95, n=5)=2.78$;

$t(P=0.95, n=4)=3.18$

Element	Added mg l^{-1}	Found mg l^{-1}	Error %	n	RSD	t_{exp}	DL (%)	Analysis by flame AAS for NBS standard reference material No. 681 has been in good agreement with the certified values (in ppm): Element AAS SD Recom. Report values ed values
Fe	.5	$.45 \pm .05$	10.0	4	.10	2.0	2.10^{-5}	
	1.0	$1.00 \pm .05$	0	5	.05	0		
Au	2.5	$2.48 \pm .05$.8	4	.02	.80	6.10^{-5}	Au 5.0 0.1 9 5-10
	5.0	$4.90 \pm .15$	2.0	5	.03	1.49		
Sb	2.0	$1.90 \pm .09$	5.0	5	.05	2.48	4.10^{-4}	
	2.5	$2.50 \pm .08$	0	4	.03	0		
Mo	2.5	$2.57 \pm .10$	2.8	4	.04	1.40	4.10^{-5}	
	5.0	$5.10 \pm .27$	2.0	5	.05	.83		
Sn	2.0	2.0 ± 0	0	5	0	0	1.10^{-3}	
	4.0	$3.9 \pm .10$	2.5	4	.03	2.00		

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Determination of the impurity composition of pure platinum metals is a very important problem of analytical chemistry. A considerable effect of some impurity elements on the operational characteristics of precious metal wares and the absence of strict correlations between the physico-chemical properties of a substance and its impurity composition requires control over a wide range of impurities in noble metals. At the present time there are no simple readily available methods for analysis of high purity platinum and rhodium with a determination of the microcomponents at a level of 10^{-7} to 10^{-5} %. Concentration of the impurities by an extractive separation of the base component makes possible to decrease considerably the detection limits of the known instrumental methods.

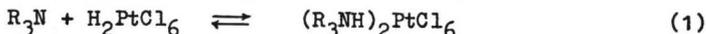
The present work is devoted to the study of the possibility of an extractive separation of the base in the analysis of high purity platinum and rhodium with subsequent spectral determination of the impurities in a highly sensitive variant using the graphite collector with 0.5% NaCl developed at the Institute of Inorganic Chemistry of the Siberian Branch of the USSR Academy of Sciences [1]. The method places rigid requirements on the quality of the matrix component separation (the purification factor must be not less than 10^3) which is due to the interfering effect of the Pt and Rh spectra as well as to the effect of the base residues on the spectral line intensities of other elements. The extractant for the matrix separation in the analysis of high purity substances must have a high capacity, efficiency, and selectivity with respect to the base element, it must be easy to purify and be practically insoluble in water.

The most effective extractants for platinum are nitrogen-containing extractants: amines, salts of quaternary ammonium bases, N-oxides of trioctylamine and α -nonylpyridine [2].

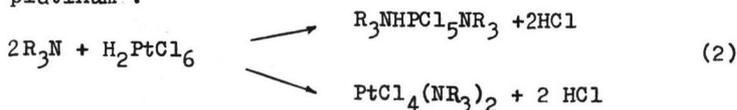
For the quaternary salts of ammonium bases the distribution coefficients of Pt(IV) are considerably affected by the counter-ion: the higher is the ion hydration energy the higher is the probability for him to go to the aqueous phase. From this point of view HCO_3^- and HC_2O_4^- forms are more preferable [3]. In the extraction with free amines the extraction can be expected to be still more effective since here there will be no competing effect of the exchanging ion at all. Fig. 1 shows Pt extraction isotherms with nitrogen-containing extractants from 0.1 mol/l hydrochloric acid solutions since it is in

such nearly neutral solutions where the extraction with the anion-exchange type extractants can be expected to be most selective due to unfavorable conditions for the existence of anionic chlorocomplexes of impurity elements. A calculation of the number of extraction stages required for a quantitative recovery of Pt(IV) from solutions with $C_{Pt} = 100$ mg/ml using the working line $y = \lambda(x - x_0)$ (x, y are Pt concentrations in organic and aqueous phases, λ is the ratio of the volumes of the aqueous and organic phases) shows that only for trioctylamine an effective single-batch extraction of Pt(IV) can be expected.

In the saturation part of the extraction curve of Pt(IV) with trioctylamine the mole ratio $R_3N : Pt$ is equal to 2.04 which is possible both in the case of formation of an ionic associate by the reaction :



and in the case of insertion of an amine into the inner coordination sphere of platinum :



Stripping of Pt(IV) from a freshly prepared organic phase with nitric acid (1:1) results in going of more than 99.0% of platinum into the aqueous phase, an observation in favour of the reaction taking route (1).

After separation of the base the concentration of Pt in the aqueous solution is 10 to 25 μ g/ml which amounts to 0.1 to 0.25% of the weight of the graphite collector containing the concentrated impurity elements. However for Al, Mn, La, Gr, Ti there is a depressing effect of Pt on the spectral line intensities at Pt content from 0.01% to 0.5%. Therefore to eliminate the interfering effect of the matrix 0.25% Pt was introduced into the reference samples.

The developed method for analysis of high purity platinum makes

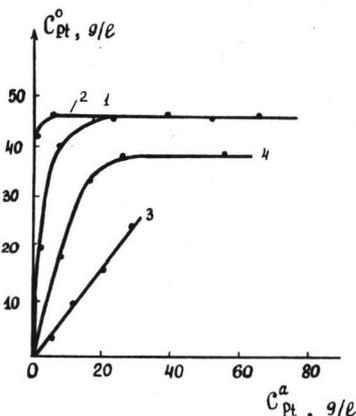


Fig. 1. Pt(IV) extraction isotherms from 0.1 mol/l HCl; $C_e = 0.5$ mol/l
 1 - $R_3RNHC_2O_4$; 2 - R_3N ;
 3 - 2-NPO; 4 - R_3NO

possible to determine 22 impurity elements (Be - at the level of $7 \cdot 10^{-8}$ %; Cd, In, Mn, Cu, Ag, Tl - $(1-8) \cdot 10^{-7}$ % ; Ba, Co, La, Ni, Pb, Ti - $(1-7) \cdot 10^{-6}$ % ; Al, Ca, Mg, Rh, Ru, Cr, Zn - $(1-2) \cdot 10^{-5}$ %; Ir, Sr at the level of $1 \cdot 10^{-4}$ %). In general, the presence of Pt in the extraction system practically does not affect the behaviour of the impurities. For Ag, In, and Tl the extraction was found to be depressed by the base presence and for Fe, Sn, V, Bi, Te coextraction is observed.

The choice of a reagent for removal of the base in the analysis of high purity rhodium is a very complex problem which is associated with the kinetic inertness and a relatively high charge of the Rh complex anions. It can be expected that the extractability of slightly hydrated polynuclear complex anions will be increased when using anion-exchange type reagents which was found in the extraction of Pt with the salts of quaternary ammonium bases [4].

Evaporation and subsequent drying of the complex halogenides of Rh(III) result in formation of polynuclear species in which the halogenide-ions act as bridges. In the aqueous solution the polynuclear complexes depolymerize, with the equilibrium state corresponding to the anion RhX_6^{3-} [5]. In the extractive dissolution of the polynuclear complexes of Rh there occurs their rapid transfer into the organic phase after which they slowly go into the aqueous phase under depolymerization. In order to retain as much as possible of rhodium in the organic phase it was necessary to find suitable conditions preventing the depolymerization of the polymeric species. It turned out that when $(\text{RhBr}_3)_n$ is dissolved directly in the extractant (TOA) in the subsequent contact with HCl solutions 99.97 % of Rh is retained in the organic phase, with some of the impurities being concentrated in the aqueous phase. Since in the presence of Rh its contents in the graphite collector of $\leq 1.0\%$ were not found to decrease the spectral line intensities of the impurities the atomic - emission determination of the impurities from the graphite

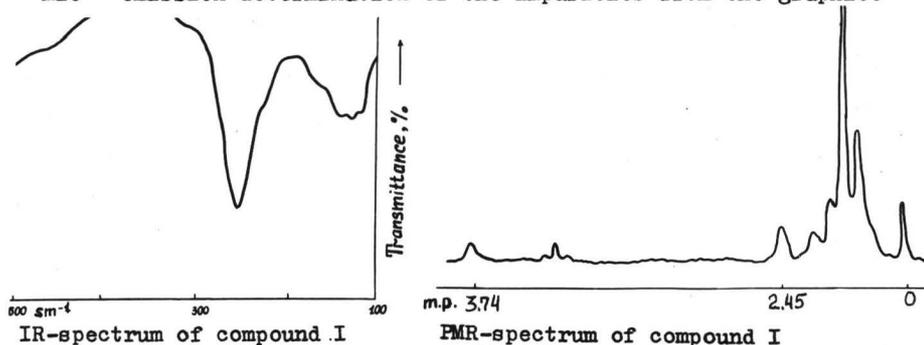
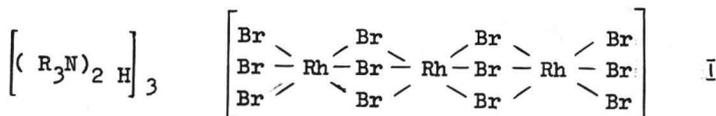


Fig. 2

collector can be carried out using a single set of the reference samples on the basis of graphite powder. The method allows determination of Be, In, Mn at the level of $(1-5) \cdot 10^{-7} \%$; Ba, Co, Ni, Ti, Cr - $(1-2) \cdot 10^{-6} \%$; Al, Ca, Mg, P at the level $(1-5) \cdot 10^{-5} \%$. The behaviour of the impurities is independent of the presence of Rh and is determined only by the concentration of the acid in the aqueous phase. The Rh compound which is formed in the organic phase when using this method of the base separation was studied by various physical methods. In Fig. 2 are shown IR and PMR spectra of compound I, which was isolated from the organic phase. The signal - 7.9 m.p. in the PMR spectrum indicates the presence of the R_3NH^+ group in the molecule of the compound under study. The polymeric nature of this compound is responsible for the presence of the absorption bands at 133 and 255 cm^{-1} corresponding to bridging and terminal Br atoms. There are no spectroscopic data indicative of the coordination of N to Rh. Therefore we can suggest existence in the organic phase of a compound corresponding to the formula



in which the cationic part is solvated. The elemental analysis data for I is presented in the table.

The developed methods for analysis of high purity Pt and Rh have better sensitivity than the direct spectral methods now in use in industry and are practically not inferior to the hardly available neutron activation and mass-spectral methods.

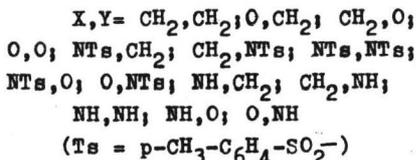
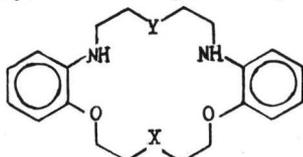
	C	H	Rh	Br
found	50.1	9.2	9.5	30.9
calculated	51.0	9.1	9.1	28.3

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The noble metals extraction with macrocyclic compounds has been only very poorly studied, though macrocycles are promisable as selective extractants. We have studied a series of 14 nitrogen-containing macrocycles in respect to 30 metals



Quantitatively or poorly extracted are only Pd, Os(IV), Pt(IV), Au(III), and Hg(II); Co, Ni, Cu, Ag, and Tl(I) demand special counterions (dipicrylaminat) for their extraction, and the following metals are not extracted (pH 1 - 10; 1·10⁻³M macrocycles in CHCl₃): Na, Ca, Sc, Ti(IV), Cr(III), Mn(II), Fe(III), Zn, Ga, Se(IV), Zr(IV), Nb(V), Ru(III), Cd, Sn(II), Sb(III), Te(IV), Ba, Ce(III), Ir(IV). This makes up a possibility for selective extraction of osmium(IV) or palladium. Their extraction has been studied in detail.

Osmium is extracted with macrocycle X=O, Y=NH in 1,2-dichloroethane (Fig.1), other macrocycles and diluents are less effective. The direct and the reverse extraction is fast (not more than 20 sek); the electron spectra show the presence of OsCl₆²⁻ in the organic phase. The electrophoresis data for fresh-prepared extracts also point at the metal presence in the anionic form. After more than 2 h storage metal migration towards the anode changes for its migration to the cathode, that can be interpreted as the formation of cationic Os(II) or (III) complexes.

The competitive processes such as the extraction of anions of the aqueous phase have been studied. Using the radioactive tracers method the chloride ion distribution coefficients vs. C_{C1} and C_L (L: X=O, Y=NH) have been obtained. The chloride ion is poorly extracted: its total concentration in the organic phase is of the order of 10⁻⁵M (D_{C1} = 1·10⁻⁴ - 2·10⁻³). Nevertheless it can seriously effect the osmium distribution.

Possible equilibria of chloride extraction with L have been suggested, and the system of equations has been compiled, including the matter balance, electroneutrality, equilibria constants, and D_{C1} expressions. The number of variables has been one more than the number of equations, so two unknown constants (extraction and dissociation

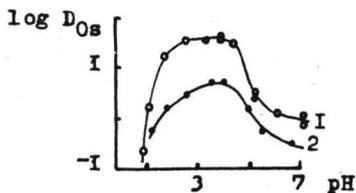


Fig. 1. Extraction of Os(IV) ($5 \cdot 10^{-7} \text{ M}$) with $1 \cdot 10^{-3} \text{ M}$ macrocycle $X=O$, $Y=NH$, from 0.04 M NaCl ; buffer or HNO_3 ; I - 1,2-dichloroethane, 2- CHCl_3

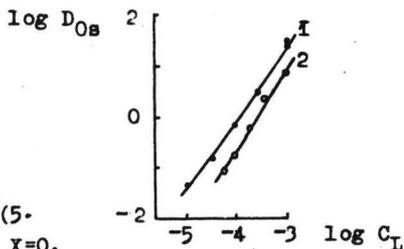


Fig. 2. Extraction of Os(IV) ($5 \cdot 10^{-7} \text{ M}$) with macrocycle $X=O$, $Y=NH$ in 1,2-dichloroethane, pH 3.8; I - 0.04 M , 2 - 0.4 M NaCl

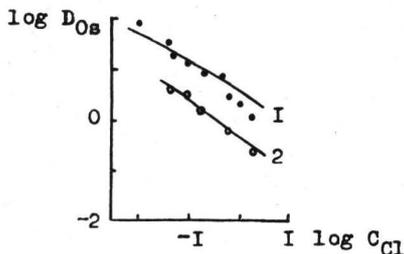


Fig. 3. Extraction of Os(IV) with macrocycle $X=O$, $Y=NH$ (L) in 1,2-dichloroethane, pH 3.8; I - $1 \cdot 10^{-3} \text{ M L}$, 2 - $3 \cdot 10^{-4} \text{ M L}$
On Fig. 2&3 curves are calculated with the found constants

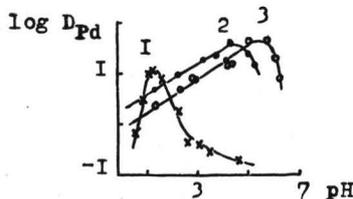
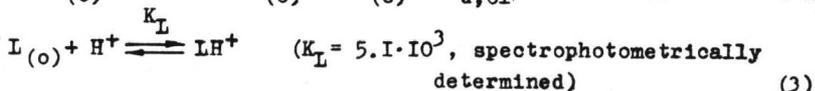
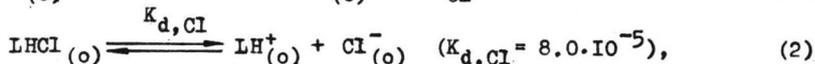
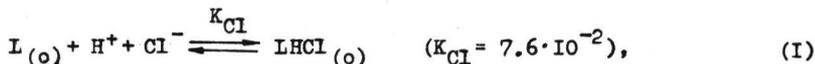


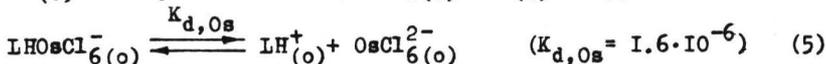
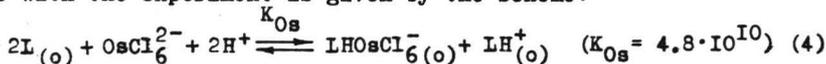
Fig. 4. Extraction of palladium ($1 \cdot 10^{-4} \text{ M}$), $1 \cdot 10^{-3} \text{ M}$ macrocycles: I - $X=Y=CH_2$ in toluene, 0.1 M NaClO_4 , 2,3 - $X=NH$, $Y=CH_2$ in CHCl_3 ; I,3 - nitrate solution, 2.5 h, 2 - chloride solution, 15 min

of the complex) have been optimised simultaneously. The following scheme is the most adequate to the experiment:



The model is true for $C_L < (1-3) \cdot 10^{-3} \text{ M}$ and $C_{Cl} < 4 \cdot 10^{-2} \text{ M}$ at constant pH 3.8.

Further the description of osmium distribution has been fulfilled as shown above, using the obtained constants (1)-(3). The best coincidence with the experiment is given by the scheme:



The curves calculated with constants (1)-(5) (Fig. 2,3) generally

fit the experimental points; worse fit is obtained for $D_{Os} - C_{Os}$ dependences.

To estimate the selectivity the distribution of other elements in the osmium extraction conditions has been studied ($1 \cdot 10^{-3} M L$, pH 3.8, $0.03 M NaCl$, 20 sek):

M	Os ^{IV}	Ru ^{III}	Ru ^{IV}	Rh ^{III}	Pd	Ir ^{III}	Ir ^{IV}	Pt ^{IV}	Au ^{III}	Hg ^{II}
$\log D_M$	1.5	-1.9	-2.1	<-1.3	-1.2	<-2.5	-1.9	0.9	0.3	1.3

The method for extractive-catalytic osmium determination is based on the o-aminophenol oxidation with hydrogen peroxide. The reaction goes in the mixture: extract(1,2-dichloroethane) - ethanol - water solution (1.1:1.0:0.14), in the presence of sodium acetate (activator). From $3 \cdot 10^{-4}$ to $0.02 \mu g/ml$ osmium can be selectively determined (the detection limit is $1.6 \cdot 10^{-4} \mu g/ml$). The determination is not hindered by $1 \cdot 10^4 - 1 \cdot 10^5$ -fold amounts of Al, Cr(III), Mn(II), Fe(II), Co, Ni, Cu, Zn, Rh(III), Ag, Se(IV), Te(IV), Pb; $(1-2) \cdot 10^3$ - of Ru(III)&(IV), Pd, Ir(IV); 600 - Pt(IV); 200 - Hg, and 100 - Au(III).

Palladium (Fig.4) is slowly extracted; the equilibrium is not attained during several hours. From chloride solutions palladium is extracted more rapidly than from nitrate ones. Electrophoresis data (macrocycle: $X=NH$, $Y=CH_2$) show that the metal is in the cationic part of the complex. The protons are shown not to be released during the extraction. The determination of Cl and Pd (by means of ^{36}Cl and ^{103}Pd) gives the composition Pd:L:Cl=1:1:2 for a solid complex and Pd:Cl = 1:2 for an extract ($L=NH, CH_2$). That is, $PdLCl_2$ (or its oligomer) is formed.

The extraction is selective; the distribution ratios of other metals are given below ($\log D$ for nitrate solutions, $1 \cdot 10^{-3} M L$, 2.5 h of phase contact):

L, cond.	Pd	Os(IV)	Pt(IV)	Au(III)	Hg	Ag	Cu	Ni	Co
NH, CH_2 in $CHCl_3$, pH 4	1.35	-0.4	-1.4 [‡]	-0.4 [‡]	-1.3 [‡]	-2.5	-1.6	-2.8	<-2.8
CH_2, CH_2 in toluene, pH I	0.95	-1.2	-1.7	-0.9	-1.0	<-2.8	<-2.4	<-3.8	<-2.8

[‡] In the presence of $1.3 M NaCl$

The method of extractive-atomic-absorption (with electrothermal atomization) determination of palladium. With the use of extraction (macrocycle: $X=NH$, $Y=CH_2$) $0.006 - 0.075 \mu g/ml$ of palladium in a solution can be determined (the detection limit is $0.003 \mu g/ml$). The below given amounts of other elements do not interfere the determination of $4 \cdot 10^{-7} M$ of palladium: Co, Ag ($2.5 \cdot 10^4:1$); Ni, Cu, Pb ($2.5 \cdot 10^3$); Hg ($1 \cdot 10^3$); Zn (250); Ru(III), Ru(IV), Pt(IV), Au(III) (25); Rh(III) (5); Os(IV), Ir(IV), Fe(III) (2.5).

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We have studied the extraction of benzene-, naphthalene-, quinoline-, indole- and phenylmethanedithiocarboxylates of palladium(II), platinum(II,IV), rhodium(II), iridium(III,IV), osmium(III,IV) and ruthenium(III) [1]. The obtained chelate complex compounds are yellow or yellow-brown and can be readily extracted with such organic solvents as chloroform, carbon tetrachloride, benzene, toluene. Butylacetate and isopentanol are the best extragents for the hydroxylic substituted dithiocarboxylates.

The light absorbtion of the extract containing dithiocarboxylate of platinum metal is usually measured in the relation with an extract obtained in an blank experiment, i.e. in absence of complex-forming substance [2]. Depending on the aqueous phase pH dithiocarboxylic acids can also pass into the extract partially or completely.

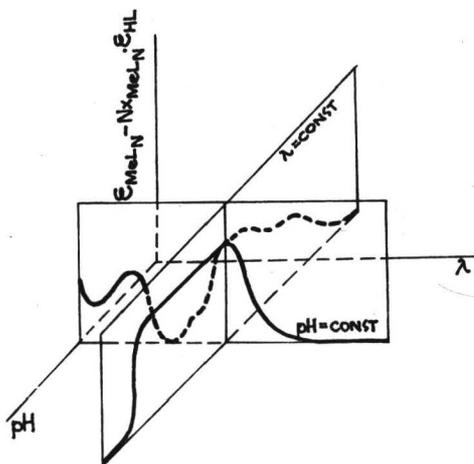
Absorbtion of the extract of the blank experiment is: $A_{ex}^0 = \epsilon_{HL} \cdot \frac{n_{L}^0}{v_{ex}} \cdot b$. Therefore, when meanning absorbtion of the extract containing dithiocarboxylate in the relation with the extract of the blank experiment the following constant is really measured:

$$A_{ex} = (\epsilon_{MeL_N} - N_{x_{MeL_N}} \cdot \epsilon_{HL}) \frac{n_{Me}^0}{v_{ex}} \cdot b; \quad \lambda = \text{const, pH} = \text{const.}$$

This constant does not depend on the reagent surplus and thus is very important for the extraction-photometric determination of platinum metals. The given relationship enables to calculate not the real molar coefficient of the absorbtion of complex dithiocarboxylate but only the difference $\epsilon_{MeL_N} - N_{x_{MeL_N}} \cdot \epsilon_{HL}$, functionally depending on the wave-length of the absorbed light and the aqueous phase pH. When describing the absorbtion of the extract by means of this difference the graphic representation is a three-dimensional diagram, having axes of the wave-length of the absorbed light, aqueous phase pH and the difference mentioned above (fig. 1).

The absorption of extracts is studied from separate sections of the diagram. If the section is examined with constant aqueous phase pH, spectral characteristics of the extract are obtained, if the wave-length of the light is constant, the pH interval of the aqueous phase where dithiocarboxylate is formed and extracted is determined. Fig. represents two sections of the tree-dimensional diagram with the dependence $\epsilon_{MeL_N - N_{x_{MeL_N}}} \cdot \epsilon_{HL}$ on the wave-length and the aqueous phase pH.

It has been found that with the exception of palladium dithiocarboxylates, preliminary heating ingredients at 95°C for 5-50 minutes is necessary in order to get maximal yield complex formation. It has been



Two sections of the three dimensional diagram showing the dependence of $\epsilon_{MeL_N-Nx} \cdot \epsilon_{HL}$ on the wave-length and pH of the aqueous phase

is found to be: PdL_2 , PtL_2 , PtL_4 , RhL_3 , IrL_3 , OsL_3 , OsL_4 , RuL_3 (L - dithiocarboxylate-ion).

It has been found that aqueous solutions of the aquahydrogenethylenediaminetetraacetatoruthenium(III) containing ions $[RuY(H_2O)]^-$ react with dithiocarboxylic acids (HL) at room temperature according to the following scheme [3]: $[RuY(H_2O)]^- + HL = [RuYL]^{2-} + H_3O^+$. The ratio Ru:L = 1:1 is determined in aqueous solutions with the mole-ratio and the shift of equilibrium methods.

As follows from the equation of complexforming reaction, the formed mixed-ligand ions are negatively charged therefore they do not undergo extraction by organic solvents. The extraction is possible in the presence of hydrophobic cations: benzenethiuronium (BTU), diphenylguanidinium (DFG), triphenylguanidinium (TFG), tetraphenylphosphonium (TFF), tetraphenylarsonium (TFA), tetraphenylpyridinium (TFP). The possibility of using various organic solvents for the extraction has been tested (table I).

Polar solvents possess higher extracting ability than non-polar solvents. With the increase of the dielectric permittivity of aliphatic alcohols their ability of extracting ionic associates rises. The ionic associates are extracted from the aqueous phase most completely by all the investigated solvents in the presence of TFF, TFA and TFP. The extraction degree of mixed-ligand complexes of ruthenium(III) in the presence of BTU, DFG and TFG considerably depends on the nature of the solvent. The reaction takes place best of all with the mixture

determined that the ligand nature influences the speed of the interaction, but the increase of its surplus accelerates the process of the formation of complexes negligably. Among the numerous studied additions formic acid was found to be the only one to accelerate slightly the complex formation. Interesting properties are demonstrated by palladium(II), whose dithiocarboxylates can be extracted even from the concentrated hydrochloric acid.

Composition of the formed complex compounds is determined by the mole-ratio, continuous-variation methods, the shift of equilibrium and by means of the Bjerrum function and Asmus method and

Table I. Extraction degree (%) of the ruthenium(III) ionic associates containing 4-dimethylaminobenzenedithiocarboxylate-ions

($t = 20 \pm 1^\circ\text{C}$; $n = 5$; $s \leq 1\%$)

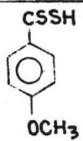
Organic Solvent	Hydrophobous cations					
	BTU	DFG	TFG	TFF	TFA	TFP
Isopentanol : chloroform (3:7)	90	100	99	100	100	100
Isopentanol	78	82	88	99	98	99
Butanol	85	88	87	92	95	95
Octanol	10	74	75	90	85	96
Chloroform	16	34	25	92	87	94
Nitromethane	-	22	15	84	84	92

(3:7) of isopentanol and chloroform and the mixture (1:1) of isobutanol and nitromethane.

It is better to use DFG as a hydrophobous cation for practical purposes because of its availability and easy purification. It has been found that quantitative extraction of ionic associates of ruthenium (III) requires 1000-fold surplus of DFG irrespective of the type of substituted benzenedithiocarboxylate-ion.

Table 2 represents the data of spectrophotometric determination of platinum metals using several dithiocarboxylic acids.

Table 2. Spectrophotometric determination of platinum metals

Reagents	Me	$\mu\text{g/ml}$	$\epsilon \cdot 10^{-4}$	λ_{nm}	Acidity
$(\text{H}_3\text{C})_2\text{N}$ -  -CSSH	Ru(III)	0,02-10,0	3,7	520	pH 2,5-6,5
	Os(III)	0,02-8,5	7,0	480	
	Ru(III)	0,1-35,0	0,8	498	pH 3,0-7,0
	Pd(II)	0,02-9,0	4,8	425	
	Ir(III)	0,05-25,0	2,8	420	pH 6,0-7,9
	Pt(II)	0,02-10,0	7,0	488	6M HCl - pH 3,0

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The possibilities of highly sensitive atomic-absorption (AAM) and atomic-emission (AEM) methods for group determination of platinum metals (PM) can be realized in the analysis of complex objects by elimination of the interfering effects of the macrobase elements by means of extractive concentration. The most effective extractants for group separation of PM are the primary aromatic amines, in particular, n-octylaniline (OA) and its easily available commercial analog - n-alkylaniline (AA) [1]. In contrast to S- and S-N-containing compounds [2,3] these extractants are able to extract quantitatively all PM independently of the oxidation state and do not require addition of labilizing additives to accelerate the extraction.

Chemistry of PM extraction with n-octylaniline. The extraction of PM with weakly basic OA is accompanied by formation in the organic phase of different species depending on C_{HCl} . Extraction of anionic acido forms of PM is observed at HCl concentrations sufficient to convert OA to $OA \cdot HCl$. Such concentrations are equal to 3M HCl for Ir, Rh, and Ru [4] and 5-6M HCl for Pt and Pd. At lower acidities the extracts contain coordination or mixed compounds. Thus for the extraction of Pd and Pt from 3M HCl, the extracts were shown, by IR and electron spectroscopy and preparatively, to contain $[Pd(OA)_2Cl_2]$ and $[OAHPt(OA)Cl_5]$. A quantitative description of the PM extraction is complicated by association of $OA \cdot HCl$ in toluene (which is the most convenient solvent for the instrumental analysis of an extract), polymerization of the extracted complexes at high PM concentrations or their dissociation at low PM contents. These processes are less pronounced in a caprylic acid media where we were able to determine the anion exchange extraction constants for Pd and Pt. But in this case the distribution coefficients (D) are by two orders of magnitude lower than for toluene solutions of OA.

Absolute concentration of PM. The optimum acidity for group extraction of PM is 2-3M HCl. A quantitative extraction of PM is observed over a wide range of their concentrations (Table 1) and at PM concentrations from 10^{-4} to $10^{-2}M$ the values of D are almost constant (25-33 for Pd and Rh, 80-90 for Pt, 100-120 for Ir and Ru, $OA \cdot HCl$ concentration - 0.5M). At a two orders of magnitude lower initial PM concentration the value of D increases to 200-250 which allows a 5 to 10-fold absolute concentration in the analysis of depleted and

highly depleted ores while retaining the extraction (R,%) at the level 91-98 % up to the ratio of the aqueous to organic phase volumes of (Aq:O) = 10:1 (Table 1). Ir and Ru in the oxidation state (III) and (IV) show practically the same values of D. From the point of view completeness of the extraction and the physical properties of the extract it is expedient to use in the subsequent analysis 0.5M toluene solution of AA. Relative concentration of PM. The study of the extraction of the macrobase elements in the analyzed objects in the range of their concentrations from 0.01 to 1M and at 1 to 3M HCl showed that the values of D are mostly at the level $n \cdot 10^{-2}$ (for 0.5 M AA), except for Zn, Sn(II), Pb (D=1-10). The value of D is independent of the metal concentrations for

Table 1. The extraction of PM with AA solutions in toluene from 3M HCl at Aq:O=1:1

C _{AA} , M	C _{PM} , M	Extraction, %				
		Pd	Pt	Rh	Ir	Ru
0.2	$2 \cdot 10^{-2}$	92	94	83	94	-
0.5	$2 \cdot 10^{-2}$	97	98	97	99	-
1.0	$2 \cdot 10^{-2}$	98	99	97	99	-
0.2	$5 \cdot 10^{-3}$	93	98	92	99	-
0.5	$5 \cdot 10^{-3}$	97	98	96	99	-
1.0	$5 \cdot 10^{-3}$	97	99	98	99	-
0.5	$1 \cdot 10^{-4}$	100	100	95	95	96
0.2	$6 \cdot 10^{-5}$	100	100	93	91	96
0.5	$6 \cdot 10^{-5}$	100	100	98	95	98
0.5	$1 \cdot 10^{-6}$	100	99	98	-	97
0.5*	$1 \cdot 10^{-6}$	99	98	97	-	96
0.5**	$1 \cdot 10^{-6}$	98	91	92	-	91
0.5***	$1 \cdot 10^{-6}$	92	91	75	-	86

*Aq:O=5:1, ** 10:1, *** 20:1

Co, Ca, Ni, increases with it for Fe, Mg, Al, Sn, Cu and Cr(III) and decreases for Mn and Zn. The distribution coefficients of Pt and non-noble metals are equal to 10^3-10^4 . The extraction of microquantities of PM against the background of the non-noble metal macroquantities studied on model mixtures simulating copper-nickel production products and on technological products is practically the same as that presented in Table 1. A fall of R to 65-70% was observed only in the case of Pd. Therefore, in the analysis use was made of a mixture of AA (0.4M) with petroleum sulfides (PS) (0.15 M) which ensures a ten-fold concentration of Pd at R=98-100%. To avoid possible effects of non-noble metals on the extract analysis and the physico-chemical properties of the extract it was washed with 2M HCl and 1M HNO₃ (to remove Pb). Approximately in accord with D of the non-noble metals, each washing produces a 10^2 -times increase of the PM concentration. After two washings the metal contents amount to less than 10 to 20 p.p.m. The PM losses do not exceed 2-3%, the overall separation coefficients of Pt and non-noble metals increase to $10^6 - 10^8$.

Interferences in the instrumental analysis of the extract. The mutual effect of PM and the effect of non-noble metals on PM in the AA and AE methods is considered.

In the flame atomization in AAM there are both the mutual effects of PM and the effects of Fe, Cu, Ni, Pb and other metals when they are present in concentrations equal to those of PM. Although these effects are of different nature they all can be eliminated by adding to the extract a buffer solution $\text{La}(\text{NO}_3)_3$ in ethyl alcohol with up to 1% of La. The measurements are carried out using reference solutions containing all PM and La. In the case of Pd the reference solutions are used without La since other PM and the non-noble metals do not affect the Pd analytical signal up to their contents of 1 mg/ml. In all cases the extractant concentrations in the reference solution and in the extract being analyzed are kept constant and equal to each other.

In the electro-thermal atomization there are no mutual effects of PM for Pd, Pt, and Rh up to a 1000-fold excess of each metal and no effects of Ir and Ru up to their contents in a 200-fold excess. In the determination of Ir and Ru a decrease in the analytical signal of these metals was established at Pt:Ru, Ru:Ir, and Rh:Ir ratios of 200:1, 10:1, and 40:1, respectively. It was also found that a 150-fold excess of Pd and Pt and a 600-fold excess of Rh, Pd, and Ir do not affect the atomic absorption of Ir and Ru, respectively. For products with an unfavourable PM ratio methods have been developed for their extraction separation. The PM analytical signal is practically unaffected by the presence of non-noble metals in amounts up to a 400-fold excess of Al, Cr, Mg, a 2000-fold excess of Au and Pb, a 8000-fold excess of Fe, Cu, Ni and other metals. Washing of the extract is needed in this case to stabilize the extract composition and the analysis conditions. For the same reasons the extractant concentration is kept constant in the extract and in the reference solution.

The atomic-emission method of PM determination in an extract involves ashing of the extract, dilution with a spectral buffer and introduction into the arc plasma by a "blow-in - spilling" method. In this method no mutual effects of PM are observed up to their 100-fold excess. The effect of non-noble metals on the PM spectral line intensities and the background is completely removed by washing of the extract. Comparison of the calibration plots obtained by extraction for each PM concentration and by dilution of extracts with known PM contents indicated their coincidence. The second technique is less labor-consuming and allows preparation of samples for several measurements. The linearity region of the calibration plots is, $\% \cdot 10^3$: Ir and Ru - 0.3 - 7; Pd and Pt - 0.3 - 14 (for Pd to 50); Rh - 0.15 - 7.

Extraction-instrumental methods of analysis. The analysis procedures involve decomposition of the products with a $\text{HCl} + \text{HNO}_3$ mixture

(samples with high Si and S contents are first treated with HF or annealed). The insoluble residue is then fused with Na_2O_2 and the melt is leached with HCl after which both solutions are added together. The extractive separation of PM is preceded by removal of HNO_3 by alternately treating the resulting solution with HCl and water (the presence of 0.5M HNO_3 in the solution decreases the value of D of Rh and Ru to 2.7 and 0.3, respectively). To increase the reliability of the analysis for products with very low PM contents (10^{-7} - $10^{-6}\%$) double-concentration methods have been developed (the first stage - to produce a Pb alloy or a Ni matte). In the analysis of the Pb alloy the PM are separated from the Pb macroquantities by thermal dissociation

with nitric acid and subsequent leaching of Pb nitrate with water. The insoluble residue containing PM and not more than 0.2% of Pb is dissolved in HCl and then the extraction is carried out (an analogous procedure is used in the analysis of products containing more than 30% Ag). The developed methods (their characteristics are given in Table 2) find application in the analysis of geochemical samples, various ores and their

Table 2. Metrological characteristics of the PM determination methods

M	Determination method	Concentration range, %	S_r
Ir	The atomic-emission method in the "blow-in - spilling" variant	$3 \cdot 10^{-7}$ - $1 \cdot 10^{-5}$	0.25-0.19
Rh		$6 \cdot 10^{-7}$ - $1 \cdot 10^{-5}$	0.20-0.09
Ru		$3 \cdot 10^{-6}$ - $1 \cdot 10^{-5}$	0.25-0.10
Pd		$1 \cdot 10^{-6}$ - $1 \cdot 10^{-5}$	0.20-0.07
Pt		$3 \cdot 10^{-6}$ - $1 \cdot 10^{-5}$	0.20-0.05
Au*		$8 \cdot 10^{-7}$ - $3 \cdot 10^{-6}$	0.25-0.10
Pd	Atomic-absorption method, air-acetylene flame	$1 \cdot 10^{-3}$ - $5 \cdot 10^{-2}$	0.09-0.02
Ru			
Rh			
Au		$1 \cdot 10^{-3}$ - $1 \cdot 10^{-1}$	0.06-0.01
Ir	Atomic-absorption method, graphite furnace	$4 \cdot 10^{-5}$ - $2 \cdot 10^{-3}$	0.15-0.02
Pt		$4 \cdot 10^{-3}$ - $1 \cdot 10^{-2}$	0.09-0.01
Rh		$5 \cdot 10^{-6}$ - $1 \cdot 10^{-3}$	0.15-0.02
Ru		$1 \cdot 10^{-4}$ - $7 \cdot 10^{-2}$	0.15-0.01

* In the case of AA+PS. mixture all gold is extracted quantitatively

concentration products, liquid and solid technological products of hydro- and pyrometallurgical stages in copper-nickel production indicating a universal character of the method for group separation of PM.

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Extraction is used in analytical chemistry of boron for: 1. separation of boron from interfering elements, 2. concentration of trace amounts of boron, 3. extraction-spectrophotometric-, 4. extraction-titrimetric determination of boron, 5. standartization of sample for spectral-, atom-absorbtion and flame-spectrophotometric determination of boron.

Recently, quite a large number of methods for extraction-spectrophotometric determination of minute quantities of boron has been developed. They are based on the formation of anionic chelate complexes of boron with ligands containing α -diols or α -hydroxycarboxylic groups, which permits to extract boron from a weak acidic or weak alkaline solution in the form of ion pairs together with basic dyes. Some examples see in Table I. Those methods are rather sensitive but not selective and require the separation of boron from most of elements of periodic system.

Table I. The extraction-spectrophotometric methods of determination of boron based on the formation of ion pairs

Chelating ligand	The basic dye	The organic solvent	pH	λ , nm	ϵ	Reference
3,5-di-tert.-butylpyroka-techol	ethyl violet	toluene	6,3-8,7	610	10^5	[17]
2-methyl-2-hydroxybutiric acid	malachite green	chlorbenzene	2,5-4,3	629	"	[27]
2,3-dihydroxy-naphtalene	cristal violet	"	3,0-7,0	595	"	[37]
mandelic acid	malachite green	benzene	2,2-3,0	633	$6,25 \cdot 10^4$	[47]
2,3-dihydroxy-naphtalene	chrompyrazol	chlorbenzene				[57]

The universal method of separation and concentration of boron is the extraction by aliphatic β -diols in organic solvent (for example CHCl_3) [67]. We have studied more than 20 β -diols C-5 - C-14, including some isomers C-9, C-10. The extraction is based on the formation of cyclic esters, which are stable towards hydrolysis and soluble in organic solvents. The extractants are effective in acidic, neutral and

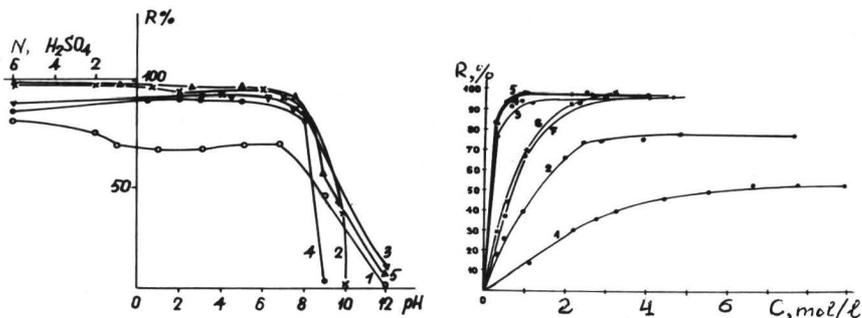


Fig.1. The dependence of boric acid extraction by β -diols in CHCl_3 (0,5M) on pH: 1.-3-methyl-1,3-butanediol, 2.-1,3-nonanediol, 3.-2,6-dimethyl-4,6-octanediol, 4.-2,2-dipropyl-1,3-propanediol, 5.-2-isopropyl-5-methyl-1,3-hexanediol

Fig.2. The dependence of boric acid extraction on the concentration of β -diol in CHCl_3 : 1 - 1,3-butanediol; 2 - 3-methyl-1,3-butanediol; 3 - 1,3-nonanediol; 4 - 2-propyl-1,3-heptanediol; 5 - 2-buthyl-1,3-octanediol; 6 - 2,4-dimethyl-2,4-octanediol; 7 - 2,4-dimethyl-2,4-nonanediol

weak alkaline media (Fig.1). The reextraction is performed by the solution of alkali (2-3%). The partition coefficient usually increases with the growth of the concentration of β -diol till saturation (Fig. 2). In some solvents (CHCl_3) the synergetic effect is observed owing to diminishing of the self association of β -diols. The extraction equilibrium is reached after 1 min. or some hours and depends on the structure of β -diol and the acidity of solution. In acidic medium it requires less time. The rate and completeness of reextraction is also dependent on the structure of β -diol.

The mineral salts, especially NaCl and MgCl_2 , have the salting-out effect, which is connected with the concentration of salt, but in some cases the time of setting-in of equilibrium is increased.

The effectivity of extraction is not connected with the concentration of H_3BO_3 in the solution, but the excess of β -diol (10x in mol) is necessary.

The type of ester (1:1, 2:1 or 3:2), which is formed depends on the structure and solubility of β -diol. In the case of more soluble and lipophilic β -diols, for example n-1,3-diols, 3-methyl-1,3-butanediol, it is a cyclic ester 1:1, in the case of less soluble in water and crystalline diols - less stable towards hydrolysis but more extractable ester 2:1. The latter β -diols are more effective as extractants. Only the threecoordinated boron is found in the extract by IR-spectroscopy. The existence of cyclic esters $\text{R}-\text{O}-\text{B}(\text{OH})_2$ and $\text{R}-\text{O}-\text{B}(\text{OR})_2$ in ex-

Table 2. Extraction properties of some β -diols in the system:

β -diol/ CHCl_3 (0,5M) - H_3BO_3 - H_2O , 25°C

β -diol	The compound formed	Limiting $\text{D}_{\text{H}_3\text{BO}_3}$	Solubility, %, 25°C	
			diol in H_2O	H_2O in diol
n-3,5-oktanediol	3:2	26	5	-
2,2,4-trimethyl-1,3-pentanediol	2:1	30	-	insoluble
n-1,3-nonanediol	1:1	9	1,22	23,83
2,2,5-trimethyl-1,3-hexanediol	2:1	31	0,52	insoluble
2-propyl-1,3-heptanediol	3:2	47	1,02	8,51
2-isopropyl-5-methyl-1,3-hexanediol	2:1	335	0,62	2,56
2,2-dipropyl-1,3-propanediol	2:1	23	0,28	insoluble
2,4-dimethyl-2,4-oktanediol	3:2	63	1,22	1,95
2,6-dimethyl-4,6-oktanediol	2:1	63	1,22	1,95
2,6-dimethyl-4,6-oktanediol	1:1	14	2,13	0,91

tracts is confirmed by the PMR-spectra upon the example of the reaction of 3-methyl-1,3-butanediol with H_3BO_3 in water - organic medium.

For all of β -diols investigated, condition may be selected, when $\text{D}_{\text{H}_3\text{BO}_3} > 20$. This allows to extract boron quantitatively by two cycles when macroamounts, and by one cycle when microamounts of boron are determined. The distinctions of diols as to solubility, rate of extraction and reextraction and so on make it necessary to use in each concrete case various diols.

Thus, one of the more appropriate β -diols for the concentration of boron is 2-isopropyl-5-methyl-1,3-hexanediol, which allows to concentrate boron in extract for 3 - 5 times.

For extraction-titrimetric determination of boron, which is based on the separation of boron from interfering elements by extraction in CHCl_3 and alkalimetric titration the extract by addition of mannitol with visual or potentiometric indication of equivalence point, the most appropriate are 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2-methyl, 2,4-pentanediol, 2,2-dipropyl-1,3-propanediol, which allow easy reextraction of boron. 2,6-Dimethyl-4,6-oktanediol, 2-propyl-1,3-heptanediol are used for titrimetric determination of boron only after reextraction.

For spectrophotometric determination of microamounts of boron with carmin or 1,1'-diantrimid only less soluble β -diols are useful, for

Table 3. The maximum possible excess of interfering ion by extraction-titrimetric determination of boron (M:B weight)

M	MBD	HD	DMOD	DDPD
Al ⁺³	170	10	interf	10
Ga ⁺³	20	75		10
In ⁺³	75	75		110
La ⁺³	150	150		70
SiO ₃ ⁻²	interf.			350
Ti(IV)			110	200
Ge(IV)	60	50		interf.
Sn ⁺²	100	160		200
Pb ⁺²	20	100		300
PO ₄ ⁻³	100	70	110	280
As ⁺³	10	100		90
Sb ⁺³	5	5		65
Bi ⁺³	100	100		300
Cr ⁺³			60	900
MoO ₄ ⁻²	300	150	50	1000
WO ₄			100	200
VO ₄ ⁺²	200	200	20	50
Fe ⁺²			125	1600
Co ⁺²			220	1500
Ni ⁺²			200	3650

MBD - 3-methyl-1,3-butanediol, ND - 1,3-nonanediol, DMOD - 2,6-dimethyl-4,6-oktanediol, DDPD - 2,2-dipropyl-1,3-propanediol.

example 2,2-dipropyl-1,3-propanediol, 1,3-nonoanediol, 2-isopropyl-5-methyl-1,3-hexanediol. All β -diols investigated can be used when atom-absorption or flame-spectrophotometry is applied, not requiring preliminary separation of boron from the extract.

The extraction of boron with β -diols is highly selective (Table 3). On this the methods of determination of boron in steel and nickelous alloys, mineral salts, inhibitors of corrosion, conservants of wood and other technical objects are based.

These methods warrant an economy of the efforts and time of the chemist - analyst.

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Extractive chromatography relates to a new research method of separation and analysis of substances. The first full review in that field was published in 1978 [1]. Sufficient results have been achieved in theory and practice of extractive chromatography applied for separation of inorganic compounds. In organic analysis extractive chromatography is not practically used although first publications on the subject appeared in the 60-th. So far there have been no systematic studies of the influence of different factors such as the supporter properties of solvent extractive agents and extracted organic compounds to the effectiveness of extractive processes, separation and concentration of compounds. However extractive chromatography is rather perspective for such important ecological problems as the development of non-reagent methods for sewage treatment, preservation of the environment from high toxic compounds, and can increase selectivity in the analysis of organic compounds.

The idea of the technique is that porous material with high specific surface ($200-400 \text{ m}^2/\text{g}$) is covered by organic solvent (effective extractive agent for individual or complex compound separation by static extraction) and the process of extraction and re-extraction runs dynamically. Thin layer of organic solvent increases the rate of extraction, provides high degree of concentration, as extractive compounds for narrow zone in column analogous to sorption zone in chromatography. The influence of different factors on the effectiveness of extractive chromatographical column with porous copolymers as a bed of extractive agent for detection of organic substances has not so far been studied.

We have studied the influence of chemical-physical properties of extractive agents, sorption ability of supporters as well as the quality of extractive agents, column parameters and the size of sorbent particles to the effectiveness of extractive chromatographical column for phenol compounds and oil products extraction from sea and fresh waters. As fresh and sea waters have principal value for human life it seems reasonable to use extractive chromatography for solving the problems connected with water protection from phenol and oil products pollution.

We have developed a number of procedures for industrial toxic substances extraction from potable, mineral and sea waters. The rela-

tions between different extractive agents and their supporters was studied with n-amylacetate, toluene, tetrachlormethane, 3-n-butylphosphate (TBP) and octane TBP mixture. Porous copolymers of styrene and divinylbenzene were used as the supporters as they contain specific groups in matrix. Copolymers of styrene and DVB swallowing results in keeping larger organic solvent than non-swallowing sorbents. Extracted compound as well as a solvent penetrate the polymer matrix retarding re-extraction. However stronger connection between extractive agent and the supporter decrease its solubility in effluent comparing with static extraction condition. These assumptions were verified experimentally with porous neutral adsorbent under studying extractive chromatographical systems used for phenol compound analysis. Correlation has been established between the quantity of organic solvents (amylacetate, heptanol, tetrachlormethane, toluene and TBP) and their surface retention, toughness, dielectrical penetration. It shows that extractive agent molecules are kept on hydrophobic surface of sorbents based on styrene and DVB due to their adsorption forces of different nature (dispersional, orientational and dipole-dipole interconnection). The increasing polarity of specific groups results in better keeping of polar solvents and becomes, for instance, for amylacetate and heptanol of a considerable value (1.8-1.6 g/g). To use toluene and tetrachlormethane as extractive agents is not reasonable because these solvents are easily washed.

By varying extractive agents a great number of sorption qualities of polymer can be produced. Thus, for example, covering the surface of neutral adsorbent polysorb-I by octane TBP mixture we observe the inversion of the alkaliphenol sorption row (Table 1). Treatment of the polysorb-I by pure TBP results in decreasing of phenol sorption in phenol-cresol-xylene row. Dilution of TBP by octane results in inversion of the row, i.e. sorption in the row is increasing. The treatment of the polysorb-I by octane decreases the sorption of the polar components. This phenomenon may be used for separation of non-polar

Table 1. Phenol sorption by polysorb-I, treated by octane and TBP alternative composition (n=3; P=0,95)

Phenols	Content of TBP in mixture with octane, % mass						
	0	10	20	30	40	50	100
Phenol	5	25	36	46	54	74	72
2-Methylphenol	29	38	64	69	75	86	64
4-Methylphenol	33	47	74	78	81	90	57
2.5-Dimethylphenol	41	61	83	87	90	90	60

substances in that case. Sorbents treated by the organic solution acquire new properties compared with non-treated ones. Such sorbents we call "combined".

The influence of specific groups to supporters ability to keep organic solvents - effective extractive agents for phenol and oil products separation - have been studied on copolymers of styrene and DVB containing nitronitryl and amid groups, and also acetyleted copolymer.

Sorbition ability of the untreated sorbents depends upon the nature of specific groups and sorbited molecules. This phenomenon hampers the effective prediction of chromatographical processes while using such sorbents. Treatment of the surface of specific sorbents scans their own adsorbition band, that is why the sorbition of phenol compounds increase in phenol-cresol-xylenol row. The established dependance coincide with the character of phenol distribution between water and amylacetate in liquid extraction. The significance of extractive agent in phenol sorbition by "combined" sorbents decreases while sorbent polarity increases (Table 2).

Table 2. Phenol sorbition by specific sorbents before (I) and after (II) treatment by amyleacetate

Sorbents	Polarity according to Rohrscheider	Sorbited phenols, %					
		Phenol		4-Methyl-Phenol		3.5-Dimethyl-Phenol	
		I	II	I	II	I	II
Polysorb-N	1255	75	80	60	86	50	90
Nitropolysorb	1078	30	58	44	77	44	88
Nitrilpolysorb	727	45	65	50	84	68	97
Acetylpolysorb	-	14	48	24	59	65	92
Polysorb-I	206	10	37	17	53	40	57

The capacity of the columns was evaluated according to the value HETP (Height of Equivalent Theoretical Plate). In practice the most important is the character of dependance HETP from the quantity of extractive agent covered the supporter as it is possible to vary this factor for optimization purposes. The value of HETP for the column with 5, 10, 20 sm layer (1 sm diameter) was found by means of front curves. It was established that ratio HETP quantity of extractive agent is shown by the curve with minimum correlative to a relationship between extractive agent and the supporter 1:1. Such relation results in maximum separation of the extractive compounds from water (95-98%) with the highest concentration coefficient (50-100%).

The present research permitted us to work out general recommendations for separation of microquantity of phenols and oil products for express-evaluation of the level of water pollution [2-4]. To detect phenols it is recommended to fill the column by neutral porous adsorbent on the base copolymer of styrene and DVB with amyacetate (1:1). The most effective effluent is the aqueous solution of chloride alkali metals alkalined by sodium hydroxide pH 12-13. The presence of phenol was found spectrophotometrically or gaschromatographically. The last way was optimized by special procedure consisting of microextractive concentration of phenols in effluent. This procedure provides the detection of phenols at $0.5-10^{-3}$ mg/l concentration. The time of analysis is not more then 0.5 h. Combined with photometrical detection of phenols extractive-chromatographical method gives us reliable and time-saving technique of evaluation of the level of water pollution in field. It may be used for all sources of water supply including sea and ocean. These methods are used to detect phenols in the water of the Baltic Sea, the Don and Volga rivers and the Baikal.

To detect oil products the surface of the supporter is covered by N-gexan. The column is also filled by gexan[5]. The contents of oil products in effluent is detected spectrofluometrically or refractometrically. The advantage of the method in question consists in time-saving and precision of analysis.

The adduced examples demonstrate broad possibilities of extractive chromatography in solving analytical and ecological problems connected with different measures directed to water protection from organic toxic substances.

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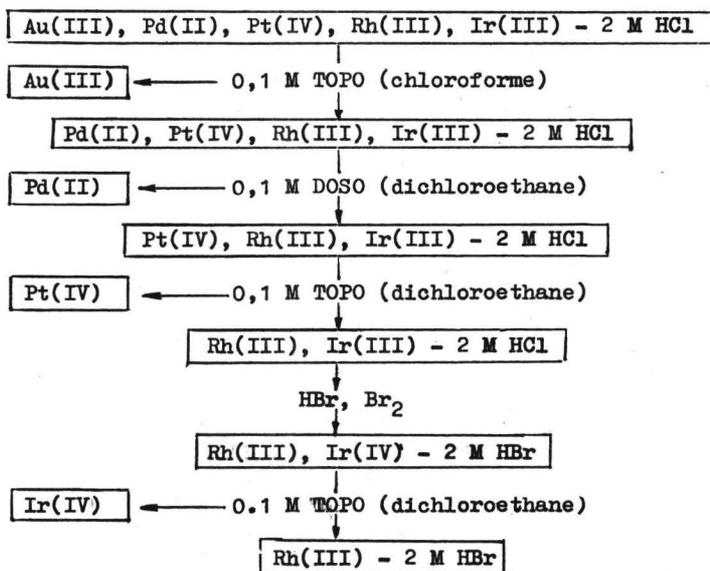
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Solvent extraction methods, especially the ones involving neutral solvating reagents are particularly useful for the separation of noble metals. This is due to the well-known advantages of extraction as separation technique and also to such properties of noble metals as the ability to form complexes with various types of ligands in aqueous solutions, occurrence in various oxidation states and differences of ligand exchange reaction rates.

A new method of separation of gold, platinum, iridium and rhodium, based on the systematic examination of the extraction of halide complexes of noble metals with trioctylphosphine oxide (TOPO) and dioctyl sulphoxide (DOSO) in different solvents, has been worked out.

The scheme of separation of Au, Pd, Pt, Ir and Rh by solvent extraction with TOPO and DOSO



The initial solution in 2 M HCl contains Au(III), Pd(II), Pt(IV), Ir(III) and Rh(III) in the form of chloride complexes. Extraction with 0.1 M TOPO solution in chloroform enables the separation of

gold. Chloroform, as solvent, diminishes the extractive power of TOPO to such an extent that the extraction of Pd(II) and Pt(IV) is impossible.

Palladium(II) is extracted from the aqueous phase after the separation of gold using 0.1 M DOSO solution in dichloroethane. In contrast to other platinum metals, only palladium(II) can be extracted efficiently from 2 M HCl medium by means of this extractant.

After the separation of palladium, the aqueous phase contains platinum(IV), iridium(III) and rhodium(III) in 2 M hydrochloric acid. Platinum is separated from this solution by the extraction with 0.1 M TOPO solution in dichloroethane.

Before the separation of iridium from rhodium, the aqueous phase medium is changed from 2 M HCl to 2 M hydrobromic acid with a simultaneous transition of Ir(III) chloride complex into Ir(IV) bromide complex. In order to carry out this operation, evaporation with hydrobromic acid in the presence of Br is necessary. Iridium(IV) bromide complex is extracted with 0.1 M TOPO solution in dichloroethane.

Results of separation of Au, Pd, Pt, Ir and Rh by solvent extraction with TOPO and DOSO

Added (ug)					Determined after separation (ug)				
Au	Pd	Pt	Ir	Rh	Au	Pd	Pt	Ir	Rh
200	20	100	100	50	195	18	93	92	54
200	100	20	50	100	197	99	22	46	92
20	100	20	100	50	19	93	20	92	52
20	50	50	100	100	20	51	48	98	96
50	20	20	200	50	46	21	19	191	48
50	50	200	50	200	49	46	195	44	207

The separation method presented in this paper has been verified on a number of synthetic mixtures of different noble metal ratios. The effectiveness of the separation has been checked by means of spectrophotometric methods and AAS. The results, shown in Table demonstrate the correctness of the applied solution.

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Extraction of metal complexes by means of organic solvents from aqueous solutions depends on complex stability, structure of its co-ordination sphere, ligand - metal bond type, and on other parameters.

We had demonstrated before that alkyl substituent attached to 2-position of 1,3-diazole ring made a steric hindrance. It does not mask, however, the donor sites of 1,3-diazoles so effectively as in case of - substituted pyridine derivatives. The effect of 2-alkylimidazole alkyl substituent on complexes formation depends on central ion properties.

Hence, we assumed that the differences in stability and structure of the complexes, resulted from the steric effect, can be utilized for the selective extraction of metal cations.

All the measurements /potentiometric, optic, and extraction/ were carried out at 298 K and at the same, 0.5, ionic strength maintained by means of KNO_3 .

Co-ordination process of 2-n-propylimidazole with Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) was analyzed also by taking into account the formation curves, i.e. the relationships between mean ligand number value and ligand concentration, $[L]$, at equilibrium. The sets of $[L]$ variables, together with the corresponding \bar{n} values, were calculated from pH values determination for the solutions containing cations of the metals investigated, and from determined dissociation constant, K_a . Precipitates had been appeared in the solutions containing Zn(II) and 2-n-propylimidazole, and this fact precluded the realization of planned investigations for Zn(II).

The determined \bar{n} and $[L]$ values were used for the formation curves, $\bar{n} = f/pL$, drawing, and for calculation of stability constants for the complexes formed in the solutions investigated. The obtained values of stability constants are listed in Table 1.

It results from the analysis of Table 1 data that the steric effect, caused by the presence of n-propyl group in 2- position of imidazole ring, differentiates the processes of formation of the complexes of all five metals investigated by causing changes in their stability and, in some cases, in the symmetry of their co-ordination spheres.

Then, we studied extraction process of the complexes for several organic extraction solvents used. Extraction process was investigated

Table 1. Stability constants of the metal complexes of 2-n-propylimidazole in aqueous solution at 298 K

Central ion	log K_1	log K_2	log K_3	log K_4
H ⁺	8,02			
Cd ²⁺	2.02 ± 0.07	2.60 ± 0.06	5.10 ± 0.07	
Co ²⁺	0.80 ± 0.03	2.50 ± 0.07	4.60 ± 0.05	
Ni ²⁺	1.37 ± 0.05	2.81 ± 0.02		
Cu ²⁺	3.71 ± 0.04	7.09 ± 0.03	9.51 ± 0.09	12.53 ± 0.03

through analysis of a relationship between the metal extraction coefficient and 2-n-propylimidazole concentration, L, at equilibrium in aqueous phase.

In order to elucidate exactly which complex from the series of one-core complexes of a given metal undergoes extraction, we determined individual partition coefficients for each of them. The values of the coefficients, found graphically from the $D = \sum_{n=1}^{n=N} P_n \alpha_n$ dependence, are listed in Table 2.

Table 2

Metal	Extraction solvent	P ₂	P ₃	P ₄	Probable composition of the complexes undergoing extraction
Cu(II)	2-Butanol			5.1 ± 0.6	$[CuL_4S_2]^{2+}$
	Benzyl alcohol			20.0 ± 2.5	$[CuL_4S_2]^{2+}$
Co(II)	2-Butanol		0.75 ± 0.08		$[CoL_3S]^{2+}$
	Benzyl alcohol		4.03 ± 0.54		$[CoL_3S]^{2+}$
Cd(II)	2-Butanol		4.68 ± 0.54		$[CdL_3S]^{2+}$
	Benzyl alcohol	2.4 ± 0.3	11.6 ± 1.5		$[CdL_2S_2]^{2+}$ $[CdL_3S]^{2+}$

It results from the Table that for Co(II) the third successive complex is extracted as a sole complex from the formed ones. The complexes with four co-ordinated 2-n-propylimidazole molecules was extracted from Cu(II) solutions. Cd(II) and Zn(II) coordination compounds acquired hydrophobic properties most quickly because the extraction begins for the second successive complex.

We showed in the last column of Table 2 the probable composition of the complexes passing to the organic phase, under assumption that

the salts containing complex cation, solvated with one or two alcohol molecules, passed into that phase. We could assume that complex cations of cobalt possessed the co-ordination number = 4 and pseudotetrahedral symmetry, since absorption bands at ca $17\ 500\ \text{cm}^{-1}$ were met in spectra of both aqueous and organic phases.

Cd(II) complexes are much less sensitive to the steric effect than the Ni(II) or octahedral Co(II) complexes. The coordination number was equal to 4 both in aqueous and organic phase.

The complexes investigated differ explicitly with susceptibility to the extraction, especially if benzyl alcohol was used. If the extraction with benzyl alcohol and 2-n-propylimidazole were accomplished in pH region $6.6 \div 7.5$, Co(II) could be easily separated from Cu(II), Ni(II), Zn(II) and Cd(II), whereas Cu(II) could be separated at $\text{pH} < 6.6$.

NUCLEAR PROCESSES

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The achievements in the development of solvent extraction are closely connected with the study of the chemical properties of the radioactive elements. Back in 1805 Bucholz [1] established, that uranyl nitrate was very soluble in diethyl ether, and forty years later French researcher Peligot [2] used ether to purify uranyl nitrate by recrystallization. A century later in 1942-44 this extractant was used in the Chicago Metallurgical Laboratory in the first experiments on plutonium separation, and then for the separation and purification of large amounts of uranium and plutonium in the course of the Manhattan Project. The discovery by Worf [3] of the capability of tributylphosphate (TBP) to extract uranium from nitrate solutions was not less important. It formed the basis of the well-known "Purex" process. The further development of extraction applied to radioactive elements can conventionally be divided into two large periods.

During the first period, which was up to the mid-sixties, the major efforts of the scientists of many countries were first of all directed to the development of the plant-scale solvent extraction processes for recovering plutonium and uranium from nuclear reactor fuels. TBP proved to be the most convenient due to its perfect extraction characteristics and commercial availability. However, it has some disadvantages with respect to radiation stability and aqueous-phase solubility. Nevertheless, up to these days TBP has been widely applied in the industrial technology. The first three volumes of the monography about the properties and numerous fields of application of this unique extractant have already been published [4].

The same period is characterized by extensive research into the extraction behaviour of practically all the radioactive elements, both natural and artificial. Various classes of extractants: neutral extractants, which form coordinationally non-solvated or solvated compounds; cation- and anion-exchange extractants with different active atoms; mixtures of extractants (synergistic extraction) were used to study the problems of the coordinational chemistry of the extraction processes, the composition of the extracted compounds, the effect of the properties of the aqueous and organic phases, kinetics of extraction and many other factors. In the USSR this work has actively been conducted in the Vernadsky Institute of Geochemistry and Analytical Chemistry, the All-Union Research Institutes of Inorganic Materials and Chemical Technology, the Radium Institute, the Kurchatov Institute of the Atomic Power, the Institute of Physical Chemistry and in some other Institutions.

In the seventies extraction was intensively developed. In that period the main efforts of scientists, along with the further development of the different aspect of the nuclear fuel cycle, were also directed to the solution of a difficult task to extract and separate trivalent actinides and lanthanides. New extraction systems and methods of substance transfer between phases (membrane extraction) were studied; more efficient and selective extractants (mono- and polydentate ones) were synthesized and studied; synergistic and sorption extraction systems were developed. Mathematical methods were used to optimize and modelize extraction processes of the radioactive elements separation.

In the recent years great success has been achieved in the study of the extraction of transplutonium elements (TPE) from the highly acidic solutions with the particular purpose to separate the long-lived americium and curium isotopes from the waste radioactive solutions. Since the atomic stations are developed at a great extend, the volume of such waste solutions is estimated to reach ~ 55000 tons by 1995, and it is supposed to reach up to 125000 tons by 2000. The isolation of the long-lived americium and curium isotopes from the waste radioactive solutions subjected to disposal is a complicated radiochemical task. Most of the known extractants do not fit the task, except for the neutral bi- and polyfunctional organophosphorus and phosphorus-nitrogen-containing compounds [5]. The most intensive work with these extractants is conducted in the USSR (Vernadsky Institute of Geochemistry and Analytical Chemistry, the All-Union Research Institute of Inorganic Materials) and in the USA (Argon National Laboratory), several papers have lately appeared in the Japan, Chechoslovakia, France, India.

More than 60 phosphorus and phosphorus-nitrogen-containing neutral bi- and polydentate extractants have been studied in the Vernadsky Institute. These reagents were synthesized by the laboratory of academician M.I.Kabachnik in the Institute of Elementoorganic Compounds of the USSR Academy of Sciences. We studied the effect of their structure, i.e. the conformation of the molecule, nature of the substituents at the atoms of phosphorus, nitrogen, in the methylene bridge; bridge composition, - upon extraction capability, selectivity and solubility of these extractants [6,7]. The first group of extractants includes the phosphorus containing bi- and trifunctional extractants with the linear bridge between the P=O groups and their derivatives, in which the hydrogen atom in the bridge is substituted by another atom or radical. The exxtractants of this group have the highest extraction capability and a high stability to radiation. With the use of these reagents the methods of the extraction isolation of TPE from highly acidic salt-containing solutions with simultaneous con-

centration to 100 times have been developed. The extractants have a typical group character and they are not very selective [6]. The second group of extractants includes bi-, tri- and tetrafunctional phosphorus-containing extractants with bridge of ortho- and metaxylene, mesitylene, durrole and other methyl-substituted aromatic compounds bonded the functional groups. The undoubtful priority of these extractants is the high selectivity, revealed in relation to different elements depending on the location of the functional groups in the aromatic compounds of the bridge [8]. The phosphorus-nitrogen-containing extractants, (dialkyl(diaryl)[dialkylcarbamoylmethylphosphine]oxides have a high extraction capability. Their priority lies in their higher solubility in organic solvents and in a relative simplicity of synthesis. These extractants are not selective as the alkylenediphosphine dioxides [7].

Along with the numerous priorities of dioxides and carbamoyls they have essential drawbacks: they cannot practically be solved in aliphatic solvents; their complexes with metals cannot sufficiently be solved in the available solvents. One of the ways to eliminate these drawbacks is to add monodentate reagents of the TBP type to the solutions of bidentate extractants. It was proved that TBP eliminates the formation of the third phase during the extraction of macroamounts of elements, besides, it leads to the non-additive increase in the TPE distribution coefficients (the synergistic effect). We have also proved that TBP addition makes it possible to use aliphatic diluents as well.

For bidentate organophosphorus extractants, a known "aryl effect" should be mentioned, which consists in the increasing of extraction capability of reagents when the alkyl radicals at phosphorus are substituted by the less electronegative ones, i.e. phenyl radicals. For the first time the "aryl effect" was only observed during the TPE and lanthanides extraction by alkylenediphosphine dioxides; then it was discovered in the course of extraction by diaryl(dialkyl)[dialkylcarbamoylmethylphosphine]oxides [9]. The "aryl effect" was believed to occur during the extraction by bidentate extractants with a methylene (or vinylene) bridge between the functional groups, and to disappear when the bridge is prolonged to ethylene. We have recently discovered the "aryl effect" in the course of TPE and europium extraction by the extractants with meta-xylene used as bridge binding two functional P=O groups (Fig.1).

Alkaline solutions also seem efficient for actinide isolation and concentration. The extraction of metals from such solutions has not practically been studied yet. Our investigations have proved the capability of actinides and many other elements to be extracted from alkali-

line solutions in the presence of the complexing agents by various classes of extractants: Aliquat 336, amines, alkyl-pyrocatechols, (DOP), alkyl-derivatives of amino-alcohols (AA), and β -diketones [10]. Several studied extractants, especially alkylpyrocatechol are characterized by a high extraction capability in relation to TPE. They are efficient for the extraction of these elements from solutions with the concentration of sodium hydroxide and carbonates of alkaline metals of being about 5-6 mol/l (Fig.2). The efficiency of the extraction

isolation of TUE is affected by the nature of complexing ligands, capable to keep elements in alkaline solutions in the soluble form. The role of complexing agents is sometimes reduced just to keep the elements in the soluble form in alkaline media (α -oxy-carbonic acids, carbonate-ions). In other cases the complexing agents (aminopolyphosphonic acids) are transferred to the organic phase together with the metal. Therefore depending on the conditions,

elements can be extracted from alkaline and carbonate solutions in the form of ionic associates, the anion part of which contains either the hydroxocomplexes of the corresponding metals or their compounds with the complexing agent. They can also have the form of chelates saturated and hydrated compounds. The methods of extraction and extraction chromatography [11] in alkaline and carbonate solutions are used to solve a number of practical tasks. Firstly, under certain conditions quantitative separation and concentration of elements can be conducted with the help of all the tested extractants. Secondly, the concentration of trivalent actinides with their simultaneous separation from the elements in other oxidation states and iron can be achieved in these systems. The selectivity of the extraction separation can

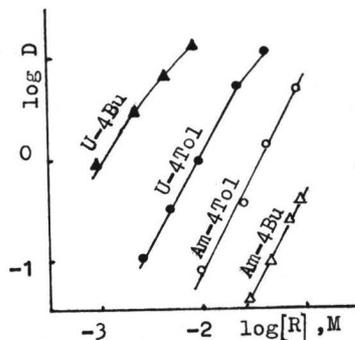


Fig. 1. "Aryl effect" in extraction of Am(III) from 3 M HNO₃

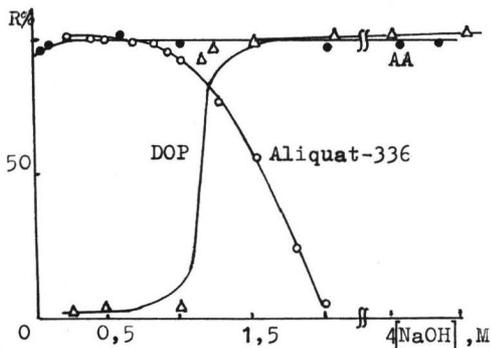


Fig. 2. Extraction of Am(III) from alkaline solutions by different extractants

be increased in two ways: by varying the alkaline concentration of the media and the contact time of phases. The best method for the trivalent americium and curium separation in carbonate media is extraction chromatography, since separation is improved due to the differences both in the values of the mass transfer coefficients and in the equilibrium process.

The membrane extraction and the use of kinetic factors open up new opportunities in the separation of radioactive elements. There are several ways to organize the process i.e. extraction with membranes, impregnated membranes and the emulsion membrane extraction. The main priorities of the membrane extraction as compared to the liquid extraction consist in the low expenditure of expansive extractants, as well as very high degrees of isolation and concentration. In some cases the membrane extraction processes are more selective. The drawbacks of the method consist in the slow rate as compared with the liquid extraction and besides in a number of cases it is only a periodical process. It is also more technically sophisticated. The electric field considerably accelerates the mass transfer of the material through the membranes. Membrane extraction is most efficient for the processing of extremely diluted solutions, including the radiochemical wastes. The most efficient method of isolation and separation of elements is the combination of membrane extraction with the use of redox reactions. A method of emulsion membrane extraction with HDEHP was developed in our laboratory for the actinide separation from concentrated DTPA solutions. Up 96% of actinide are transferred to emulsion in the course of the extraction, while not more than 1% of americium can be isolated by one contact, when liquid extraction is applied.

The methods of separation using various oxidation states of the separated elements are the most selective [12]. Thus the conditions of the tetravalent americium extraction by secondary amines from nitric and sulphuric acids solutions in the presence of phosphotungstate ions were found in our laboratory for the first time [13]. A high degree of americium (both micro and macroamounts) separation from curium and other trivalent elements is achieved. Tetravalent berkelium can be quantitatively extracted from mineral acid solutions by many extractants: organophosphorus ones and β -diketones; and in the presence of heteropolyanions they can be extracted by primary, secondary, tertiary amines and quaternary ammonium bases.

The pentavalent americium can be isolated from solutions of various composition by extraction with TTA, 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP), HDEHP and ammonium pyrrolidinedithiocarbamate. With the use of PMBP and HDEHP the macroamounts of pentavalent americium were extracted for the first time, its absorption spectra in the organic media were taken, and the data on its stability were obtained. The

separation factor of americium and curium in the course of the pentavalent americium extraction by PMBP and HDEHP makes $(3 \div 6) \cdot 10^3$. Using the mixtures of extractants (PMBP or TTA with TOPO, picrolonic acid with sulphoxides from low acidity solutions) the trivalent actinides are extracted with high distribution coefficients, while the pentavalent americium remains in the aqueous phase.

Thus a conclusion can be drawn, that extraction has played and is still playing an essential role in the development of the chemistry of radioactive elements, particularly actinides. On its basis highly efficient methods of isolation of radioactive elements from the material of various nature, both technological and analytical, have been developed by this time. The extensive experimental data accumulated in this field has made it possible to draw important conclusions on various aspects of the theory of the extraction processes. It can be stated that the use of new efficient and selective extractants and systems, new ways of conducting extraction processes and knowledge about their kinetics will give important information about chemical properties of radioactive elements and prompt efficient ways of their isolation, separation and concentration.

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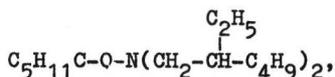
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To decrease the cost of the irradiated nuclear fuels reprocessing, it is necessary to simplify the process and to limit the amounts of radioactive wastes. The use of new extractants could fulfill these requirements. Completely incinerable extractants and nonbasic solvent regeneration are favourable to wastes limitations. Highly selective actinides extractants towards fission products are necessary to simplify the chemical processes. The carboxylic acids amides are good candidates for such programm [1 - 3]. We will survey the extraction chemistry of N, N-dialkylamides which are a promising alternative to TBP and of N,N'-tetraalkylmalonamides [4, 5]. They are good extractants of the actinides ions including trivalent ones and could be an alternative to the polyfunctional extractants.

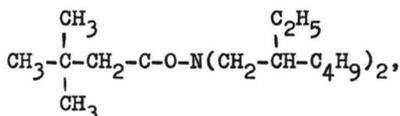
N,N-dialkylamides properties. The selection of N,N-dialkylamides as a function of the solubility of nitrate uranyl adducts in aliphatic hydrocarbons has been carried out. It has been found that the amides containing the radical 2-ethyl hexyl as the nitrogen substituents form adducts which are highly soluble in hydrocarbons like normal or ramified dodecan (TPH). Nitric acid forms the adducts HNO_3L_2 , HNO_3L and $(\text{HNO}_3)_2\text{L}$ where L represents an amidic extractant. IR spectroscopy indicates that L and HNO_3 are linked by hydrogen bond.

Depending of the aqueous acidity, the extraction of uranium (VI) occurs via two mechanisms [4] $\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{L} \rightarrow \text{UO}_2(\text{NO}_3)_2\text{L}_2$ from low acidity media and $\text{UO}_2^{2+} + 3\text{NO}_3^- + \text{H}^+ + \text{L} \rightarrow \text{UO}_2(\text{NO}_3)_3\text{HL}$ for higher acidic solutions. These two cases can be distinguished by the U-V spectroscopy of the organic phase. The spectra of the two U(VI) species are shown in Fig.1.

Plutonium (IV) extraction is sensitive to the nature of the C=O substituent. The difference between linear (DOHA),



and branched (DOTA),



hexanamides is illustrated by the

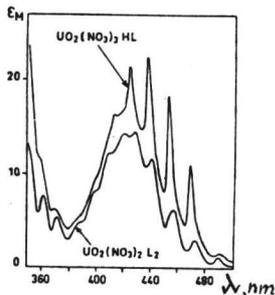


Fig. 1. U(VI) U.V-vis. spectra (1M amide into TPH. Acidic and neutral solutions)

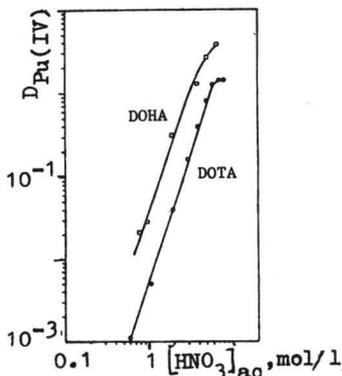


Fig. 2. $D_{Pu(IV)}$ between 0.5M DOHA □ DOTA ○ into TPH and aqueous HNO_3 solutions

Pu(IV) distribution ratios plotted as a function of HNO_3 concentration in Figure 2. U(VI) distribution ratios do not vary so much by changing the C=O substituent; so the branched substituent on the carbonyl offer possibilities of (U(VI)-Pu(IV) coextraction from highly concentrated nitric acid and U(VI)-Pu(IV) separation at lower acidities (Figure 3).

This branched hexanamides give better fission product separations as shown by Figure 4 extraction curves.

Radiolysis and hydrolysis are important for practical applications in the field of nuclear fuels. We investigated the stability of 1M DOHA in TPH mixed twice a day with one volume of aqueous 4N HNO_3 or 0.5N HNO_3 . It can be seen Figure 5 that the disappearance of DOHA is correlated to the hexanoic acid production which is the main degradation product. The hydrolysis of DOHA and TBP are compared in Table 1, it can be seen that the two extractants are rather stable. Small dif-

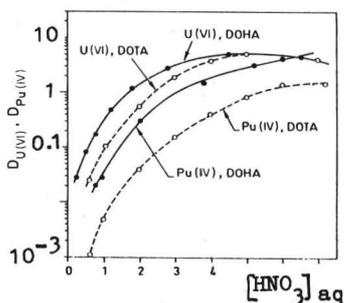


Fig. 3. Distribution of Pu(IV) and U(VI) between DOTA or DOHA and aqueous HNO_3

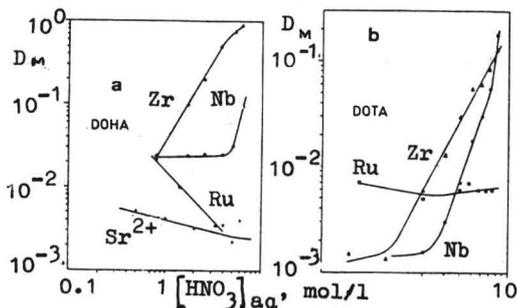


Fig. 4. D_{FP} between 1M DOHA (a) or 1M DOTA (b) in TPH and aqueous nitric solutions

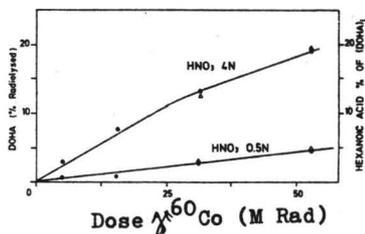


Fig.5 . Of % 1M DOHA radiolysed and hexanoic acid yields dose rate in the presence of 4N and 0.5N HNO₃

ferences in the figures are probably due to analytical incertainties and a better comparison necessitates improvements in these technique.

Table 1

Hexanoic acid (HA) and N,N-di(2-ethyl)hexylamine (DEA) yields in the hydrolysis of DOHA at 110°-115°C in the presence of aqueous HNO₃ (stirred solutions) and comparison with TBP hydrolysis

HNO ₃ , mol.l ⁻¹	Time, hours	DOHA, mol.l ⁻¹	HA, mol.l ⁻¹	DEA, mol.l ⁻¹	TBP, mol.l ⁻¹	HDEP, mol.l ⁻¹
0.5	4	0.95	0	0		
4	1	0.95	0	0		
4	4	0.94	0.015	0		
0.5	4				1.08	0.0008
5	4				1.08	0.0047

A mixer-settler test of a first reprocessing cycle has been carried out using 1M DOHA in TPH as extractant Although DOHA is not the best choice for U(VI)-Pu(IV), partition at low acidity has been tempted in order to precise the problems linked to U-Pu non reductive partition. The flow-sheet for this experiment is shown schematically in Figure 6 and the main results are contained in Table 2. The partition battery was not 100% efficient because of the slow Pu(IV) back-extraction kinetics which was too low for the liquids flux used. All the other operations were satisfactory and show that N,N-dialkylamides are promising extractants for the future.

Polyfunctionnal amides properties. The use of N,N-dialkylamides as an extractant for the nuclear fuels reprocessing suggests to investigate the extractive properties of polyamides in order to extract also the trivalent actinides ions contained in the radioactive wastes solutions. The pioneer work of Siddall [5] showed that Ce(III) was

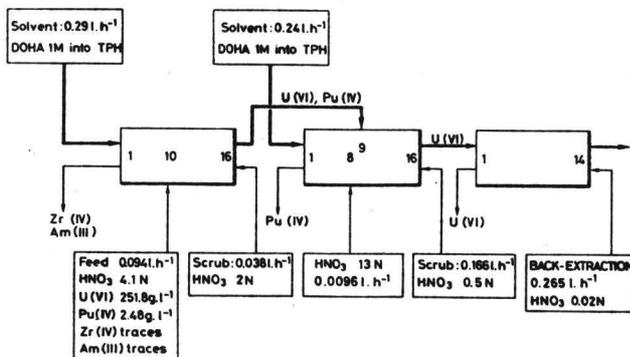


fig.6 . Flow sheet for a first reprocessing cycle using 1M DOHA in TPH

Table 2

Results of a mixer settler first cycle reprocessing separation using 1M DOHA in TPH as solvent

Operation	Element	Feed (g.l ⁻¹)	Raffinate (% of feed in each step)
Extraction		Aqueous phase	Aqueous phase
	U(VI)	251.8	0.015
	Pu(IV)	2.48	0.14
	Zr(IV)	Traces	99.5
	Am(III)	Traces	99.5
Partition		Organic phase	Aqueous phase
	U(VI)	81.7	0.37
	Pu(IV)	0.805	95.5
Back-Extraction		Organic phase	Aqueous phase
	U(VI)	44.7	99.9
	Pu(IV)	0.0198	95.2

poorly extracted by N,N'-tetrabutylloxalamide, N,N'-tetrabutylglutaramide and N,N'-tetrabutylsuccinamide. In a first step we selected malonamides proper to extract Am(III) from aqueous nitric acid [6, 7]. It has been found that N,N'-dimethyldialkylmalonamides are the best Am(III) extractant because of their chelating properties. It was found further that the substitution of a methyl hydrogen by an alkyl or oxyalkyl radical improves the extractive behavior of diami-

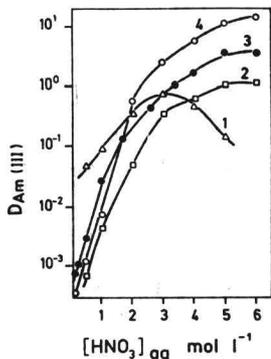


Fig.7. Am(III) distribution (8). ratios between aqueous HNO_3 and various 0.5M diamide $(\text{CH}_3\text{C}_4\text{H}_9\text{NCO})_2$ CHR in TPH with R =
 1) H, also C_8H_{17} instead of C_4H_9
 2) C_6H_{13} 3) $\text{C}_2\text{H}_4\text{OC}_2\text{H}_5$ 4) $\text{C}_2\text{H}_4\text{OC}_2\text{H}_5\text{-OC}_6\text{H}_{13}$

des. This feature is illustrated by Figure 7 plots. Diamides show good prospects as actinides extractant from radioactive wastes. Others metal ion extraction are given at this conference [8].

Conclusion. New non-organophosphorus extractants are appealing in the nuclear fuels reprocessing field because of their complete incinerability and the nature of their radiolytic products which do not alter the process. Their extraction chemistry presented here is encouraging to pursue the research and development since several advantages over the PUREX process can be seen immediately. Among them are non reductive U-Pu partition; better fission product decontamination, better U(VI) back-extraction ... Solvent regeneration which is not yet known will be the next important step to corroborate the interest of amides.

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N,N-disubstitute aliphatic amides are promising extractants for such actinides as uranium, neptunium and plutonium. On the other hand these amides are poor extractants for fission products. These valuable properties indicate that amides could find application in the nuclear industry. From this point of view amides can be considered as alternative extractants to tri-n-butylphosphate (TBP).

Advantageous properties of amides and extraction experiments with amides have been described in the literature [1,2]. Good extraction properties of amides imply that they could be used in extraction chromatography for separation purposes [2].

The present work aimed at examination of the behaviour of some actinides on chromatographic columns containing newly synthesized N,N-dihexylcyclohexylbutyramide (denoted as DHCHBA) and N,N-di-sec-butylcyclohexylbutyramide (DSBCHBA) as extractants. Special attention was focussed on the separation of the various oxidation states of actinides by these amides. In acidic aqueous solutions light actinides attain the following four oxidation states: An(III), An(IV), An(V), An(VI).

From among these oxidation states Np(III) and Pu(V) are not present in ordinary aqueous solutions since they are unstable and easily oxidized by the air.

The existing literature extraction data for plutonium and neptunium are, in general, at variance. This is caused by the difficulties in removing Np(V), Pu(III) and colloidal plutonium from aqueous solutions. The comparatively large experimental errors associated with the extraction data obtained, e.g., for hexavalent plutonium have been indicated by McKay [3].

It is to be emphasized that column extraction chromatography applied in this work enables to obtain true extraction

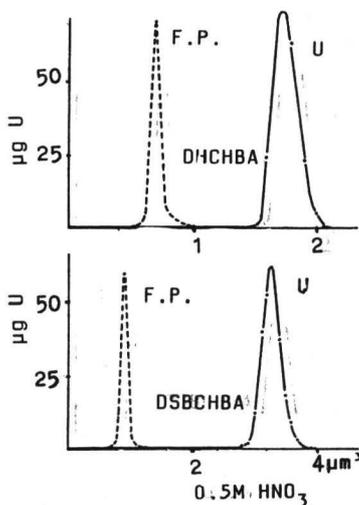


Fig.1. Separation of fission products and uranium on the amide columns

data for actinide elements because each oxidation state of these elements can be separated as an individual chromatographic peak.

Experimental

The chromatographic columns used throughout the work were prepared applying the procedure elaborated earlier in our Department [4,5]. Silicon treated kieselguhr "Hyflo-Super Cell" was mixed with an appropriate amount of the amide extractant (20% w/w), diluted with a volatile diluent, e.g. hexane, the latter being carefully evaporated. The length of the column bed was about 10 cm and the column diameter was ~0.3 cm. The volume of the samples introduced into the column was about $10^{-2} \mu\text{m}^3$. The eluting agent was 0.5M HNO_3 . The flow rate of the eluant was about $9 \cdot 10^{-3} \mu\text{m}^3 \text{cm}^{-2} \text{min}^{-1}$. All the experiments were carried out at room temperature. The alpha activity of the studied actinides was measured using a liquid

scintillator consisting of a mixture of 5 g dm^{-3} PPO and 25% (v/v) of HDEHP in toluene. Identification of the particular γ - and α -energies was performed with the help of γ - and α -ray spectrometry using a multichannel analyser (ORTEC-Model 7150). Uranium was determined spectrophotometrically with the Arsenazo-III method.

Oxidation of neptunium and plutonium to the hexavalent state was performed by means of NaBrO_3 in 1.0M HNO_3 . $\text{NH}_2\text{OH} \cdot \text{HCl}$ was used as the reducing agent for Pu(III). No catalytic reagents were used. The reduction process lasted for about 24 hrs at room temperature. It should be mentioned that U(VI), Np(V), Pu(IV) and Am(III) are the most stable valence states of the actinide ions in the aqueous solutions used.

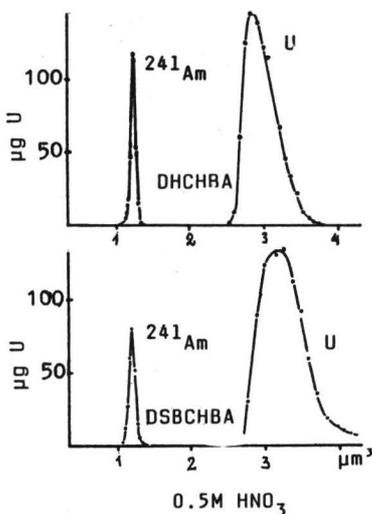


Fig.2. Separation of Am(III) and uranium on the amide columns

The amides used in this work were synthesized in the NRC Baghdad. The amides have the following characteristics:

	n_D^{293}	$d^{298}(\text{kg m}^{-3})$	b.p.(K)/Pa
DHCHBA	1.4700	944	429-435/400
DSBCHBA	1.4735	952	407-409/800

the purity of the amides was better than 96%.

The distribution ratio, D , of the actinides were calculated from the elution curves according to the formula [6].

$$D = \frac{V_{mr} - V_m}{V_s} = \frac{V_r}{V_s}$$

where: V_{mr} - total retention volume, V_m - mobile phase volume, V_r - retention volume, s - stationary phase volume. The reproducibility of the results was about 5%

Results and discussion

From the previous studies [1,2] it is known that the N,N -disubstituted alkyl amides are not extracting fission products from nitric acid solutions. This fact enables clean separation of fission products from uranium, as can

be seen in Fig.1., where ^{137}Cs and ^{144}Ce were separated from 0.1 mg of uranium. Similarly to the trivalent lanthanides (Ce , Eu) also Am(III) can be separated from uranium, and an example of such a separation is

presented in Fig.2. The separation of the various valence states of plutonium and neptunium on the amide columns can be seen in Figs.3 and 4, respectively. Pu(III) is not retained on the column and is eluted in the free volume of the column.

The calculated distribution ratios of the particular valence states of the actinides are listed in Table. It is seen that di-sec-butylcyclohexylbutyramide extracts the hexavalent actinides much better than does the DHCHBA

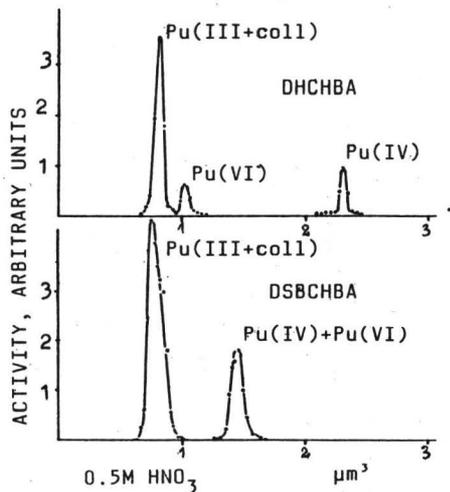


Fig.3. Separation of plutonium in different oxidation states on the amide columns

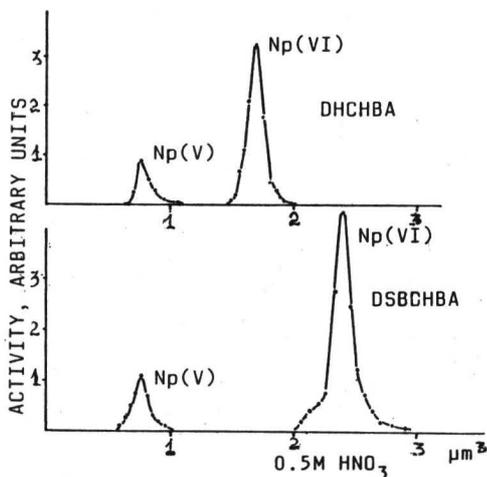


Fig.4. Separation of neptunium in different oxidation states on the amide columns

extractant, which on its turn, is more efficient for Pu(IV). The better extraction of the hexavalent actinides by DSCHBA, as compared with DHCHBA may be due to the increased electron density on the carbonyl oxygen caused by the sec-butyl radicals. Since the extraction mechanisms of metals by amides and TBP are similar therefore, for a comparison, also column extraction data, under comparable experimental conditions, for TBP are given in this Table.

It is worthy of notice that the amide columns demonstrated a good characteristics and stability. The height equivalent to the theoretical plate (HETP) ranged usually from 0.2 to 0.5 mm. The amide columns could be used for several runs.

Distribution ratios for actinides in different oxidation states calculated from column experiments. 0.5M HNO₃ was used as the eluant

Extractant	U(VI)	Np(VI)	Pu(VI)	Pu(IV)	Am(III) ¹⁾
DHCHBA	9.62	8.55	1.43	14.3	0.005
DIBCHBA	20.3	16.2	5.16	6.80	0.016
TBP	9.92	9.91	1.65	12.7	1.27

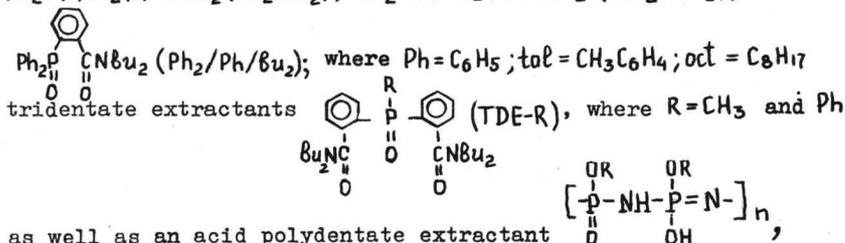
1) From liquid-liquid extraction with undilute amides and TBP from concentrated nitric acid.

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At present in the USSR, USA and other countries bi- and polydentate organophosphorous extractants have aroused interest due to their ability to extract residues of actinides from Purex liquid waste without its special conditioning [1-5]. We have studied a series of bi-, tri- and polydentate extractants: diphosphine dioxides $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{PPh}_2$ (abbrev. 4Ph); $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{Poct}_2$ (2Ph2oct); $\text{oct}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{Poct}_2$ (4oct); $\text{tol}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{Ptol}_2$ (4tol); $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2(\text{O})\text{PPh}_2$ (4Ph(CH₂)₂); $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_3(\text{O})\text{PPh}_2$ (4Ph(CH₂)₃); $\text{Ph}_2\text{P}(\text{O})(\text{CH}=\text{CH})(\text{O})\text{PPh}_2$ -cis (4Ph(CH=CH)cis); carbamoylphosphine oxides $\text{oct}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{CNBu}_2$ (oct₂/Bu₂); $\text{Ph}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{CNBu}_2$ (Ph₂/Bu₂); $\text{tol}_2\text{P}(\text{O})\text{CH}_2(\text{O})\text{CNBu}_2$ (tol₂/Bu₂);



where $n=2-4$; $\text{R}=\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$ is poly-2 ethylhexylphosphonitrile acid (P2EHPNA). With these extractants extraction can be further improved through the use of the effect of anomalous aryl stability increase (AASI) found by us [1]. The essence of the effect is the following. Our experiments showed, e.g. [6,7], that when extracting with neutral monodentate extractants the extraction ability (EA) was reduced with an increase of the substituent electronegativity (X) in an extractant molecule. This is explained by the fact that complex form by an acceptor-donor mechanism (the donor is the oxygen extractant); as X grows, the substituents draw off the electron density from the oxygen, its donor ability decrease. Correspondingly, the complex stability and, hence, EA are reduced, e.g. in the phosphine oxides R_3PO -phosphate $(\text{RO})_3\text{PO}$ series, since $X_{\text{R}}=2.0$ and $X_{\text{RO}_{\text{eff}}}=2.5$.

However, on extraction with diphosphine dioxides and carbamoylphosphine oxides it turned out that the replacement of alkyl substituents with more electronegative phenyl (X=2,3) or tolyl ones the Am distribution coefficient (α_{Am}) did not only reduce out, on the contrary, improved it by two orders (fig.1a, 0.01 mole/l solutions of dioxides in dichloroethane (DCE) [1-3]. The same is observed for the extraction with 0.05 mole/l solutions of carbamoylphosphine oxides in dichloroethane (fig.1b). The similar effect is observed in the extraction of uranium (VI) and Pu(IV) with solutions of dioxides and carbamoylphos-

phine oxides in dichloroethane (fig.2). However, one should distinguish between the true AASI (when both the distribution coefficients and

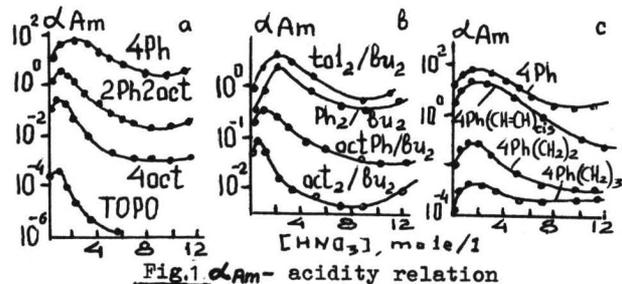


Fig.1 α_{Am} - acidity relation

equilibrium constants grow through the acid extraction weakening and the growth of the free extractant concentration while the equilibrium constants decrease)

grow, i.e., the complex stability increases which is observed in the extraction of An(III) and Ln(III) and the visible AASI (when the distribution co-

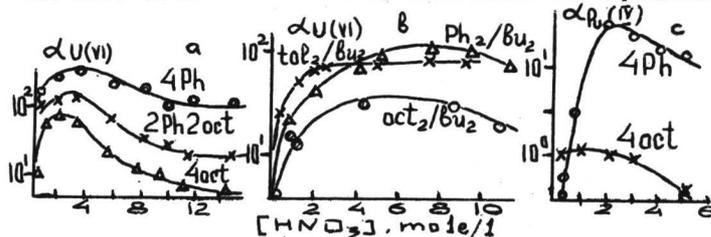


Fig.2 α_U, α_{Pu} - acidity relation

were introduced (fig.1,2). Studies were carried out to find out the reasons of this anomaly. It turned out that in accordance with the expectations the donor ability of phosphoryl oxygen of an isolated ligand decreased with the introduction of aryl groups into an extractant molecule which is confirmed by the growth of the PO IR frequency and a decrease in the extraction of monodentatically coordinated nitric acid when going from 4 oct to 4 Ph. The stability increases the moment a sixmember cycle closes and bidentatically coordinated metal complex forms. This effect is associated with the chemical nature of aryl groups: when the latter are replaced by groups of the same electronegativity but of a different nature, e.g., $Cl(CH_2)_2$, it disappears. When aryl groups are separated from phosphorus with a CH_2 -group the effect disappears; the same takes place when the methylene bridge is replaced by the ethylene and propylene ones and the effect is restored when the vinylene bridge is introduced (fig.1c). This means that the electron density is delocalized from the aryl groups to the cycle. It can be also assumed that a system of conjugated bonds forms, the cycle is "aromatized". Whatever the causes are, the effect of AASI is very useful for the extraction of actinides from liquid waste.

The main difficulty in using the above compounds results from the poor compatibility of those extractants and particularly their complexes (with lanthanides) with hydrocarbon diluents. One of the ways is to introduce alkyl substituents into benzene nuclei, i.e., to use diphosphine dioxide 4 tol [8] and carbamoylphosphine oxide tol_2/bu_2 [9].

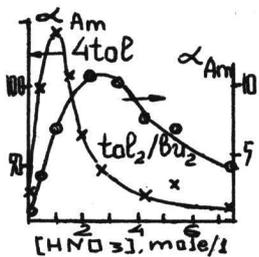


Fig. 3. α - $[HNO_3]$ relation

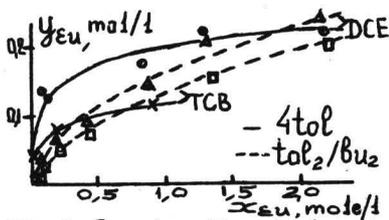


Fig. 4. Eu extraction isotherms

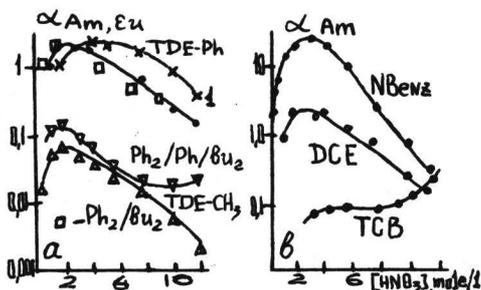


Fig. 5. TDE extraction (Am, curve 1-Eu)

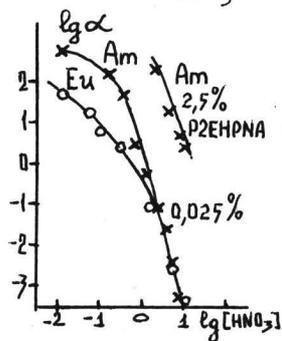
However, these compounds are also poorly soluble in paraffin diluents. To extract from solutions close in their composition to liquid waste (e.g., 3 mole/l HNO_3 and 40g/l Eu) the required extractant concentration is 0.3-0.5 mole/l. To provide the compatibility isoparaffin with 20% octyl alcohol and 1 mole/l TBP are needed. Due to the alcohol α of Am greatly decreases. To increase α_{Am} trichlorobenzene (TCB) as a diluent was used. The isotherms of the micro Am extraction in the presence of 10 g/l Eu with 0.3 mole/l solutions of 4 tol and tol_2/bu_2 in TCB were taken (Fig.3). The distribution coefficients remain rather high, i.e., at the phase flow ratio 1:1 one-two stages are sufficient for the full Am extraction.

Extraction of europium nitrate macroamounts with the indicated bidentate extractants was also studied (Fig.4). It is established that along with the known tri- and disolvates found by us earlier in the extraction of Am and Eu microamounts monosolvate is also formed (y_{equil} exceeds 0.15; i.e., $Z = y/L_0 > 0.5$ which points to the presence of some solvate 1:1), i.e., solvates $Eu(NO_3)_3 \cdot L_q$ where $q=1,2,3$ are formed.

The Am and Eu extraction with two tridentate compounds has been studied (Fig.5,a, 0.05 mole/l in DCE). The replacement of methyl radical by phenyl one results in a significant improvement of the extraction; the true AAST is observed. As compared to the bidentate analogue Ph/Ph/ bu_2 a considerable extraction improvement is observed which points to a tridentate coordination; this is also confirmed by IR-spectra. A strong effect of a diluent on extraction with TDE-Ph is noted (Fig.5b).

The advantage of the extractants discussed consists in the extraction of actinides (III) at the level of An (IV,VI) [1] as well as in the possible simultaneous suppression of HNO_3 extraction and improvement of actinides extraction through the introduction of aryl substituents. Apart from the difficulties associated with a diluent the disadvantage is a low selectivity; following the co-extraction of An and Ln special operations are required to separate them.

Of the class of polydentate extractants poly-2 ethylhexylphosphonitrile acid (P2EHPNA) suggested in [10] was studied. As it can be seen from fig.6 P2EHPNA as distinct from D2EHPA effectively extracts americium from a highly acidic medium: $\alpha_{\text{Am}}=7$ at the P2EHPNA=2.5% (in dodecane) and $X_{\text{HNO}_3}=5$ mole/l. The composition of the resultant complexes



was established; the P2EHPNA extraction constant for Am is 10^8 times higher than D2EHPA one. This is likely a result of the linear character of P2EHPNA polymers (no dimerization that binds PO and OH centres), transformation to the imide form, containing only OH groups and the possible bi- and polydentate coordination of metals.

Fig.6. P2EHPNA extraction

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Dialkyl(diaryl)[dialkylcarbamoylmethyl]phosphine oxides (CMPO) is known can be used successfully for concentrating of transplutonium elements (TPE). The disadvantages of these extractants are a low solubility of metal complexes in organic diluents and an incompatibility with diluents.

It was shown [1,2] that these disadvantages could be overcome by addition of tributylphosphate (TBP), which had good compatibility with many diluents. The objective of this study was to determine regularities in changes of TPE distribution ratios (D_{TPE}) and values of their deviation from additivities (S), concentration of all the system compounds and both the nature of CMPO and diluent.

We used extractants of general formula: $R'R''P(O)CH_2C(O)NR_2'''$ where $R'=R''=Ph, Tol, Bu, BuO$ or $R'=Ph, R''=BuO; R'''=Et$ or Bu . Extractants are given in accordance to substituents at phosphorus and nitrogen atoms, respectively.

It was shown that in case of Am(III) extraction from 3M HNO_3 by 0.025M solutions of all CMPO the addition of TBP gave nonadditive en-

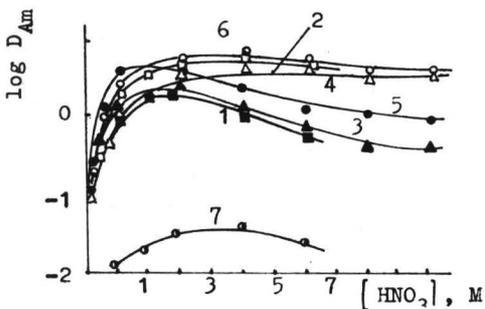


Fig.1. Acid dependency for Am(III) extraction by 0.05M Ph_2Et_2 (1), Ph_2Bu_2 (3), Tol_2Et_2 (5) and their mixture with 1.5M TBP (2,4,6) in DCE; (7)-1.5M TBP in DCE

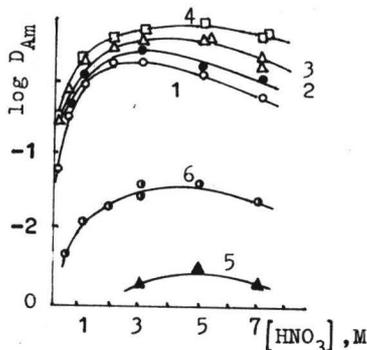


Fig.2. Acid dependency for Am(III) extraction by 0.05M Ph_2Et_2 (1) and a mixture of 0.05M Ph_2Et_2 and 0.05M TBP (2), 0.5M TBP (3), 1.5M TBP (4); (5)-0.5M TBP; (6)-1.5M TBP. Solvent-DCE

hancement of D_{Am} ($S > 1$). The study of Am(III) extraction over a wide range of nitric acid concentrations shown both synergistic ($S > 1$) and antagonistic ($S < 1$) effect could be taken place in the systems (Fig.1). Therefore the degree of D_{Am} increasing, S and its manifestation region (e.g. $[TBP] : [CMPO]$ ratio and $[HNO_3]$) depend on CMPO individual.

The influence of $[TBP]$ on Am extraction using a mixture of extractants from HNO_3 solutions of various concentration is shown in Fig.2. From Fig.2 it is obvious that dependency of D_{Am} and S on $[TBP]$ is the higher the stronger $[HNO_3]$.

Fig.3 gives $[CMPO]$ influence upon Am extraction in the presence of TBP. It is shown that increasing of D_{Am} takes place only when the ratio of $[TBP]$ to $[CMPO]$ is high, the antagonistic effect is observed under smaller ratio and higher $[CMPO]$ and $[HNO_3] < 2$ that can be seen from Fig.1 (curves 3-6).

Fig.4 shows that solvent nature is of great importance in Am extraction by a mixture of extractants. Under the same conditions $[HNO_3] < 2M$ we observed the synergistic effect both with *o*-xylene (curves 5,6) and 1,2,4-trichlorobenzene (TCB) (curves 3,4) and antagonistic effect with dichloroethane (DCE) (curves 1,2).

Fig.5 shows that addition of TBP also results in D_{Eu} increasing in the presence of macroamounts of Eu(III). It was shown that upon TBP

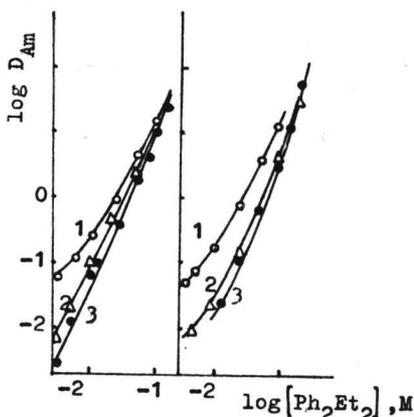


Fig.3. Distribution ratio of Am(III) vs. molarity of Ph_2Et_2 from 3M (a) and 7M (b) HNO_3 by a mixture of 1.5M TBP (1) and 0.025M TBP (2) with Ph_2Et_2 . (3)- Ph_2Et_2 in DCE

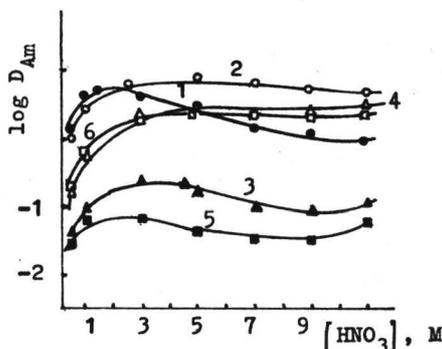


Fig.4. Acid dependency for Am(III) extraction by 0.05M Tol_2Et_2 (1,3,5) and a mixture of 0.05M Tol_2Et_2 and 1.5M TBP (2,4,6) in DCE (1,2); 1,2,4-TCB (3,4) and *o*-xylene (5,6)

addition the sediment didn't form that took place in the system with alone CMPO and $[Eu] > 0.3M$.

It will be expressed some views about the nature of synergistic effect in these systems. It is known that with increasing of $[HNO_3]$ extraction mechanism of Am with CMPO is changed: in weakly acid solutions $Am(NO_3)_3 \cdot nCMPO$ is extracted, in highly acid - $H^+Am(NO_3)_4 \cdot nCMPO$. On changing $[HNO_3]$ and complexes composition the role of TBP and nature of synergistic effect are changed.

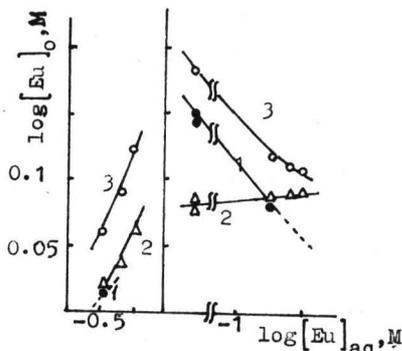


Fig.5. Dependency of Eu(III) amount in organic phase (a) and D_{Eu} on extracting by 0.1M Tol₂Et₂ (1), 2M TBP (2) and a mixture of 0.1M Tol₂Et₂ and 1M TBP (3) on Eu(III) concentration from 3M HNO₃

Conclusion

In case of TPE extraction by a mixture of CMPO and TBP D_{Am} deviation from additivity is observed, which values are connected with CMPO nature and solvent. Synergistic effect increases with enhancement of $[TBP] : [CMPO]$ ratio and $[HNO_3]$. The appearance of antagonistic effect takes place under large $[CMPO]$ and low $[HNO_3]$.

Differences in synergistic effect values in case of extraction by a mixture of extractants from low and high nitric acid concentration depend on changing of extracted complexes composition with CMPO ($Am(NO_3)_3 \cdot nCMPO$ and $H^+Am(NO_3)_4 \cdot nCMPO$, respectively) and the role of TBP in deviation from additivity.

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Introduction

The extraction of actinides with tertiary arsine oxides has been studied in detail in relation to the partition of U, Th, Np and Pu in different oxidation states between aqueous nitric acid solutions and solutions of aliphatic and aromatic arsine oxides (1). It has been shown that all the tertiary arsine oxides investigated are powerful extractants of transuranium elements and have extraction constant values ranging from 10^8 - 10^{11} . These values exceed by more than three orders of magnitude the constants for the extraction of the actinides by the isomeric phosphine oxides and are among some of the highest of all those known at the present time (2). In fact, no data are available concerning the pentavalent oxidation state of the actinides. As has been known, the element Pa(V) has the most stable oxidation state and therefore, is chosen for this study, where the extraction behaviour of Pa(V) with Ph_3PO and Ph_3AsO in chloroform from nitric acid solutions is investigated.

Experimental

Ph_3PO and Ph_3AsO were of purum grade and supplied by Fluka. Chloroform and all other chemicals were of A.R. purity grade and obtained from BDH (England). The radiotracer ^{233}Pa (27.4 d) was separated from neutron irradiated $\text{Th}(\text{NO}_3)_4$ samples by diisobutyl ketone (3).

Extraction procedure

The details of the extraction procedure were described elsewhere (4). The distribution ratio, D , was determined at $25 \pm 1^\circ\text{C}$, and defined by

$$D = \frac{\text{counting rate (cpm) per ml of the organic phase}}{\text{counting rate (cpm) per ml of the aqueous phase}}$$

Results and discussion

In the present study, the main two factors affecting the distribution ratio, D , i.e. nitric acid and extractant concentrations are followed at constant conditions of the other factor. As shown in Fig. 1, at constant Ph_3PO concentration, $D_{\text{Pa(V)}}$ increases with the increase in HNO_3 concentration from 1 - 9M by three orders of magnitude. At constant concentration of Ph_3AsO , $D_{\text{Pa(V)}}$ increases with HNO_3 concentration by one order

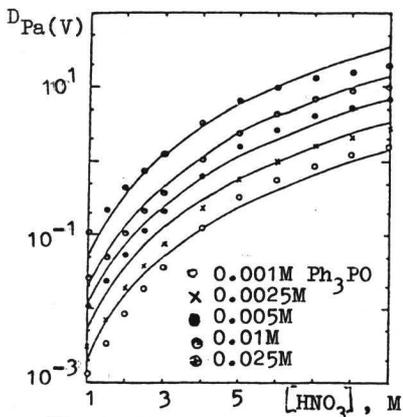


Fig. 1. Effect of HNO_3 conc. on $D_{\text{Pa}}(\text{V})$

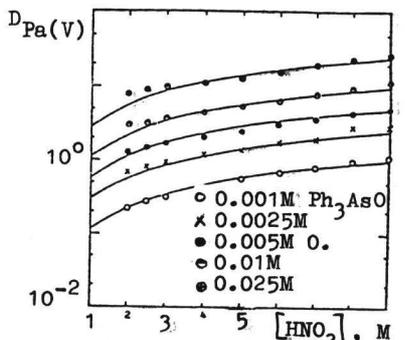


Fig. 2. Effect of HNO_3 conc. on $D_{\text{Pa}}(\text{V})$

of magnitude, Fig. 2. The aforementioned extraction behaviour for both extractants is repeatedly obtained at different extractant concentrations which indicates that the extraction stoichiometry for a specific extractant is the same irrespective of the concentration used. From Fig. 3 and 4, the logarithmic relation between $D_{\text{Pa}}(\text{V})$ and $[\text{extractant}]$ is linear with slope one. This was carried out at 3 different $[\text{HNO}_3]$, indicating that the extracted complex species accommodate only one extractant molecule mainly all-over the studied HNO_3 concentration range.

To get deeper insight about the extraction mechanism and the nature of extracted species, the logarithmic relation between $D_{\text{Pa}}(\text{V})$ and $a_{\pm} \text{HNO}_3$ ($a_{\pm} \text{HNO}_3 =$ mean molar activity of HNO_3) is presented in Fig. 5 and 6 for Ph_3PO and Ph_3AsO , respectively. In case of Ph_3PO , two straight lines of slopes 2 and 1 are obtained, suggesting the extraction stoichiometry

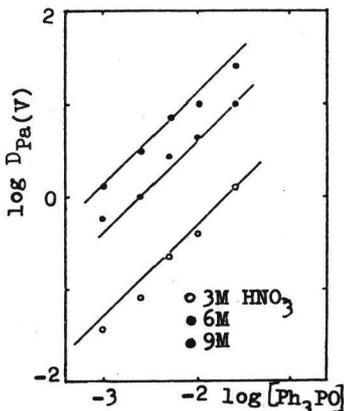


Fig. 3. Effect of Ph_3PO conc. on $D_{\text{Pa}}(\text{V})$

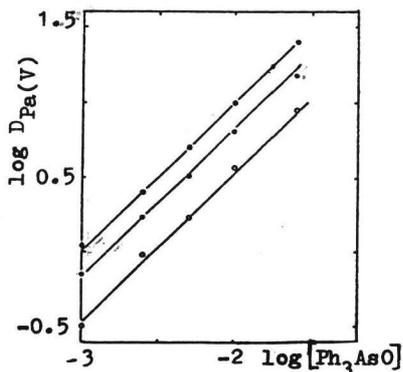


Fig. 4. Effect of Ph_3AsO conc. on $D_{\text{Pa}}(\text{V})$

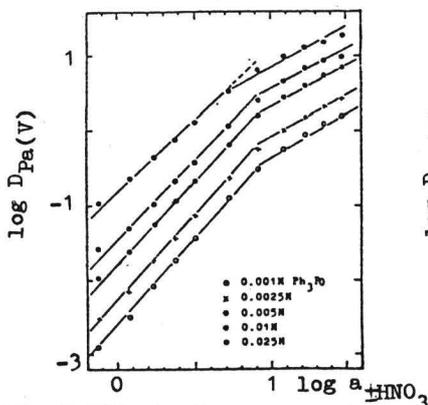


Fig. 5 Effect of $a_{\pm\text{HNO}_3}$ on $D_{\text{Pa(V)}}$

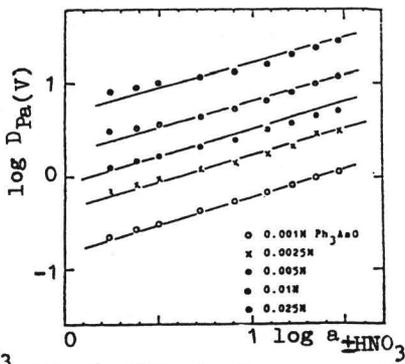
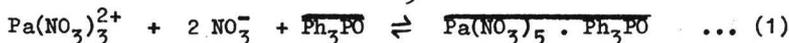


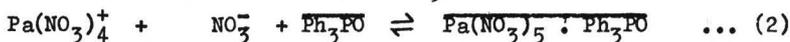
Fig. 6. Effect of $a_{\pm\text{HNO}_3}$ on $D_{\text{Pa(V)}}$

proceeds via :

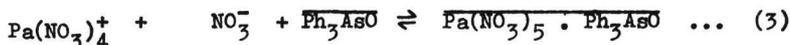
i. at lower HNO_3 activity, $\log a_{\pm\text{HNO}_3} \leq 0.7$



ii. at higher HNO_3 activity, $\log a_{\pm\text{HNO}_3} > 0.7$



In case of Ph_3AsO , Fig. 6, a group of almost parallel straight lines of slope ≈ 1 , all over the studied HNO_3 activity range are obtained. This clearly indicates that the extraction stoichiometry proceeds via



The formation constants of the proposed extraction were not evaluated since the interaction of HNO_3 with the two extractants is not clear at high acid and extractant concentrations (5). However, it is found that an empirical equation can satisfactorily represent the extraction data. This is achieved by considering the effect of both nitric acid and extractant concentrations on the distribution ratio. A general expression for this dependency is given as follows :

$$D_{\text{Pa(V)}} = k_1 \cdot [\text{extractant}]^{k_2} \cdot [\text{HNO}_3]^{k_3} \quad \dots (4)$$

or

$$\log D_{\text{Pa(V)}} = \log k_1 + k_2 \log [\text{extractant}] + k_3 \log [\text{HNO}_3] \quad \dots (5)$$

The values of the constants k_1 , k_2 and k_3 are calculated by fitting equation (4) with the experimentally obtained D-values; Fig. 1 and 2 and the best fit for both Ph_3PO and Ph_3AsO is obtained, with the following two equations :

$$\log D_{\text{Pa(V)}} = 0.27 + \log [\text{Ph}_3\text{PO}] + 3 \log [\text{HNO}_3] \quad \dots (6);$$

with $s = 0.18$, and

$$\log D_{\text{Pa(V)}} = 2.05 + \log [\text{Ph}_3\text{AsO}] + \log [\text{HNO}_3] \dots (7);$$

with $\delta = 0.01$, where

δ is the error square sum, defined by :

$$\delta = \sum \left[\frac{D_{\text{exp}} - D_{\text{calc}}}{D_{\text{exp}}} \right]^2.$$

The solid lines drawn in Fig. 1 and 3 are obtained from equation (6), whereby the corresponding lines in Fig. 2 and 4 are obtained from equation (7). The error square sum of the data indicates the good validity of the empirical equations deduced with respect to the experimental results obtained. The difference in the values of the constants obtained between Ph_3PO and Ph_3AsO systems can be related to the different interactions between each extractant, nitric acid, the diluent and the Pa(V) -species.

Comparing equations (6) and (7), the value of $k_1(\text{Ph}_3\text{AsO})$ is much higher than that of $k_1(\text{Ph}_3\text{PO})$. This is reflected by the high extraction of Pa(V) with Ph_3AsO than with the same concentration of Ph_3PO up to 7.5M HNO_3 . The high capability of Ph_3AsO over Ph_3PO can be attributed to the high electron donating power of oxygen in Ph_3AsO than the oxygen in Ph_3PO based on the low electronegativity of As than P. However, the difference in the electronegativity of As(2.18) than P(2.19) is rather small (6) and cannot account for such pronounced difference in the extractability between Ph_3AsO and Ph_3PO . Structurally, arsenyl group involves cooperative interaction between the arsenic and the oxygen in the $\text{>As}^+ - \text{O}^-$ σ -bond and the $p_{\pi} - d_{\pi}$ conjugation of the unshared electron pairs of oxygen with the highest vacant 4d orbitals of arsenic. As a result, the $\text{>As} \cdots \text{O}$ bond acquires partial double bond character. This can formally explain the high extraction power of Ph_3AsO over Ph_3PO .

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The selection of conditions for the extraction separation of metals is associated with the determination of the effect of molecular structure of an extractant on the extraction equilibrium. One of the contributing factors may be the characteristics of the substituents, i.e. their nature, size, mass and symmetry of these radicals. Studies of the effect of the composition of amines on their extraction ability concentrate in the first place on an assessment of the induction effects of the substituents which determine the nucleophilicity of nitrogen atom.

The effect of the extractant structure may be described quantitatively with sufficient accuracy by means of one- or several-parameter equations which express the important characteristics of the system affecting the extraction properties within the series under investigation. A correlation of experimental data with the effect of the individual factors shows that extraction series may be described by means of two-parameter equation of the following type

$$\log K = \log K_0 + Q \sum \sigma + \delta \sum E_S, \quad (1)$$

where K is the extraction constant of given system, K_0 is a constant accepted as a standard, Q and δ are constants for all the systems of the series which differ only in the nature of the substituents bonded to the functional group, σ and E_S are parameters characterizing the induction and steric effects of the substituents in the investigated type of an extraction series. Values σ and E_S (taken over from literature) were mostly obtained from measurements of organic substrates. A number of equations of type (1) have been determined for each series with given experimental values of distribution ratios and sums $\sum \sigma$ and $\sum E_S$ which have been evaluated from tabular data for amine in question. Application of this method with special reference to the extraction of lanthanides by benzyldialkylamines is illustrated in Table.

A one-parameter correlation equation including only one of these parameters was always used to assess the contribution of the induction and steric effects involved in a particular series. Data show that the one-parameter correlation $\log D_{Me} - \sum \sigma$ is valid only for benzyldialkylamines with the number of carbons equal to 4 - 8, where the linear dependence of $\log D_{Me}$ on $\sum \sigma$ was found for Ce(III) and Eu(III).

Literature does not provide sufficient data on E_S set constants which would allow to express the steric effects peculiar to amines. The values of E_S constants for the individual substituents were chosen on the basis of steric constants published in literature [1-4] and modified values which approximate those of Hansch sets. E_S values for substituents which have not been published in literature were added on the basis of the established rules.

Induction and Steric Constants and Theoretic Values of D_{Ce} , D_{Eu} and $\alpha_{Ce/Eu}$ Calculated for Tertiary Benzylalkylamines and Dibenzylalkylamines

Amine	$\Sigma\sigma$	ΣE_S	D_{Ce}^{exp}	D_{Ce}^{cal}	D_{Eu}^{exp}	D_{Eu}^{cal}	$\alpha_{Ce/Eu}^{cal}$
BDEN	0,02	4,81	1,6		2,8		
BDBuN	-0.04	5.07	9.7	10.10	4.5	4.75	2.13
BDHeN	-0.06	5.17	6.4	8.24	3.7	3.93	2.10
BDON	-0.08	5.41	4.2	4.63	3.0	2.46	1.88
BDNoN	-0.10	5.57	3.6	3.21	1.9	1.81	1.77
BDLN	-0.13	5.71	2.2	2.41	1.2	1.39	1.73
DBBuN	0.31	5.25	2.2	2.51	2.7	2.71	0.93
DBON	0.29	5.42	1.4	1.69			
DBHeN	0.30	5.30	1.9	2.26			

As amine extraction follows the pattern of an equilibrium reaction where induction effects are always involved to a lesser or greater extent, as corroborated by the correlation the authors have found for $\Sigma\sigma$ and ΣE_S , expressed by means of a two-parameter equation. As regards the extraction of Ce(III) by tertiary benzylalkylamines, with $\log D_o = 6.7$ the following constants have been evaluated: $Q_{Ce} = -1.1$ and $\delta_{Ce} = 6.7$. In the case of Eu(III) extraction, with $\log D_o = 5.1$, the constants are: $Q_{Eu} = -0.2$ and $\delta_{Ce} = 0.87$. A comparison of values D_{Ln} obtained by calculation with experimental data is given in Table. As it is evident from Table, the two-parameter correlation facilitates description of the extraction experimental data obtained for alkylamines, and it may also serve as a basis for the analysis of the individual factors peculiar to the structure of the extractant and their selectivity. This description, however, only applies to a specific class of extractants and it is not universal.

As regards the extraction of two elements, the log of the separa-

tion factor ($\log \alpha_{1,2}$), expressed by means of equation (1), gives the following expression

$$\begin{aligned} \log \alpha_{1,2} &= \log D_{O1} - \log D_{O2} + [\varphi_1 - \varphi_2] \sum \sigma + [\delta_1 - \delta_2] \sum E_S = \\ &= \log \alpha_{1,2}^0 + \varphi_{1,2} \sum \sigma + \delta_{1,2} \sum E_S. \end{aligned} \quad (2)$$

It is therefore possible to draw the conclusion that the effect of the extragent structure on the separation factor can be described by means of these correlation equations. The values of $\varphi_{1,2}$ and $\delta_{1,2}$ coefficients and the corresponding values of the separation factors can serve as an indication of the influence of the induction and steric effects of substituents on the separation process selectivity.

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Solvent extraction of americium in higher oxidation states is widely used for americium separation from other actinides and is especially promising for americium separation from curium [1]. When using traditional solvent extraction systems americium in higher oxidation states is unstable in organic phase due to reduction in the presence of organic extractants and solvents. In this respect it was of interest to use two-phase systems based on polyethylene glycol free of organic solvents for americium extraction in higher oxidation states.

Extraction of trivalent actinides has been studied previously in the following systems: polyethylene glycol (PEG) - ammonium sulfate - water - arsenazo III and PEG - potassium carbonate - water - alizarine complexone [2-3]. Extraction of americium in higher oxidation states by PEG has been investigated from concentrated carbonate solutions in the presence of alizarine complexone (AC). Americium has been established to quantitatively pass into the PEG phase at AC concentrations more or equal 0.02 M. In this case the efficiency of americium isolation is constant for different oxidation states when taking trace amounts of americium (10^{-6} - 10^{-7} M); and distribution coefficients of americium (IV), (V) and (VI) differ significantly from those of other actinides in the same oxidation states (see Table 1). It apparently

Table 1. Distribution coefficients of actinides in case of extraction into the PEG phase from K_2CO_3 (40 mass %) in the presence of 0.02 M AC

Metals	Am(III)	Cm(III)	Am(V)*	Np(V)	Pa(V)	Am(VI)*	U(VI)	Am(IV)*	Pu(IV)
D	43.7	127.8	7.3	0.15	0.12	33.2	0.05	40.8	13.4
*Initial oxidation states of Am prior to extraction									

results from trace amounts of americium (IV), (V) and (VI) to be unstable in this system and to reduce to americium (III).

Behaviour of macroamounts of americium ($\geq 10^{-3}$ M) in higher oxidation states in carbonate solutions was studied using spectrophotometry. Americium was electrochemically oxidized to a hexavalent state. Fig. 1 shows the absorption spectra of americium in potassium carbonate solution recorded after oxidation and addition of PEG and AC. The data obtained indicate a quantitative americium oxidation to americium (VI) and no change in valence state of americium caused by PEG. After complexone addition to this system absorption bands appear in solution

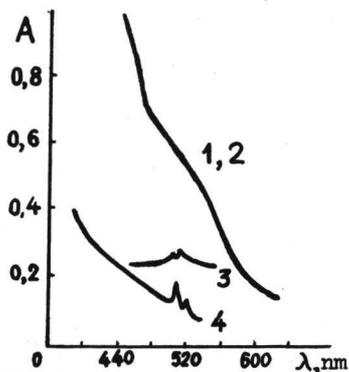


Fig. 1. Absorption spectra of Am carbonate solution: 1 - after the oxidation, 2 - after the contact with PEG, 3 - after the addition of AC, 4 - after the contact of Am with AC during 26 hours

absorption spectrum of Am(VI) which are characteristic of Am(III) (maximum at 508 nm) and Am(V) (maximum at 518 nm). These spectra show that macroamounts of Am(VI) are reduced by AC giving mainly Am(V). Under a prolonged contact with the extractant the part of Am(III) does increase. Fig. 1, curve 4 shows that the spectrum recorded in 26 hours corresponds mainly to Am(III) absorption spectrum in carbonate solutions. Macroamounts of Am(V) were obtained by electrochemical reduction of Am(VI). Spectrophotometry has shown that Am(V) not move into the PEG phase containing 0.02 M AC nor reduce to Am(III). This enabled us to develop a separation method of macroamounts of Am(V) from Cm in carbonate solutions. α - Spectra

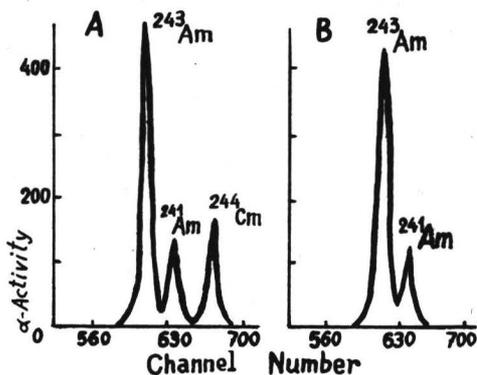


Fig. 2. α - Spectra of the initial solution of Am(V) and Cm (A) and of the salt phase after the extraction by PEG in the presence of AC (B)

of an initial solution and that of a saline solution recorded after curium extraction by PEG are shown in Fig. 2. α - Spectrum shows practically no curium in the saline phase. Separation factor of Am and Cm is more than 100 for one extraction cycle by PEG containing AC.

Americium extraction in the PEG - ammonium sulfate - water - arsenazo III system has been studied.

Conditions have been found in this system for quantitative extraction of Am(V) by PEG. Americium extraction as a function of equilibrium salt phase pH is given in Table 2.

A quantitative americium extracti-

on is observed at pH 4-5 in the presence of 10^{-3} M arsenazo III. A spectrophotometric study has shown Am(V) to form a complex with arsenazo III of a 1:1 composition. Three absorption bands are observed in the absorption spectrum of a sulfate solution containing arsenazo III (1.1×10^{-4} M) and Am(V) (5.4×10^{-4} M) which have maxima at 550, 580 and 670 nm (see Fig. 3). These absorption bands remain in the solution absorption spectrum of PEG after Am(V) extraction, but unlike sali-

Table 2. Distribution coefficients of actinides as a function of pH in case of extraction by PEG in the presence of 10^{-3} M arsenazo III

pH	Am(III)	Am(IV)*	Pu(IV)	Am(V)*
2.1	0.30	-	16.6	-
2.6	0.31	1.04	-	-
2.8	0.95	-	36.6	-
3.0	1.50	5.20	-	0.23
4.0	46.20	57.51	59.7	52.72

*Initial oxidation states of Am prior to extraction

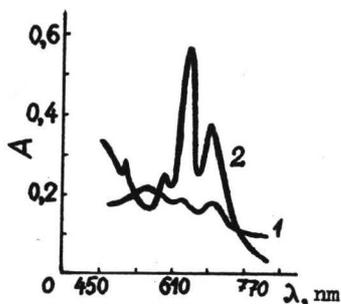


Fig.3. Absorption spectra of Am(V) complexes with arsenazo III in $(\text{NH}_4)_2\text{SO}_4$ solution (1) and PEG (2)

ne solutions a small shift is observed in characteristic absorption bands to a long-wave region: 580, 620 and 680 nm. Optical densities of Am(V) solutions with arsenazo III in PEG are much higher than those in saline solutions. The molar extinction coefficients of Am(V) complex in the PEG solution are 1×10^4 at 620 nm and 1×10^3 $\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 680 nm. One can clearly see in the spectra two absorption bands at 517 and 718 nm belonging to Am(V) together with those characteristic of americium complex with arsenazo III. There are no absorption bands characteristic of Am(III) in the spectrum of the PEG phase. This indicates no reduction of Am(V) upon extraction by PEG containing arsenazo III. A spectrophotometric study of Am(VI) extraction has shown Am(VI) to reduce to Am(V) under the contact with arsenazo III, Am(V) being subsequently extracted by PEG.

It was interesting to study the behaviour of Am(IV) in the system under consideration since arsenazo III complexes with four-charged metal cations are more stable than those with triply-charged cations. The PEG solution has been found previously to quantitatively extract tetravalent plutonium and thorium at lower pH values of saline solutions than trivalent actinides. However, at low pH values of a saline solution distribution coefficients of Am(IV) are not much higher than those of Am(III) (see Table 2).

Thus, two-phase aqueous systems based on polyethylene glycol can be widely used for extraction isolation and separation of americium in different oxidation states.

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Actinides in carbonate solutions form various complex compounds, the content and the stability of which being affected by the concentration and relation of the components, the pH value and other factors. The formation of the anion complexes of the following composition is typical for TPE: $\text{Am}(\text{CO}_3)_2^-$ ($\lg\beta=11.44$); $\text{Am}(\text{CO}_3)_2(\text{OH})^{2-}$ ($\lg\beta=15.56$); $\text{Am}(\text{CO}_3)_3^{3-}$ ($\lg\beta=13$); $\text{Am}(\text{CO}_3)_3(\text{OH})^{4-}$; $\text{Am}(\text{CO}_3)_4 \cdot (\text{OH})^{6-}$; $\text{Cm}(\text{CO}_3)_4(\text{OH})^{6-}$ [1]. Taking into consideration the variable composition of carbonate complexes of actinides in the aqueous phase, one can expect that extractants of different classes will essentially affect the content of the compounds in the organic phase. Primary amines (N-decylamine (DA)) extract TPE and REE from carbonate solutions in the form of ion associates of $(\text{RNH}_3)_3 \cdot [\text{M}(\text{CO}_3)_3]$ composition including metal tricarbonato complex as anion [2-3]. Chelating reagents (β -diketones (PhMBP, HTTA); alkylpyrocatecholes (DOP, TAP) extract trivalent TPE and REE in the form of intracomplex coordinationally saturated and hydrolyzed compounds of the type of $\text{M}(\text{PhMBP}) \cdot n\text{H}_2\text{O}$; $\text{M}(\text{TTA})_3 \cdot n\text{H}_2\text{O}$ [4-5]; $\text{Na}_2[\text{MDOP}_2(\text{OH})(\text{H}_2\text{O})]$ [6-7].

In that case carbonate-ion is not the necessary component of the extracted compounds, but only a complexing agent, which confines the hydralizing elements in the low alkaline media in the soluble form. Since the extraction process of the intracomplex compounds and the disintegration of the complex compounds in the aqueous phase take some time, the role of the kinetic factors, especially in metals with alkylpyrocatechole, is essentially increased [8]. As the experimental data show, the rate of mass transfer is determined by slow chemical reactions, which take place both in the volume of the aqueous phase and at the phase boundary. Although the increase in the pH of the initial solution facilitates these reactions, the possibility of the formation of the interphase film grows. To avoid the effect of the interphase film on the mass transfer rate, the extraction should be conducted with high content of the alkaline metal carbonate. Firstly, the increase in the content of potassium carbonate and alkali increases the concentration of the intermediate hydroxocarbonate complexes, which are responsible for the velocity of the beginning of the reaction, and secondly, it allows to avoid the accumulation of the products of hydrolytic polymeri-

zation in the zone of the reaction. Therefore, by varying the concentration of caustic potassium, one can achieve quantitative isolation of americium even from a saturated solution of K_2CO_3 [7] (Fig.1). The most part of the studied extractants rather highly extract

both macro- and micro-amounts of elements from carbonate solutions. As the same time the extracts, saturated with metals, based on DA, PhMBP, TAP, with the concentration of the order of $n \cdot 10^{-2} M$,

can only be obtained by concentration, since TPE carbonate compounds, as well as REE, are comparatively poorly soluble in carbonate solutions.

Extraction from carbonate solutions can be used not only for TPE isolation, but also their separation. Like in the case with alkaline solutions, the sequence of actinide isolation from carbonate solutions in decreased in the series $M(III) > M(IV) > M(V) > M(VI)$, according to the degree of oxidation. It is clearly manifested on Fig.1-2 where the comparison is made between the metal extraction with alkylpyrocatecholes [7] and β -diketones [4-5]. Since hexavalent and tetravalent elements are extracted worse than trivalent elements, in these systems rather high separation factors ($n \cdot 10^4$) for pairs Am(III)-U(VI); Cm(III)-U(VI); Am(III)-Pu(IV); Cm(III)-Pu(IV).

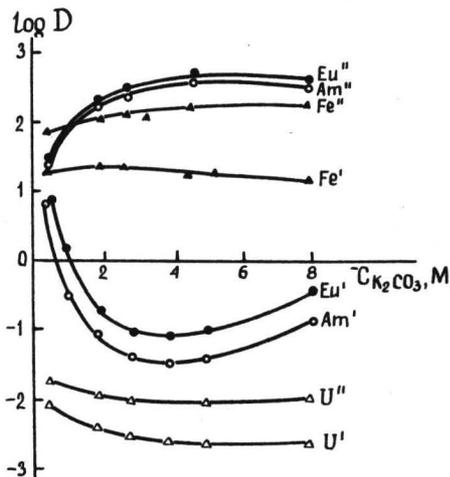


Fig.1. Extraction of metals from K_2CO_3 (M') solutions and the mixture of K_2CO_3 and 2 M KOH (M'') by 0.04 M DOP in toluene

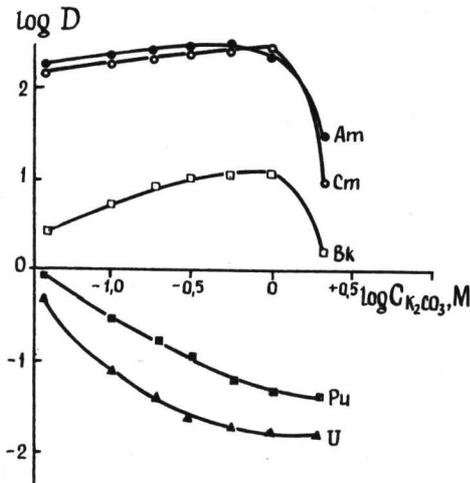


Fig.2. Extraction of metals from K_2CO_3 solutions with 0.1 M PhMBP in MIBK

The selectivity of the extraction separation can be increased by two ways: by varying the alkalinity of the media and the time period of the phase contact. Thus, adding small amounts of caustic potassium into the carbonate solutions not only enhance the extraction of many elements, but also increases the factors of americium separation from berkelium, cerium and other elements, except europium ($D_{Am}/D_{Eu} < 2$).

Among the agents tested for the extraction separation of Am-Cm, TAP is practically the only agent, which extracts curium and californium from carbonate solutions better than americium ($D_{Cm}/D_{Am} = 2.2$) [8-9]. Additional possibility of separating these elements occurs during the re-extraction by potassium carbonate mixtures and salts of aminopolycarbonic acids. The comparison of the kinetic activity of the studied re-extracts has shown that DTPA content essentially effect the rate of the re-extraction of the elements under study, and the increase in its concentration at constant K_2CO_3 content leads to a sharper increase in the rate of curium re-extraction against americium. Under the optimal conditions the re-extraction rate constants of these elements differ in more than an order.

The efficiency of the separation of trivalent elements grows during the transfer from a single static extraction to extraction chromatography due to the differences both in the values of equilibrium constants and the values of the mass transfer coefficients [8]. By varying the content and the rate of the penetration of the solution through the column with fluoroplast-4, impregnated with 5% TAP in toluene, the fractions were obtained at the stages of sorption, washing and desorption, containing ~90% of curium and 1% of americium.

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The main part of the most efficient techniques for recovery and purification of the transuranium elements are based on a combination of solvent extraction with redox cycles. Dealing with the trace quantities of an element, solvent extraction technique is widely used for studying redox properties, complex formation and other processes taking place in aqueous solution. The results obtained and their interpretation in all cases depends very much on the experimental conditions and the way of the data treatment.

Any redox equilibrium supposes existence of at least two oxidation states in a system. For a simplicity we shall confine ourselves to consideration of two forms, Me(Ox) and Me(Red), being in a reversible equilibrium. Here we shall operate by such a practical parameters as: relation of analytical concentration of oxidized- and reduced forms

in an aqueous phase, $\alpha = \frac{[Me(Ox)]_a}{[Me(Red)]_a}$ and in a solvent extraction system as a whole, $A = \frac{[Me(Ox)]_a + [Me(Ox)]_o}{[Me(Red)]_a + [Me(Red)]_o}$; distribution coefficients of the both

forms $D_{ox} = \frac{[Me(Ox)]_o}{[Me(Ox)]_a}$ and $D_{red} = \frac{[Me(Red)]_o}{[Me(Red)]_a}$ and experimentally determined distribution coefficient of the element under consideration:

$$D = \frac{[Me(Ox)]_o + [Me(Red)]_o}{[Me(Ox)]_a + [Me(Red)]_a} \quad (1)$$

As shown in [1], the relations connecting all these parameters with each other can be obtained by simple transformation of the above expressions in to:

$$\alpha = \frac{D - D_{red}}{D_{ox} - D} \quad (2); \quad A = \alpha \frac{D_{ox} + 1}{D_{red} + 1} \quad (3); \quad D = \frac{\alpha D_{ox} + D_{red}}{1 + \alpha} \quad (4)$$

Speaking about the influence of solvent extraction on the redox equilibria, we should always compare the concentration relations of oxidized and reduced forms in an initial aqueous solution, " α^o ", and in a final solvent extraction system as a whole, "A". In the paper we shall consider three practical aspects, resulting from the mutual consideration of solvent extraction- and redox equilibria.

I. Solvent extraction technique for studying redox equilibria. There are two cases, which should be considered here:

- when the solvent extraction process is not accompanied by any redox reaction and result in a simple distribution of existing Ox- and Red-forms between aqueous and organic phases;

- when the solvent extraction process is accompanied by a redox reaction. In the first case the concentration relation of oxi-

dized and reduced forms in the initial aqueous solution is equal to the corresponding relation in the solvent extraction system as a whole i.e. $a^\circ = A \neq a$. The second case is characterized by the conditions, when the concentration relation of the oxidized and reduced forms in the aqueous solution before the start of extraction process and after the attainment of an extraction equilibrium, remains unchanged, i.e. $a^\circ = a \neq A$. This case is a rather frequent one, when in an aqueous solution a redox potential, "E", is supported continuously by an introduction of a redox agent or by an electrochemical device.

The results of the analytical consideration of the equations(2,3,4) for both cases and their variations are summarized in Table .

The equations for the calculation of "a°" from the solvent extraction data

System	General form $D_{\text{ox}} \neq D_{\text{red}}$	At the conditions when.	
		$D_{\text{ox}} \gg 1; D_{\text{red}} \ll 1$ $D_{\text{ox}} > D > D_{\text{red}}$	$D_{\text{ox}} \ll 1; D_{\text{red}} \gg 1$ $D_{\text{ox}} < D < D_{\text{red}}$
Type I	$a^\circ = \frac{(D - D_{\text{red}})(D_{\text{ox}} + 1)}{(D_{\text{ox}} - D)(D_{\text{red}} + 1)}$	$a^\circ = A \approx D$	$a^\circ = A \approx \frac{1}{D}$
Type II	$a^\circ = \frac{D - D_{\text{red}}}{D_{\text{ox}} - D}$	$a^\circ \approx \frac{A}{D_{\text{ox}}} \approx \frac{D}{D_{\text{ox}}}$	$a^\circ \approx \frac{D_{\text{red}}}{A} \approx \frac{D_{\text{red}}}{D}$

The conditions of the applicability of a solvent extraction technique and the corresponding equations for the calculation of a° -values are represented in Table I as well. When all the distribution coefficients are known, the solvent extraction technique is applicable for both types of system, but the equations for the calculation of "a°" are different, depending on the type of the system. In case II even for approximate calculations it is necessary to know not only apparent distribution coefficient but the distribution coefficient of the most extractable form as well.

The possibilities of application of solvent extraction technique for evaluation of formal redox potential of Bk(IV)/Bk(III) couple at the condition when $D_{\text{Bk(IV)}}$ is not known exactly and possible mistakes in data interpretation are considered in detail in work [1] .

II. The condition selection for stabilization of an element at the desirable oxidation state. As follows from eq.(3), relation "A" in an extraction system can differ from relation "a°" by a factor of several hundreds or thousands. For example, an oxidant continuously acting during extraction process provides 1% oxidation of a metal ion in

aqueous phase, i.e. $a^\circ = 0,01$. At $D_{ox} = 10^4$ and $D_{red} = 0,01$ oxidation degree in the whole solvent extraction system according to eq.(3) will be 99%. Generally in the systems with $D_{ox} \gg 1$ and $D_{red} \ll 1$ an oxidant, which can not be predicted on the basis of its properties in monofase aqueous solution, may be very efficient [2]. On the other hand, in case of reduction back-extraction procedure even relatively strong reductants (usually active in aqueous solution) may be inefficient for quantitative transfer an element into aqueous phase. For example, at electrochemical oxidation of Bk(III) directly in extraction-chromatography column (with 10% HDEHP on carbonfibre) complete oxidation and sorbtion of Bk take place at potential +1,4 V [3] (which is 130 mV lower than the formal potential of Bk(IV)/Bk(III) in corresponding medium). Berkelium stripping by electrochemical reduction takes place at 1,0 V and less. When using TBP as an extractant, which under similar conditions has much lower distribution coefficient for Bk(IV), the corresponding potentials increase up to 1,7 V and 1,3 V.

III. Extraction radiopolarography for determination of redox potentials of Transuranium ions. The main advantage of this technique is an opportunity to determine formal potentials of the elements, which are not available in weighable quantities.

Suppose " E_f° " be a formal redox potential of $Me(Ox)/Me(Red)$ in a solution and "E" be a potential, which could be supported in the solution by an electrochemical device. Let us introduce and extractant predominantly extracting the element in a definite oxidation state. When solvent extraction process is equilibrated equations(2-4) are valid. On the other hand the concentration relation of oxidized and reduced forms, "a", will be determined by the Nernst equations Substituting eq.(2) into the Nernst equation, we obtain:

$$E_f^\circ = E - 2,3 \frac{RT}{nF} \lg \frac{D - D_{red}}{D_{ox} - D} \quad (5)$$

Knowing the potential E and the corresponding distribution coefficients, the value of E_f° can be determined on the basis of eq.(5). In practice a dependence of the apparent distribution coefficient, "D", upon the solution potential is interesting to draw. To obtain this dependence let us solve eq.(5) relatively D and represent the resulting expression in a log.-form:

$$\lg D = \lg D_{ox} + \lg \frac{e^{\frac{nF}{RT}(E - E_f^\circ)} + \frac{D_{red}}{D_{ox}}}{e^{\frac{nF}{RT}(E - E_f^\circ)} + 1} \quad (6)$$

The plot of $\lg D$ versus E represents an S-shaped curve. The values of " $\lg D$ " change within the limits of D_{red} and D_{ox} . The inflection point of the curve, $E_{1/2}$, is determined by double differentiation

of eq.6:

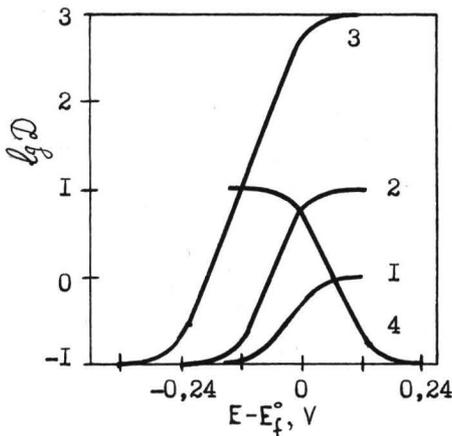
$$E_{1/2} = E_f^{\circ} + 2,3 \frac{RT}{nF} \lg \frac{D_{ox}}{D_{red}} \quad (7)$$

and corresponds to

$$\lg D_{1/2} = \frac{\lg D_{ox} + \lg D_{red}}{2} \quad (8)$$

The determination of the inflection point coordinates from eq.(8) and the relation $\frac{D_{ox}}{D_{red}}$ from the experimental data permits us to calculate the value of E_f° using eq.(7).

The best way to control the potential of the solution is to use an electrochemical cell with a working electrode of large surface, which simultaneously serves for supporting the organic phase. The technique was successfully tested 4 in the determination of the formal redox potential of Bk(IV)/Bk(III) couple.



The theoretical dependence of the apparent distribution coefficient "D" upon the oxidation potential, "E", at the conditions:

- 1) $D_{red} = 0,1, D_{ox} = 1,0$;
- 2) $D_{red} = 0,1, D_{ox} = 10$;
- 3) $D_{red} = 0,1, D_{ox} = 10^4$;
- 4) $D_{red} = 10, D_{ox} = 0,1$

In all cases $n = 1$

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Trivalent americium and curium are known to behave very similar to each other in chemical reactions. For this reason up to now the separation of Am and Cm has been a task not easily to be accomplished. Attempts have been made to use the higher oxidation states of americium (Am-V, Am-VI) for its separation from curium which under appropriate conditions remains trivalent or tetravalent in solution [1]. There are a lot of two-phase systems with different chemical behaviour of Am(VI) and Cm(III) or Am(V) and Cm(III) and, consequently, high separation factors have been achieved. If the oxidizing conditions have been chosen to establish pentavalent americium in solution, a precipitate of $K_3AmO_2(CO_3)_2$ can be used to separate Am from Cm which is remaining in the liquid phase. In extraction systems Cm(III) can be transferred into an organic phase containing di(2ethylhexyl)phosphoric acid (HDEHP), 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 or 2-thenoyltrifluoroacetone and Am(V) will be left in the aqueous solution [2]. After oxidizing americium to the hexavalent state and establishing the corresponding conditions in solution Am(VI) can be extracted by HDEHP and Cm(III) is retained in the aqueous phase [3]. In all the separation procedures mentioned the problem concentrates on how to hold americium in the higher valence during the time of separation.

In connection with americium-curium-separation by liquid-liquid extraction problems of oxidizing Am to the higher valence states by using ammoniumperoxidisulphate in the presence of silver ions as a catalyst have been investigated. The different oxidation states of Am have been identified spectrophotometrically by the help of characteristic absorption peaks of the species present.

The results presented in Table 1 demonstrate a slow and incomplete oxidation of Am to the hexavalent state by $(NH_4)_2S_2O_8$ (in the presence of Ag^+) at room temperature. By performing the oxidation at elevated temperatures ($80^\circ C$) one can reach the complete oxidation to Am(VI) within 10 minutes, but the hexavalent state will be stable only for a few minutes. Another condition consists in a rather low acidity of the solution. Already in 0.5 M HNO_3 only 85 % of Am(VI) have been found. Therefore conditions of better stability of hexavalent americium should be elaborated. In this context the influence of potassium phosphorwolframate has been thoroughly investigated.

Potassium phosphorwolframate ($K_{10}P_2W_{17}O_{61}$, KPW) has become well known as a strong inorganic complexing agent capable of stabilizing

Table 1. Experimental results on oxidation of americium
(Conditions: 0.001 M Am, 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.01 M AgNO_3)

N	Concentration of HNO_3 , M	Temperature, $^{\circ}\text{C}$	Time to maximum of oxidation, min	Result of oxidation	
				Valence state	Degree %
1	0.1	25	360	Am-VI	80
2	0.1	80	10	Am-VI	100
3	0.5	80	8	Am-VI	85

the higher valence states of actinoides in solution [4]. The results collected in Table 2 give an impressive picture of the enormous influence of KPW on the oxidation of Am by means of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of silver ions. Obviously, the ratio of KPW to Am is of high importance and determines the final valence state of Am under the given conditions. When comparing the data of the first three lines of Table 2

Table 2. Influence of potassium phosphorwolframate (KPW) on the oxidation of americium

(Conditions: 0.001 M Am, 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.01 M AgNO_3)

N	Concentration of HNO_3 , M	Temperature $^{\circ}\text{C}$	KPW/Am ratio	Time to maximum of oxidation, min	Result of oxidation	
					Valence state	Degree %
1	0.1	25	5.0	imediately	Am-IV	100
2	0.1	25	0.2	15	Am-VI	100
3	1.0	25	0.2	40	Am-VI	100
4	2.0	25	0.2	90	Am-VI	35
5	2.0	25	0.6	15	Am-VI	100
6	2.5	25	0.6	20	Am-VI	100
7	2.5	50	0.6	15	Am-VI	75
8	2.5	50	1.0	15	Am-VI	65
9	3.0	25	0.2	170	Am-VI	15
10	3.0	25	0.6	120	Am-VI	75
11	3.0	50	0.6	45	Am-VI	16
12	3.0	70	0.6	20	Am-VI	8
13	4.0	70	0.6	no oxidation		

with those of Table 1 one should be convinced of the possibility of oxidizing Am completely to Am-VI at room temperature and up to a concentration of HNO_3 of 1 M by the aid of KPW. But the amount of KPW should be substoichiometric in relation to Am, otherwise Am-IV would be stabilized rather than Am-VI (see run No. 1 of Table 2). It should be mentioned that Am-VI is stable for a long time (up to two days) in the presence of the quantity of KPW following from the data of Table 2. Even at higher concentrations of HNO_3 (up to 2,5 M) the quantitative oxidation of Am to Am-VI by $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{Ag}^+$ can be accomplished, provided that the mole ratio KPW/Am has been increased to 0.6. Somewhat astonishing, but a rise in temperature so useful in oxidizing Am without KPW has been shown to lower the degree of Am-VI in the presence of KPW (see runs No. 6-8 and 10-12 of Table 2). At higher concentrations of HNO_3 (more than 2.5 M), no conditions for oxidizing Am to Am-VI have been found.

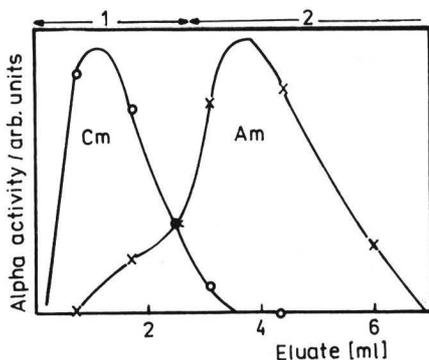
In real separation problems one should expect Am-Cm to be accompanied by other ions, e. g. by salting-out agents (Mg^{++}) or by elements of the rare earth group (Ce^{3+}). Therefore the influence of other ions on the oxidation of Am under the conditions outlined above has been investigated. It follows from the data of Table 3 that foreign ions introduce additional complications into the oxidation process because it will be more difficult to establish the right concentration of KPW. Under the conditions of 100 % oxidation to Am-VI (see Table 2) the yield of Am-VI decreases drastically in the presence of macroquantities of $\text{Mg}(\text{NO}_3)_2$. Fortunately, this influence can be overcome up to a certain concentration of the possible salting-out agent by an increase in the amount of KPW. Also, if cerium is present in a concentration tenfold that of Am, conditions of the complete oxidation to Am-VI have been found lying within a rather narrow range of the KPW concentrations. Thus, the amount of KPW

Table 3. Influence of other ions on the oxidation of Am in the presence of KPW (Cond.: 1M HNO_3 , 25°C, 10^{-3} M Am, 0.1M $\text{S}_2\text{O}_8^{2-}$, 0.01M Ag^+)

N	Ion and its concentration	KPW $\text{Mx}10^4$	Time to maximum of oxidation, min	Result of oxidation Valence state, degree (%)
1	1,0 M Mg^{++}	2	180	Am-VI (75)
2	1.0 M Mg^{++}	4	90	Am-VI (95)
3	1.0 M Mg^{++}	6	60	Am-VI (100)
4	2.0 M Mg^{++}	6	200	Am-VI (15)
5	2.0 M Mg^{++}	10	150	Am-VI (20) / Am-IV (30)
6	0.01 M Ce^{3+}	6	360	Am-VI (5) / Ce-IV (100)
7	0.01 M Ce^{3+}	100	180	Am-VI (25) / Ce-IV (100)
8	0.01 M Ce^{3+}	150	180	Am-VI (100) / Ce-IV (100)
9	0.01 M Ce^{3+}	200	5	Am-IV (100) / Ce-IV (100)

should be at least 150 % of the concentration of Ce, but already an increase to 200 % will result in Am-IV instead of Am-VI.

Attempts have been made to use the results outlined above for the separation of Am and Cm from solutions of spent nuclear fuel in an analytical scale. A special method of solvent extraction - extraction chromatography - with tributylphosphate (TBP) or solutions of HDEHP in n-heptane as the stationary phases and HNO_3 solutions as the mobile phases has been applied. In the system TBP/1M HNO_3 , 0.3 M $\text{Mg}(\text{NO}_3)_2$ the partition coefficient (K_p) of Am-VI is 20 whereas all the other species of Am (Am-V, Am-IV, Am-III) are scarcely extracted with $K_p < 0.1$. An even much stronger extracting power for Am-VI was measured with HDEHP, an 0.2 M solution of which should take up Am-VI from an aqueous phase 0.05 M in HNO_3 with $K_p \sim 250$ [57]. In the solvent extraction systems mentioned above and in the oxidizing conditions Cm remains trivalent (or tetravalent with KPW) and is not extracted. In Fig. an example of the extraction chromatographic separation of tracer concentrations of Am and Cm from a rare earths fraction of fission products is shown. A Celite column has been impregnated with 0.2 M HDEHP in n-heptane. The oxidation at 80°C has been performed with 0.01 M AgNO_3 , 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.1 M HNO_3 without KPW. After 15 min. and chilling in an ice-bath the solution has been loaded on to the column and quickly eluted by the aid of overpressure.



Extraction chromatographic
Am-Cm separation with 0.2 M HDEHP.
Column: 4 mm i.d., 100 mm length.
1- oxidizing solution, 2- 1M HNO_3

When collecting the whole 1M- HNO_3 -Am fraction some percent of Cm activity is still present. The last portions of the eluate are free of Cm. With tracers Am and Cm no enhancement of the separation by KPW has been found. Our explanation is the strong dependence of the resulting valence state of Am from the mole ratio KPW/Am and up to now attempts have failed to establish the desired ratio by taking into account the alpha activity of the initial solution.

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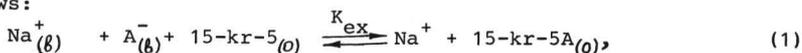
Extraction techniques are most suitable in isolating pure radioactive isotopes from targets irradiated by nuclear particles in cyclotron or nuclear reactor.

In isolating radionuclides the irradiated target is dissolved, the extraction of the radionuclide from the solution is carried out. Two extraction techniques are mostly used:

a) the aimed isotope is selectively extracted; the organic phase being washed, it is then extracted back into a suitable aqueous solution, or
 b) the extraction removal of the target material and some radionuclides (impurities) is carried on to result in the isotope being produced in aqueous phase. After used are also some other techniques for additional purification of the radionuclides obtained. In using solid extraction chromatography the first method is preferable, i.e. to extract the aimed radionuclide separating it from the target material and impurities. For producing pure radioactive isotopes we used liquid extractants in suitable diluents and solid one based on tributylphosphate. Tributylphosphate and other oxygen - containing organic solvents, amines and salts of quaternary ammonia bases, crown ethers and other reagents in diluents were used as liquid extractants. Irradiation of targets on high-energy cyclotrons of p , d and α -particles commonly results in long-lived radionuclides of two or more elements. Isolation of two or three radionuclides from one irradiated target is more reasonable and less expensive.

As an example, let us consider the technique for isolating sodium-22 and aluminium-26 from cyclotron irradiated targets made of magnesium or its alloys. Isolation of sodium-22 was performed by 15-crown-5 solvent extraction, that of aluminium-26 by 10 vol.% trioctylamine of oxalic acid $[(C_8H_{17})_3NH]_2C_2O_4$ in solution of chloroform in benzene or toluene.

Sodium extraction by 15-crown-5 solution in diluent proceeds as follows:



where K_{ex} is an extraction concentration constant, A - is usually an organic acid anion. Of common use is sufficiently strong picric acid.

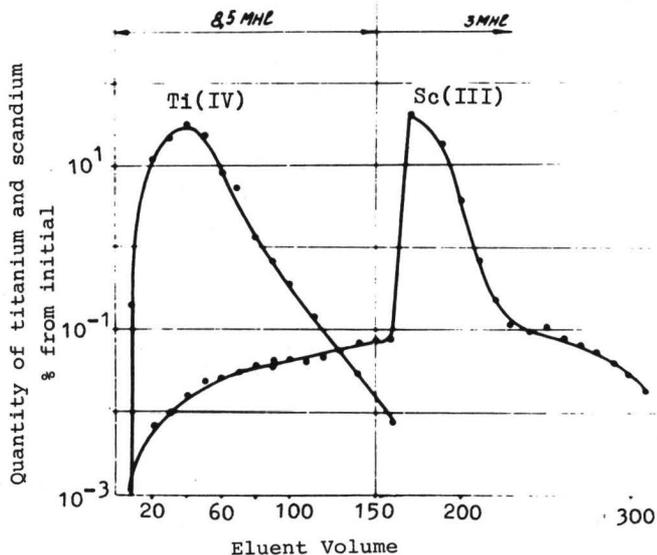
As was shown by our investigations the following dependence for hydrocarbons and their chloro derivatives is observed

$$K_{\text{ex}} = a + b/\epsilon, \quad (2)$$

where ϵ - is dielectric of diluent of crown ether. The use of chloroform as a crown - ether doluent results in rather a big value of constant of 15-crown-5 sodium picrate extraction ($\lg K_{\text{ex}} \approx 4,00$). Greater extraction constant values are also observed for triphenyl methane dyes for bromthymol blue in particular ($\lg K_{\text{ex}} \approx 4,9$). Values of sodium distribution coefficients may be doubled provided that lithium hydroxide solution extraction is applied. Lithium is very weakly extracted by 15-crown-5.

Selective extraction of aluminium (III) from weakly acidic solutions by trioctylamine of oxalic acid is caused by formation of its stable oxalate complexes. Only iron (III) is also well extracted by this extractant. The magnesium target being dissolved in 2,5 M sulphuric acid (excess in relation to magnesium 1,02-1,03) and pH of 1,0+1,5 being established by ammonia. Aluminium-26 is extracted by 0,02-0,03 M solution (TOAH) $2\text{C}_2\text{O}_4$ in benzene or toluene with 10% of chloroform, the organic phase is washed by 0,02 M solution of oxalic acid. Back extraction of aluminium-26 is made by 6 M HCl. Sodium-22 is then extracted by chloroform solution where the concentration of 15-crown-5 is 0,2 M and that of picric acid is 0,1 M; the organic phase being washed, it is then extracted back by water. The isotope yield is over 95%, the purification coefficient from radioactive and non-radioactive impurities being 10^5-10^6 .

Let us now consider the production of vanadium-48,49 and scandium-46 from cyclotron irradiated titanium targets by means of extraction and tributylphosphate solid extraction chromatography. Values of scandium (III) and titanium (IV) distribution coefficients were determined at their different concentrations from solutions of hydrochloric acid of different concentration on solid tributylphosphate reagents in static and dynamic conditions. At any concentration of hydrochloric acid scandium (III) values of distribution coefficients are much larger than those of titanium. On the basis of these and model experiments the following techniques for producing vanadium-48,49 and scandium-46 were proposed. Titanium target is dissolved in hydrochloric acid with chlorine and titanium (IV) is obtained in the solution. On addition of potassium chlorate vanadium-48,49 is extracted by dipropylketone and extracted back by diluted hydrochloric acid, the aqueous solution with hydrochloric acid concentration of about 8,5 M being passed through the column 1,2 cm in diameter and 20 cm long filled with solid tribu-



Elution of scandium-46 and titanium (IV) from solid tributylphosphate reagents

tylphosphate at the rate of 0,5-0,6 ml/min. Titanium (IV) is totally washed by 150-200 ml 8,5 M hydrochloric acid and then scandium-46 is eluted in 30-40 ml 3 M hydrochloric acid. The isotope yield is over 95% radiochemical isotope purity being over 99% the amount of inactive impurities of many elements being less than 0,05-0,5 mg/ml solution. Typical elution curves are given in Fig.

Let us consider the techniques for isolating technetium-95 m and technetium-96 and molybdenum-93 from α -particle irradiated niobium targets. Irradiated niobium is dissolved in a teflon vessel with hydroxide melt at 240-280°C. The melt is dissolved in water with hydrogen peroxide, then technetium isotopes are extracted by $5 \cdot 10^{-4}$ M solution of nitrate (chloride, bromide) of ethyltrioctylammonium in toluene. Technetium back extraction is carried on by 1 M ammonium carbonate solution after 70% dilution of the organic phase by amyl or hexyl alcohol. And then on reducing cesium hydroxide concentration molybdenum-93 is also extracted by QAB salt.

Thallium isotopes, thallium-201,202 are produced by proton and deuteron irradiation of mercury. Using isotopeenriched mercury it is possible to produce thallium-201 containing negligible amounts of other thallium isotopes. Irradiated mercury is dissolved in nitric acid. On

addition of hydrochloric acid and sodium chloride thallium-201 and gold isotopes are extracted by an ether (chlorex, di-n-butyl ether, etc.). The organic phase being washed by chlorine saturated hydrochloric acid thallium-201 and gold isotopes are extracted back by a weak solution of sodium hydroxide. Gold isotopes are quantitatively removed from a weakly acidic solution by metallic copper cementation. We have developed the similar technique to produce thallium-201 from thallium via lead-201. The irradiated thallium target is dissolved in 5 M sulphuric acid and on addition of sodium chloride the target material - thallium is quantitatively removed by multiple extraction by chlorex or another ether. Thallium-201 after it's accumulation from lead-201 is extracted by the same ether and extracted back by water or a weak alkali solution. Thallium-201 yield over 90% may be expected.

In conclusion, the techniques for producing silver-105 from α -particles irradiated rhodium targets may be given.

Cyclotron irradiated rhodium is melted with tin in a graphite crucible. The cooled melt is treated by hydrochloric acid to result in total dissolution of tin, and then amorphous rhodium is dissolved in sulphuric acid, silver-105 is extracted from 2-3N, H_2SO_4 by 0,05% dithizone solution in carbon tetrachloride, 91-94% of silver-105 being extracted at one extraction with rhodium separation coefficient $(3-4) \cdot 10^4$. Silver-105 yield is no less than 85% with isotope purity 95% (5% of silver-106 impurity).

We also developed extraction techniques for isolating the radio-nuclides of tungsten- 181, tungsten-178, osmium-185, rhodium-102 and others.

GROSS AND RADIATION YIELDS OF PHENOL DERIVATIVES IN NITROBENZENE SYSTEMS WITH AQUEOUS PHASE AND ITS USE FOR EXTRACTION OF NIOBIUM

10-13

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Radiolysis of nitrobenzene is of interest because nitrobenzene is used as an extraction solvent for radiocesium recovery [1]. It was indicated that the radiolysis of extractants should be investigated in the presence of an aqueous phase [2,3], and the theory of the radiolysis in two-phase systems was elaborated by us [4,5]. As a consequence of the theory an a priori "two-phase additivity rule" for radiation yields in emulsions was formulated [5]. Its importance was demonstrated on the nitrobenzene-water systems. Partial radiation yields in the phases being different, the autoradiolysis in actual systems depends also on the phase ratio and specific activity of aqueous and organic phases and it cannot be predicted accurately from the data obtained from irradiation of separated or even statically contacted phases [4]. In the present work we investigated the formation of nitrophenols in irradiated emulsions of nitrobenzene, established partial and gross radiation yields of phenols and nitroaniline.

Table 1. Gross radiation yields of the products. The phase volume ratio is varied from 1:9 to 5:5

Product	T^G at aqueous phase		
	H ₂ O	1.5 M-H ₂ SO ₄	3M-HNO ₃
p-nitrophenol	0.25-0.53	0.36-0.45	0.05-0.14
m-nitrophenol	0.41-0.95	0.61-1.37	unmeasurable
p-nitrosophenol	-	unmeasurable	0.04-0.07
2,4-dinitrophenol	-	-	0.26-0.29
2,5-dinitrophenol	-	-	0.27-0.42
o-aminophenol	0.14-0.58	0.23-0.50	-
m-aminophenol	0.12-0.37	0.17-0.40	-
p-aminophenol	0.15-0.48	0.19-0.47	-
o-nitroaniline	-	-	0.27-0.47

Nitrobenzene phase was found to be several times more reactive than the aqueous one in respect of the phenols and aniline derivatives formation. The yields for organic phase (G_{II}) indicate that the latter one is a more reactive phase, i.e. the products are formed preferably

in nitrobenzene saturated by water. However, a contribution of the aqueous phase to the gross radiation yields is far from being negligible for all the products, except perhaps the aminophenols in pure water. In 3 M-HNO₃ solution about 30-50% of dinitrophenols and o-nitroaniline is produced in aqueous phase.

Finally, products of radiolysis of nitrobenzene-water systems were

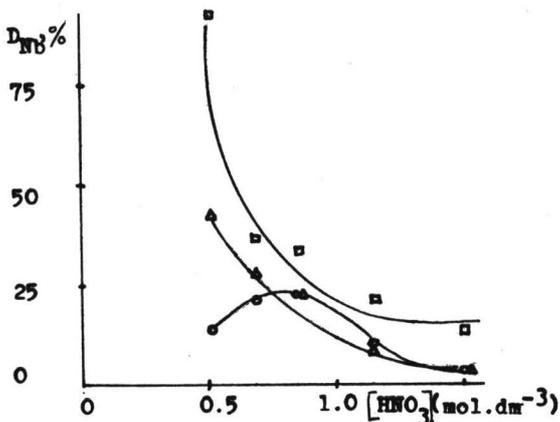
Table 2. Partial radiation yields of the products. G_I-aqueous phase, G_{II}-organic phase

Product	Aqueous phase		
	H ₂ O	1.5 M-H ₂ SO ₄	3M-HNO ₃
p-nitrophenol	G _I 0.16±0.02	0.33±0.02	0.04±0.01
	G _{II} 0.97±0.07	0.55±0.08	0.22±0.02
m-nitrophenol	G _I 0.39±0.05	0.40±0.01	unmeasurable
	G _{II} 1.63±0.15	2.15±0.33	unmeasurable
p-nitrosophenol	G _I -	unmeasurable	0.04±0.01
	G _{II} -	unmeasurable	0.09±0.02
2,4-dinitrophenol	G _I -	-	0.26±0.01
	G _{II} -	-	0.29±0.01
2,5-dinitrophenol	G _I -	-	0.25±0.02
	G _{II} -	-	0.55±0.03
o-nitroaniline	G _I -	-	0.23±0.01
	G _{II} -	-	0.63±0.01
o-aminophenol	G _I 0.02±0.008	0.16±0.003	-
	G _{II} 1.02±0.030	0.74±0.010	-
m-aminophenol	G _I 0.06±0.002	0.11±0.004	-
	G _{II} 0.60±0.010	0.61±0.010	-
p-aminophenol	G _I 0.07±0.004	0.12±0.004	-
	G _{II} 0.80±0.10	0.75±0.010	-

investigated as an extractant for separation of niobium. The best results were obtained with o-aminophenol, p-aminophenol and o-nitroaniline. In Fig. is D_{Nb} as a function of concentration of nitric acid for o-aminophenol (○), p-aminophenol (▲), and o-nitroaniline (◻). Aqueous phase was: 0.1 ml 0.9x10⁻⁴M ⁹⁵Zr in 6 M HNO₃ + 0.1 ml 1.7x10⁻² M Zr(NO₃)₄·5 H₂O in 6 M HNO₃ + z ml 1.5 M HNO₃ (z was varied from 0.86 ml to 4.2 ml). Total volume of aqueous phase was 5.0 ml. Organic phase was 5.0x10⁻³M phenol + 5.0x10⁻²M HDCC (dicarbonyl cobaltic acid).

D_{NB} as a function
of concentration of nitric acid

(○) o-aminophenol;
(△) p-aminophenol;
(□) o-nitroaniline



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The paper discusses possible modifications of the aqueous technology for reprocessing high burn-up (~100 GWday/t) and short cooled (3-6 months) nuclear fuel; presents the results of R&D work carried out at pilot plants. The major difficulty - the possible destruction of an extractant during processing solutions of the activity of the order 10^3 Ci/l - is obviated through the usage of short-residence time centrifugal extractors (CE). The studies into the extraction kinetics showed that the chemical reactions of TBP extraction of many elements is accomplished in the time of order tenth parts of a second [1]. This fact permitted us to expect rather a high extraction of valuable elements in a cascade of CE.

High efficiency CE's for the radiochemical processes (Fig.1) are being developed from the base designs [2] and can be serviced with manipulators. Feed solutions are fed through pipes 1 to a labyrinth mixer-blower 2 where they are agitated and forced into a mixing chamber 3. Emulsion is fed to rotor 4 where it is divided under the action of centrifugal forces. The divided liquids are directed into circular collectors of a fixed body 5, then they gravitate from the extractor. Rotor unit 4 with drive 8 is remotely replaced by a reserve one. The extractor can be also used for slow mass transfer processes [3]. The needed time of phase contact is ensured through an installation of mixing chambers 3 having different volumes [4]. The mass transfer effectiveness in CE using a 30% TBP in synthin-uranium- HNO_3 system is more than

6 95%. The effectiveness can be raised through
7
8
5
4
1
2
3
recirculation [3]. The disperse aqueous phase recirculation, e.g., during UO_2^{2+} extraction from a sulphuric acid solution by D2EHPH increases the mass transfer effectiveness from 75% to 94% at the time of a phase contact 7s. A severe problem is a possible formation of a second organic phase at a high Pu concentration that is caused by a limited solubility of TBP-Pu solvates in a diluent (normal paraffine hydrocarbons -NPH). A series of experiments were carried out to select extractants having an extraction ability at the level of TBP, but forming solvates with actinides(IV) compatible with a diluent. On the basis of work [5] a conclusion is drawn [6-9] that trialkyl phosphates (TAP) are advisable, if their hydrocarbon chain is optimized, i.e.,

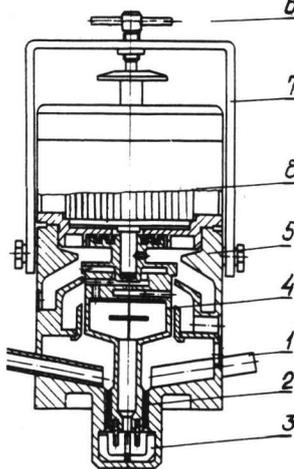


Fig. 1. Centrifugal extractor

elongated and the isostructure is used. The first member of the series - triisoamyl phosphate (TIAP, $n_c=15$) was found to give solvates with Pu(IV) that are compatible with a diluent, however, solvates with Th(IV) form a second organic phase. Diisobutylisooctyl phosphate (DIBIOP, $n_c=16$) turned out to be the first versatile extractant for actinides(IV); its solvates with both Pu(IV) and Th(IV) are compatible with NPH; solvates of actinides(IV) with triisohexyl phosphate (TIHP, $n_c=18$) do not give the second phase [6-9]. The above three extractants were tested in a cascade of CE along with TBP (a further increase of n_c seemed to be inadvisable due to difficulties involved in washing from long-chain destruction products). It should be noted that in the USA TIAP, TIHP and triisooctyl phosphate ($n_c=24$) were recommended. Successful checking of the latter in hot cells was reported [10], methods of the effective washing from destruction products were developed.

Now consider the results of the experiments.

Fuel used. The fuel (20% Pu, 80% U) of the BR-10 and BOR-60 of the burn up to 10% (~100 GWday/t) cooled for 3 months to 2 years was reprocessed.

Shearing of fuel before dissolution. The method of chopping can be used and in some experiments it was used, however, when handling fuel cooled for less than 1 year modification of some aggregates that would provide for high-speed chopping, or thermal methods with the help of which a fused structural material would be separated from fuel [11] are required. Being an alternative to mechanical processes these methods are applied to fuel held practically for any period of time. As the experiments performed in pilot facilities show, the fusion of stainless structural materials at 1450-1550°C in the inert atmosphere makes it possible to reach adequate process parameters; the capture of steel by fuel does not exceed 3%, plutonium losses with the separated steel are 0.01%, those with ceramic lining are 0.02%; the total yield of fuel components is 99.9%.

The combination of shearing with the oxidation permits removal from the fuel (before its dissolution) and localization of up to 99% tritium as well as a larger portion of Kr, Xe, ^{131}I , ^{129}I , Ru and other nuclides.

The dissolution was performed in 8-9 mole/l HNO_3 at $100 \pm 5^\circ\text{C}$ for 6 hours. The S:L ratio was chosen based on condition of receiving 250 g/l (U+Pu) in a final solution (prior to mixing with scrubbing water). Additions of F were required for the final dissolution of hardly soluble residues as dependent on their Pu content.

The clarification of solutions was performed in two stages: a coarse one (up to 30-100 mg/l content of dissolver residues) on a centrifuge, a fine one (up to 5 mg/l) using filtration through a metal powder.

The clarification centrifuge development [12] showed that the separation of fine dissolver residues from the feed solution (about 90% particulates < 3 μm dia) the separation factor of the order of 10^3 is

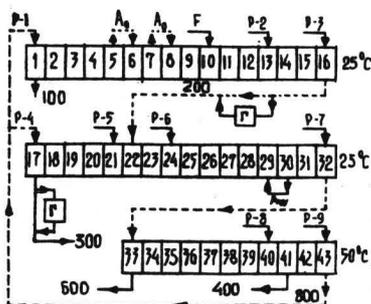


Fig. 2. The scheme of the process (the dotted line - an extractant). Γ - a thorough gamma-absorbtimeter; A - a thorough alpha-radiometer on organic (A_o) and aqueous (A_w) flows

adequate to clarify solutions up to 30-100 mg/l. After centrifugation the feed solution contained up to 100 mg/l residues. The filtration characteristics of the solution were determined using stainless steel powders of two fractions (grain dia 0.3-0.4mm and 0.4-0.6mm). At the layer height of 400mm and specific throughput $6 \text{ m}^3/\text{m}^2$ the filtration rate was 1.3 and 2.2 m/h (P=300mm water column), respectively: based on these data the solution was filtered through a three layer powder filter 32mm dia, with the total layer height being 600mm. The essentially full clarification was reached under the load $1-5 \text{ m}^3/\text{m}^2$ (the capacity of 1.2 l/h).

Extraction process (the first cycle) was checked in the 43 CE's cascade. The

Table 1. Composition of Feed Flows

Feed to stage N	Index	Flow	Chemical composition	Flow rate l/h
10	F	Feed aqueous	4.3 m/l HNO_3 , 165 g/l U, 23 g/l Pu	0.97
1	P-1	Fresh (recycling) extractants	30-40% TAP mixed with normal paraffins ($\text{C}_{10}-\text{C}_{16}$) (Pu < 0.1 mg/l, U < 1.5 mg/l)	2.0
13	P-2	Strong acid scrubbing	10 m/l HNO_3 (10 g/l NH_4VO_3)	0.12
16	P-3	Weak acid scrubbing	0.5 m/l HNO_3	0.27
17	P-4	Fresh extractant	Composition see P-1	0.80
21	P-5	Acidification of U scrubbing zone	10 m/l HNO_3 , 0.05 m/l $\text{N}_2\text{H}_5\text{NO}_3$	
24	P-6	Main reductant	0.6 m/l HNO_3 , 75 g/l U, including 70 g/l U (IV), 0.2 m/l $\text{N}_2\text{H}_5\text{NO}_3$	0.26
32	P-7	Auxilliary reductant	0.15 m/l HNO_3 , 11 g/l U, including 10 g/l U (IV), 0.18 m/l $\text{N}_2\text{H}_5\text{NO}_3$	0.46
40	P-8	Uranium stripping agent	0.015±0.005 m/l HNO_3	3.2
43	P-9	Washing	5% Na_2CO_3	0.40

Outcoming Flows

Index	Flow	U	Pu	HNO_3 m/l	Others
100	Aqueous-tail solution	2.4 mg/l	0.5±0.4 mg/l	4.3±0.2	-
200	U, Pu - extract	68 g/l	12 g/l	-	-
300	Pu - product (strip)	0.4 g/l	35 g/l	7.1±0.3	0.07 m/l
400	Soda solution from washing	5 mg/l	1 mg/l	-	30 mg/l ΣPO_4
600	U - product (strip)	54 g/l	0.06 mg/l	-	-
800	Recycling extractant	1.5 mg/l	0.09 mg/l	-	52 mg/l ΣPO_4

scheme (Fig.2) incorporated the co-extraction of U and Pu (stages 1 - 10), two-zonal scrubbing-10 mole/l HNO_3 (11-13) and 0.5 mole/l HNO_3 (14) separation of U/Pu using U(IV) as a reducing agent (17-32), stripping of U (33-40) and soda washing of an extractant (41-43). The composition and the flow rate are given in table 1; up to 10 g/l of ammonium vanadate were introduced into the strong-acid scrubbing flow to oxidize Np to Np(IV).

Contact time (residence time in a mixing section) was 2-3s at stages 1-16 and 21-32; 5-6s at stages 17-21 and 33-40; 10s at stages 41-43. The separation time was 20 ± 5 s.

The results of the experiments performed using TBP, TIAP and TIHP are listed in table 2. The data of the DIBIOP extraction differed insignificantly from the presented ones.

Table 2. Characteristics of I cycle performed in CE and mixer-settlers using spent FBR fuel, TBP, TIAP and TIHP

Characteristics	Experiments in mixer-settlers	Experiments in CE			
		30% TBP	30% TBP	36% TIAP	40% TIHP
Extractant					
Losses with aqueous and soda solutions, %	U	0,052	0,007	0,008	0,006
	Pu	0,0056	0,004	0,004	0,004
	Np	<1,9	<4,6	<5	<4,6
Decontamination factor of U from Pu (DF U/Pu)	$6 \cdot 10^5$	up to $1,5 \cdot 10^5$			
DF Pu/U	up to 15	40 - 660			
DF U/ γ	$2,5 \cdot 10^5$	$1,2-1,5 \cdot 10^5$	$1,5 \cdot 10^5$	$1,6 \cdot 10^5$	
DF Pu/ γ	$1,3 \cdot 10^4$	$1,3 - 4,0 \cdot 10^4$			
DF U/Np	>100	>11	>12	>12	
Consumption of U(IV) per stripping, kg/kg	1,4	1,0	1,0	1,0	
Saturation of extractant in I unit, g/l of (U+Pu)	83	82 ± 2	83	82	
Accumulation of acid alkyl-phosphates in extractant (prior to washing), mg PO_4 /l	≤ 22	<10	<10	<11	
Content of these products in recycling extractant after washing, mg PO_4 /l	4 - 8	5,1	5,0	6,0	
U content of recycling extractant, mg/l	1,6	1,5	1,5	1,4	
Frequency of phase exchange in I cycle	≥ 12	70-26-87 for I-II-III units			

The direct extraction from the feed aqueous solution of the 300 - 900 Ci/l activity was for U and Pu - 99.99%, Np - up to 98% (goes to the plutonium product solution). In the CE experiments the decontamination factors from γ, β -emitting fission products - were: for U-REE $> 7.7 \cdot 10^6$; Ru, Rh - $3.1 \cdot 10^3$; Cs $> 5.1 \cdot 10^6$; Sb $> 6.1 \cdot 10^5$; Zr, Nb - $3.0 \cdot 10^4$. For

$\text{Pu-REE} > 2 \times 10^6$; $\text{Ru, Rh} - 1.8 \times 10^3$; $\text{Cs} > 7.8 \times 10^5$; $\text{Sb} > 9.3 \times 10^4$; $\text{Zr, Nb} - 4.5 \times 10^2$. In the experiment described the number of phase exchange was 60-100 (in the I unit), 20-40 (in the II unit) and 80-110 (in the III unit). See fig.3 for the concentration profile in unit I under one of the conditions.

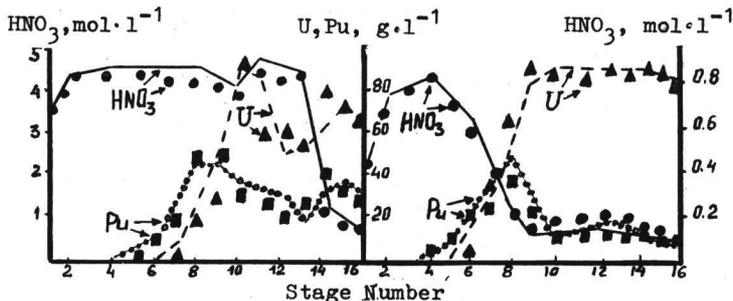


Fig.3. Distribution of U, Pu, HNO_3 over the stages of the first unit (the regime with 15% Pu (VI): $X_{\text{HNO}_3}^{\text{F}} = 4$ mole/l, $X_{\text{HNO}_3}(\text{P2}) = (6$ mole/l), $X_{\text{U}} = 125$ g/l, $X_{\text{Pu}} = 13$ g/l). The dots - the experiment, the lines - the calculation by the model [17] with the refining in equation 21 the ionic strength $J = X_{\text{HNO}_3} + X_{\text{Pu}}$ without taking account of uranium

On the Reductive stripping. A decrease of the consumption of U(IV) from 1.4 to 1.0 kg/kg and a decrease of the phase contact time by a factor of several tens as compared to the experiments in the mixer-settler did not interfere with the high-quality purification of U from Pu and actinides from fission products.

On the distribution of Np. In the absence of an oxidation agent the short contact time in the extraction zone did not allow an adequate co-extraction of Np with U and Pu, due to this fact more than 50% Np remained in the aqueous-tail flow. The introduction of a weak oxidation agent - V(V) - resulted in essentially a quantitative extraction of Np with U and Pu in unit I. The oxidation process is so fast that the oxidation agent was worked for a short period of contact on 13 stages (only 30 s in the mixing chambers). Further on Np left together with Pu product. Comparisons between the reprocessing of fast breeder reactor mixed fuel in pilot mixer-settler and centrifugal extractors (table 2) show that the latter units solve not worse than mixer-settler the problems of quantitative extraction, decontamination from fission products and mutual separation of actinides using the same number of stages - and all this is done at 2-3 s phase contact in the CE mixing chamber. As compared to the results received in mixer-settlers the less radiation-chemical destruction of an extractant (when going from pilot to full-scale extractors this difference increases several

times), the practicability of quantitative extraction of Np, decrease of U(IV) have been confirmed. The version of the electro-chemical separation of U/Pu was also successfully checked in the CE cascade. The 2-nd extraction cycle was also checked (the additional uranium DF 10^2 was reached). The use of TIAP and TIHP practically did not change the performance of the flow sheet, the use of DIBOP slightly improved it. The limits for Pu broke away.

Finally, experiments were performed on high extraction of trans-plutonium elements and lanthanides from the first cycle raffinates (directly and after concentration by evaporation) using bidentate organophosphorus compounds (for their properties see the stand paper by Rozen A.M. et al at this conference as well as [13,14]). Using tetratolymethylene diphosphine (0.5 mole/l in trichlorobenzene) practically full extraction with 5-fold concentration was reached in a single stage, the extraction with ditolylbutyl-carbamoylphosphine oxide (tol_2/bu_2) required 5-6 stages.

Preparation of mixed fuel. Mono- and polydisperse fractions of oxide microspheres prepared by a sol-gel process, are suitable for the re-fabrication of fuel in the form of granules and pellets. The absence of a dust permits the activity to be localized within the working equipment (see [15,16]). Among the versions of sol-gel processes the method of internal gel-formation seems promising. True or colloidal mixed high concentration U and Pu solutions are subjected to spheroidization in the organic phase. The solid phase precipitates as microspheres as a result of the pre-introduction of donors of ammonia - hexamethylenetetramine and urea- into the aqueous phase, containing metals. With a temperature increase both inorganic and organic constituents polymerize quickly in a drop of the working solution. An organo-mineral phase forms which as a result of washing with an aqueous solution of ammonia and treatment transforms to a stoichiometric compound (oxide).

The main difficulty was in the engineering for the process. The fact that drops of an aqueous working solution formed above the surface of a heated disperse phase resulted in the formation of very fine drops-satellites that interfered with the hydrodynamic and gravitational conditions of the operation of a gelation column. The unloading of the microspheres, their washing with ammonium, transportation to the subsequent technological operations were performed batchwise, which did not provide for the remote control of the process as a whole. The quality of the mixed U-Pu oxide microspheres was not stable which did not permit the guarantee of the quality of the product fuel. The investigations under way are primarily aimed at the preparation of monodisperse fractions of microspheres through a new

organization of a drop formation process, the continuous unloading of microspheres from the gelation column, washing and transportation to the subsequent thermal operations.

Conclusion. The experiments carried out in the pilot facilities show that the pyrochemical removal of clads, the use of short-residence time centrifugal extractors and extractants with the optimized hydrocarbon chain permit with confidence the employment of the aqueous reprocessing technology in the shortened version of the external fuel cycle.

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The effect of Pu accumulations in the Purex first cycle high active extraction and scrub extractors HA and HS was first described in detail by Rozen [1]. A variety of process conditions may cause such accumulations: reduced solvent flow, reduced TBP concentration, increased high active feed concentrations or flow, low acidity etc. The Pu accumulations in a counter-current extractor occur by loading the solvent close to its theoretical limit. An insufficient solvent supply creates a "bottleneck" for organic Pu transport under usual flowsheet conditions and Pu is forced to the aqueous phase. Close to the raffinate loading is low and Pu is extracted again. This recycling allows Pu to accumulate. The smaller the solvent deficit, the slower the build-up of the Pu peak, but the larger its maximum concentration. A large solvent deficit causes a rapid propagation of the peak towards the aqueous raffinate outlet. The peak deflates rather rapidly when its tail reaches the raffinate. As a consequence the maximum peak concentrations increase with increasing extractor length.

Recently Schön et al. [2] observed peak concentrations of up to 40 g Pu/l (LWR feed composition, conventional flowsheet) in the miniature pulsed column facility MINKA (column length 350cm). Theoretical calculations using the computer code VISCO [3] predict possible transient peak concentrations for technical size columns in excess of 80 g Pu/l under the most unfavorable conditions. Even though the build-up time of several days will hardly pass unnoticed a potential criticality problem exists and requires additional design restrictions or at least highly reliable safety instrumentation.

Standard Purex flowsheets for the HA/HS extractors favor the possibility of Pu accumulations: U(VI) has the highest extractability and expels all other species from the solvent at high loadings. Extensive studies using VISCO in order to minimize Pu accumulations predicted a possibility to completely avoid this risk. The overall HA extractor temperature or at least the temperature at the location of the "bottleneck" has to follow:

$$T \geq \{(0.06676U - 0.3367P - 327.4H) \cdot \exp[0.00008179H \cdot (U+P)] \cdot H^{-0.9999}\} + 401 \quad (\text{equ.1})$$

T is in °C, U and P are the aqueous U and Pu feed concentrations resp. in g/l, H is the HNO₃ feed concentration (M/l). This minimum extractor temperature does not depend on TBP concentration. It reflects the temperature and concentration conditions for which the distribution coefficient of Pu(IV) becomes larger than the distribution coefficient of U(VI). If the condition in equ.1 is met, Pu(IV) forms the strongest TBP-complex of all species involved. It therefore expels U(VI) from the organic phase and Pu cannot be recycled any more within the extractor: Pu accumulations in the HA extractor are reliably avoided. There may be uranium accumulations instead but even for FBR feed composition they will amount to only a few g/l and will be of no practical significance.

Equ.1 reflects the fact that the distribution coefficient ratio D_{Pu}/D_U increases with increasing temperature, increasing acidity and increasing metal

concentration. The equality in equ.1 holds if $D_{Pu}/D_U=1$ defining the critical temperature T_c for Pu accumulation. No Pu accumulations can occur at $D_{Pu}/D_U \geq 1$ (or $T \geq T_c$). T_c will be the lower the larger the feed concentrations are. For composite extractors such as HA and HS the composite feed concentrations (e.g. HAF blended with HS-reflux) have to be inserted in equ.1.

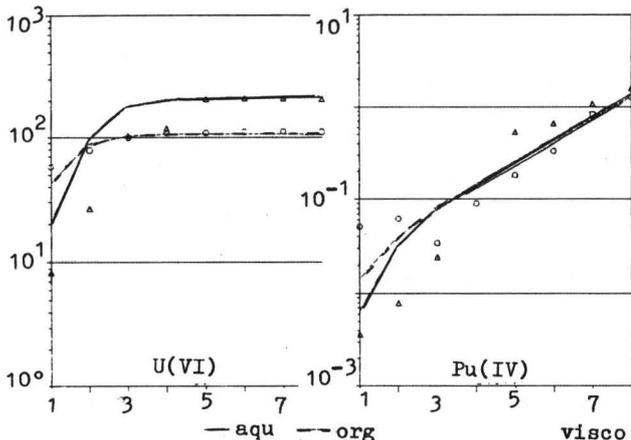


Fig.1

Fig.1 shows the U and Pu concentration profiles in g/l for a small lab scale 8-stage mixer settler operated at 50°C. HAX (30%TBP, 258ml/h) enters at stage 1, HAF (150ml/h, 211 gU/l, 2.35 gPu/l, 5.26M HNO₃) enters at stage 8. Theory and measurement are: aqueous = solid lines and triangles, organic = dashed lines and circles.

Fig.2 shows measured and calculated concentration profiles for an operating temperature of 18–20°C with all other conditions kept identical to fig.1. While the feed composition U/Pu is 90, raffinate U/Pu is 2300(!) in the 50°C experiment shown in fig.1, and 60 in the low temperature test of fig.2. A further test run at 20°C and 3M HNO₃ ($T_c=45^\circ\text{C}$) increased Pu to U/Pu=15 in the raffinate and showed the expected Pu accumulation of 7g/l in stage 4. The 18–20°C experiment shown in fig.2 was operated

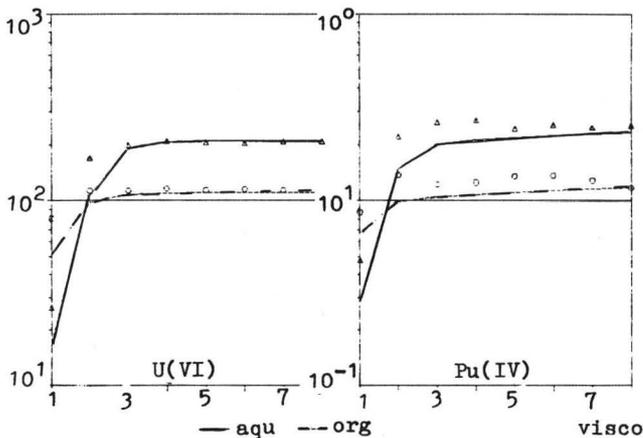


Fig.2

almost at $T_c=20.4^\circ\text{C}$. U and Pu show a very similar behavior and there is even a slight indication of a Pu peak. A further experiment in the 350cm A column of MINKA was run at a nominal 20°C using the feed composition of figs.1–2. But in this column the heat of extraction resulted in a temperature of 37°C at the location of the

"bottleneck" which is in favor of the new process: no Pu accumulation was observed and the raffinate ratio was $U/Pu \approx 130$.

These results demonstrate that not only Pu accumulations are reliably avoided by the new process but that in the case of a maloperation Pu is even depleted in the

raffinate stream (it is by no means necessary to have U losses as large as in the tests of figs.1-2 to avoid Pu peaks). This allows to exploit the advantages of an ultra high loading process reducing the risk of Pu losses. As demonstrated in the ORNL work [4] the position of the U extraction flank can be kept constant by automatic control using suitable in-line sensors (temperature, light absorption etc.). Instead of keeping the flank position close to the feed point [4] it can be moved close to the raffinate, dependent on how large U losses can be tolerated. The reward is a highly enhanced fission product decontamination.

Fig.3 shows measured and calculated U and Pu profiles for an 8-stage HA extractor (stages 1-8) and an 8-stage HS extractor (stages 9-16). HA is operated at 50°C. HAX (29%TBP, 327 ml/h) enters at stage 1, HAF (145 ml/h, 230 gU/l, 2.87 gPu/l, 120 mgNp/l, 1 gZr/l, 1 gNb/l, 320 mgRu/l, 5.05M HNO₃) at stage 8, HAS (65 ml/h, 3M HNO₃) at stage 16. No

Pu accumulation is observed in HA where the new process conditions apply (T_c=33°C). HS is operated at 25°C, while T_c for the HS extractor is 59°C and Pu accumulates indeed.

Fig.4 shows the measured concentration profiles of Zr and Nb. Ordinates are % of the feed concentration. Both species form weaker TBP complexes than U(VI) and therefore accumulate in the lower stages of HA where solvent loading decreases. The mechanism for this build-up is the same as for Pu(IV) in a conventional flowsheet as described above.

Excellent decontamination is achieved since the tails of the accumulations do not extend to the organic product. Ru does not even accumulate and is found 100% in the raffinate as was to be expected.

In the example of figs.3-5 Np(VI) and Np(V) are reduced in HS predominantly to

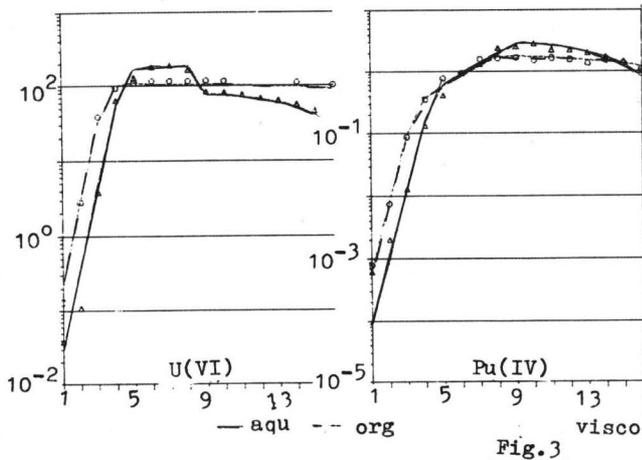


Fig.3

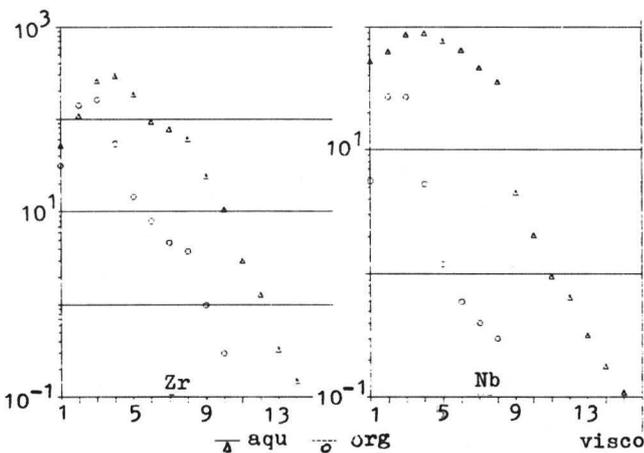


Fig.4

Np(IV) by operating the HS scrubber with electroreduction at a current density of about 6 mA/cm². Under these conditions Pu(IV) and U(VI) are also reduced in small quantities but they are rapidly reoxidized in the HA extractor as can be seen from the small Pu losses to the aqueous raffinate. Fig.5 shows the measured concentration profiles along with Np calculated as Np(IV) (left plot) and Np(VI) (right plot); Np redox reactions are not yet implemented in VISCO. From the Np slope in the HS part (stages 9-16) of fig.5 it is obvious that little Np(VI) is present in the scrubber,

whereas in HA Np is predominantly hexavalent. Np(IV) entering HA reoxidizes, the tailing in stages 1 and 2 is attributed to the almost inextractable Np(V) leaving with the raffinate. The Np accumulation is caused mostly by Np(VI) but due to electroreduction a Np(VI) tail cannot extend into the organic product: Np is quantitatively removed from the product.

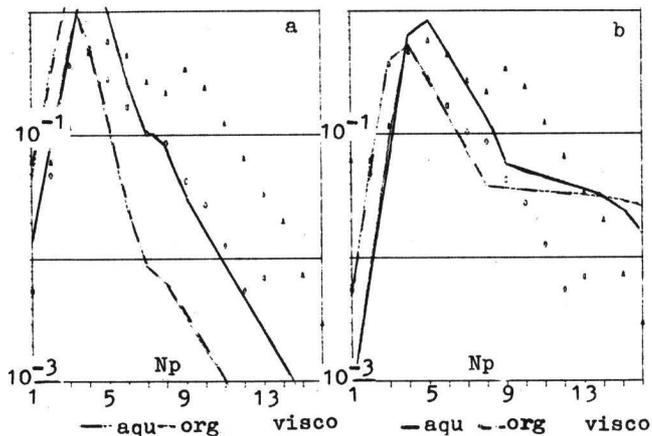


Fig. 5

Tc behavior was also studied in the new process. High temperature and high acidity are opposed to a good separation in the presence of Zr [5] and Tc was almost completely found in the product. Electroreduction did not reduce major amounts of Tc(VII) in the scrubber. Without Zr about 80% Tc was removed. Further experiments to reduce the Tc extraction factor at a lower organic to aqueous flow ratio are in preparation.

Increased solvent degradation was expected for the new process. The measured concentrations of HDBP were 20 to 30 mg/l and seem to be only slightly increased as compared to the conventional process.

The new process will be run with high burn-up/short cooling time FBR fuel in 1988. By the presented results we are encouraged to continue our efforts to design a one cycle Purex process [6].

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TRIBUTYLPHOSPHATE-N.DODECANE AND NITRATE SYSTEM: EXPERIMENTS AND ITS
ANALYSIS BY MATHEMATICAL MODEL

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INTRODUCTION

In the PUREX process of the spent fuel reprocessing, the actinide elements and the fission products distribute between the organic and the aqueous phases depending on the concentrations of various components involved in the system. Therefore it is not surprising to have been pointed out that some elements e.g., plutonium(1-5), zirconium(6), are entangled to the extraction-reextraction cycle in the extraction scrub stages by the action of the other components which change their distribution ratios, and result in accumulation in the process or deterioration of DF. Thus a process design of PUREX inevitably needs an assessment of such phenomena for criticality safety and high DF. One of the novel methods to analyse the recycle phenomena is a simulation study of the process by computer code. A mathematical model for PUREX process EXTRA.M has been developed to analyse transient behavior of uranium, plutonium and nitric acid in the mixer-settlers.

In order to clarify parameters which control accumulation of Pu(IV) or U(IV) in the 30 vol.% TBP-n.dodecane-HNO₃-U(VI) system, a parameter survey was carried out using mathematical models DIST and EXTRA.M. Then the computed results of U(IV) buildup were compared with the results of laboratory experiments by miniature mixer settlers being put special emphasis on the modification of the EXTRA.M to improve simulation.

RESULTS AND DISCUSSION

Effects of Parameters on Recycling of U(IV) or Pu(IV)

Specifically, plutonium builds up in a co-decontamination process of PUREX due to high loading of U(VI) of the organic solvent and subsequent split of Pu(IV) to the aqueous phase. Thus the negative salting-out effect of U(VI) on distribution of Pu(IV) plays an essential role for recycle of Pu(IV).

Our distribution model DIST(7) expresses distribution ratios of metal M as

$$D_M = P1 C_N^{P2} / \{ 1 + P3 C_N^{P4} + P5 C_N^{P6} C_{U6} + \sum_T f_1 \} \quad (1)$$

where C_N and C_{U6} denote the aqueous concentrations of total nitrate ions and uranyl ion, respectively. The $P1$, $P2$, ... are parameters of which values are determined by the best fit procedures in the DIST based on the experimental data, and $\sum_T f_1$ signifies the degree of (self-)salting out effect of the other components than U(VI).

Buildup of Pu(IV) or U(IV) will occur provided that a highest D value and D value at the highest organic concentration of U(VI) (\bar{C}_{U6}) of the extraction process are respectively higher than and lower than 1. Magnitude of D depends mainly on parameter $P1$, and a dependency of D value on \bar{C}_{U6} is related to parameters $P5$ and $P6$ of the eq.(1) expressing the salting out effect of U(VI). As an example of DIST calculation, Fig.1 a), b) show dependencies of D_{U4} and D_{Pu4} on \bar{C}_{U6} as a function of $P5$ value for 30

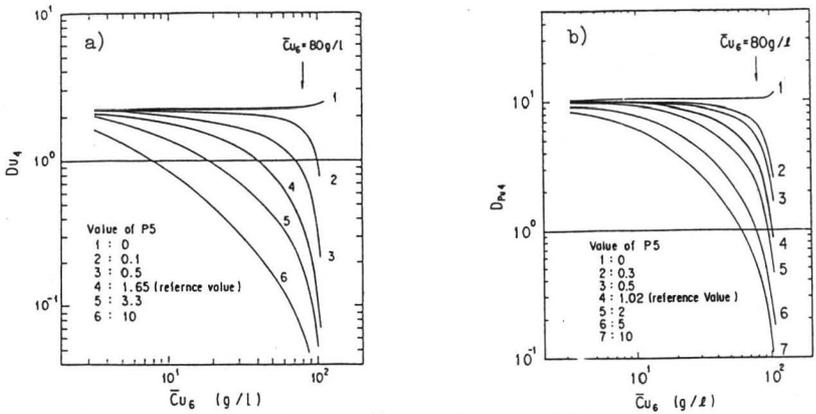


Fig.1. Dependencies of D_{U4} and D_{Pu4} on \bar{C}_{U6} as a function of P5 value in the extraction system of 30 vol.% TBP-n.paraffin-3M HNO₃. a: U(IV), b: Pu(IV)

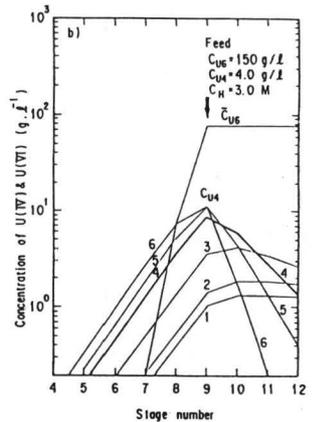
vol.%TBP-n.paraffin-3M HNO₃ system. The reference values adopted in the EXTRA.M are listed in Table. From curves 4 of Fig.1 a),b), it is understood that the highest \bar{C}_{U6} necessary for U(IV) or Pu(IV) buildup in the process is larger than 40 g/l or 102 g/l, respectively. And in case of an assumed process of which highest \bar{C}_{U6} value is 80 g/l, accumulation will occur with P5 value larger than 0.5 (curves 3 to 6) for U(IV) and 5 (curves 6 and 7) for Pu(IV), where D is lower than 1. Figure 2 shows \bar{C}_{U6} profile of the assumed process and variation of C_{U4} profile with P5 value. It is clearly shown that only curves 3 to 6 have shape of accumulation mode.

Parameter P1 determines not only magnitude of D_M but also slope of a curve of C_M profile appeared in front of the high \bar{C}_{U6} zone. Thus C_{Pu4} profile (P1=22.9) is more sharpened in shape than that of C_{U4} (P1=4.06). For the accumulation of Pu(IV), a highest value of \bar{C}_{U6} must reach near saturation of 30% TBP solvent. The \bar{C}_{U6} profile under that condition of the process is usually unstable, because the amount of U(VI) input by the feed flow does not balance to that flown out with the organic solvent and a high \bar{C}_{U6} zone with a \bar{C}_{Pu4} peak in the front moves between the scrub section and the organic inlet stage during operation. Since D_{U6} defines \bar{C}_{U6} , particularly at the organic outlet stage, it determines the mass balance of U(VI) of the process and consequently width of the high \bar{C}_{U6} zone.

Reference parameter values obtained by DIST and used for EXTRA.M computation

	Reference parameter value					
	P1	P2	P3	P4	P5	P6
D_{Pu4}	22.9	2.90	5.38	1.85	1.02	2.28
D_{U4}	4.06	2.68	2.14	2.12	1.65	2.35

Fig.2. C_{U4} and \bar{C}_{U6} profiles of the assumed extraction process showing variation of C_{U4} profile with P5 value



Comparison of Experimental Results and EXTRA.M Calculation for U(IV)-Buildup

Counter-current extraction of U(IV) and U(VI) was carried out with mini-mixer settlers. Reference flowsheet is shown in Fig.3. Buildup of U(IV) would not occur if \bar{C}_{U6} of the feed is lower than 75 g/l, because \bar{C}_{U6} will not exceed 40 g/l where D_{U4} is approx. 1 as seen from curve 4 in Fig.1 a). During the course of the extraction based on the reference flowsheet, the accumulation of U(IV) was observed in front of the high \bar{C}_{U6} zone, peaks of \bar{C}_{U4} and C_{U4} appeared at 8th and 9th stages, respectively. Time dependency of both \bar{C}_{U4} and C_{U4} profiles in the extractor agreed very well with those calculated during whole period of operation.

To examine reliability of parameters of D_{U6} used for EXTRA.M, the flowsheet conditions changed after concentrations of the components in the mixer settlers having reached steady state so as to observe growth of the high \bar{C}_{U6} zone with time, which is important in case of Pu(IV) buildup. Conditions changed are

- i) 30% increase of feed flow,
- ii) 30% decrease of solvent flow,
- iii) decrease of scrub acid from 3M to 0.5M.

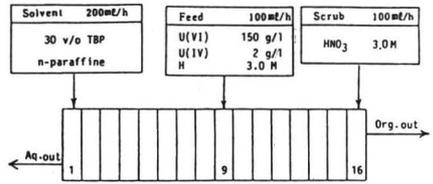


Fig.3. Reference flow sheet for experiments of U(IV) accumulation

Figure 4 shows an example of the results of experiments (points) and that of EXTRA.M (lines). After being decreased solvent flow rate, the high \bar{C}_{U6} zone expanded toward solvent inlet stage with time as seen Fig.4 a) and U(IV) accumulated at the front top as seen in Fig.4 b). Measurement of temperature along stages, Fig.5 a), demonstrated that a maximum temperature rise occurred at the stage where an exhaust U(VI)-extraction took place and consequently the highest C_{U4} appeared (Fig.5 b)). Because calculated shapes of both \bar{C}_{U4} and C_{U4} profiles agreed very well with the experiments, parameters of D_{U4} were considered to be almost satisfactorily reliable. However, behavior of the expanding high \bar{C}_{U6} zone did not always agree well with prescribed by EXTRA.M.

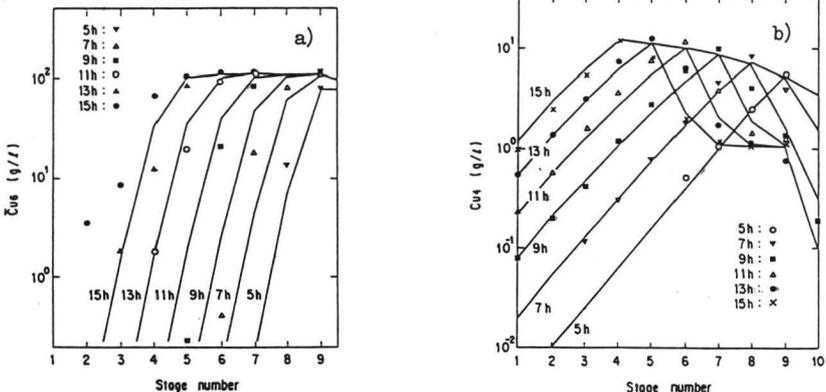


Fig.4. Change of \bar{C}_{U6} and C_{U4} profiles with time by a 30% decrease of solvent flow rate from the reference flowsheet. a: U(VI), b: U(IV)

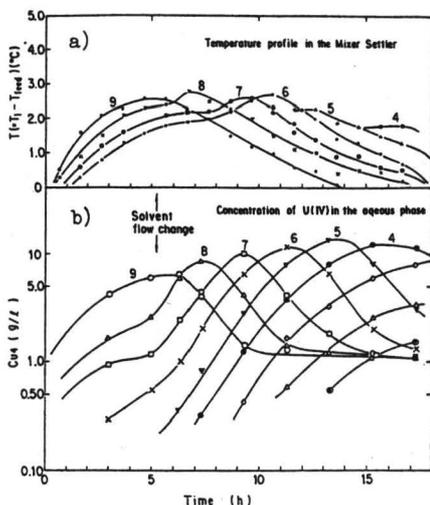


Fig.5 Change of temperature profile during extraction showing the highest temperature appearing at the stage of a highest C_{U4} . Numerals on the figure ; stage number

As being discussed above, behavior of the high \bar{C}_{U6} zone is determined by the mass balance of U(VI) of the process. Assuming that the feed composition and its flow rate are constant, the mass balance depends mainly on the \bar{C}_{U6} value and over-flow rate of the organic product. Measurement of \bar{C}_{U6} value at the 16th stage during the run showed some differences from those calculated and fluctuations to some extent. Since the organic overflow rate varies with the operation factors, i.e., flow rate of the feed solvent, interfacial level of the settlers etc., a key parameter for the U(IV) buildup during very stable operation might be D_{U6} , especially in the system of high \bar{C}_{U6} . Therefore, parameter values of D_{U6} equation were reassessed by DIST solely with the experimental data of high \bar{C}_{U6} systems. The EXTRA.M computation with the revised parameter values improved the simu-

lation of the behaviors of the high \bar{C}_{U6} zone in the extraction.

It must be pointed out that growth of the third phase of U(IV) during the extraction run is important for the analysis of abnormal situation. Upon forming the third phase, it appeared initially at the settler where the highest \bar{C}_{U4} was observed, but split to several stages with time and prediction of the fate of U(IV), i.e., concentration profile, a maximum concentration to be reached, and rate of growth of the peak, by the present model became impracticable, because the EXTRA.M includes no information about chemical characteristics of the third phase of U(IV) and Pu(IV). One of the mostly needed subjects for the assessment of Pu buildup in the PUREX process from a view point of criticality safety is to establish a precise model to simulate the behavior of the third phase of tetravalent actinide elements.

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Introduction. Np-237 is formed from reactions of neutrons with uranium during irradiation of nuclear fuel and as the daughter product, by α -decay, of Am-241. During PUREX reprocessing, neptunium will be distributed throughout the waste and product streams of the process. For the development of waste management strategies, it has become essential to be able to predict the pattern of neptunium distribution in a given reprocessing flowsheet so that possible re-routing can be considered.

Neptunium Chemistry and Behaviour. In nitric acid solutions, neptunium can occur simultaneously in 3 stable oxidation states: Np(IV), Np(V) and Np(VI). These inter-convertible oxidation states, exhibit different extraction behaviour into the reprocessing solvent (TBP-diluent) resulting in the dispersion of neptunium throughout the process. The route taken by neptunium in reprocessing is therefore not simple and will depend upon the precise conditions of the process. Four key aspects of the solvent extraction process need to be examined:

(i) the equilibrium distribution of neptunium oxidation states resulting from dissolution of the fuel and chemical conditioning.

The dissolution of spent nuclear fuel in nitric acid and under reflux conditions, provides an oxidising medium that will result in the higher oxidation states, Np(V) and Np(VI) as the predominant neptunium species. Chemical conditioning with nitrite, used substantially to convert all plutonium to Pu(IV), will provide conditions for the reduction of Np(VI) to Np(V). The relative proportions of Np(V) and Np(VI) in the feed are generally dominated by the nitric-nitrous acid redox equilibria:



The equilibrium constant, K , is given by:

$$K = \frac{[\text{Np(VI)}]}{[\text{Np(V)}]} \left(\frac{[\text{HNO}_2]}{[\text{H}^+]^3 [\text{NO}_3^-]} \right)^2, \quad (2)$$

where K increases from $3.2 \times 10^{-4} \text{ M}^{-1.5}$ in 1 M acid to $9.3 \times 10^{-4} \text{ M}^{-1}$ in 4 M acid at 25°C (1);

(ii) the distribution of neptunium oxidation states between the organic phase and reprocessing acids.

Under reprocessing conditions, Np(V) remains in the aqueous phase while Np(IV) and Np(VI) are extracted into TBP-n alkane. Distribution measurements between nitric acid and differing compositions of TBP-diluent have been reported (2); Figure 1 illustrates typical data points.

In the UK, the use of sulphuric acid to strip Pu(IV) from the solvent has been studied for fast reactor fuel (PFR) reprocessing. The presence of sulphate anions will also decrease the distribution coefficients of neptunium (3,4); illustrated in Figure 2;

(iii) the oxidation of Np(V) by nitrous acid in the extraction stages of the process.

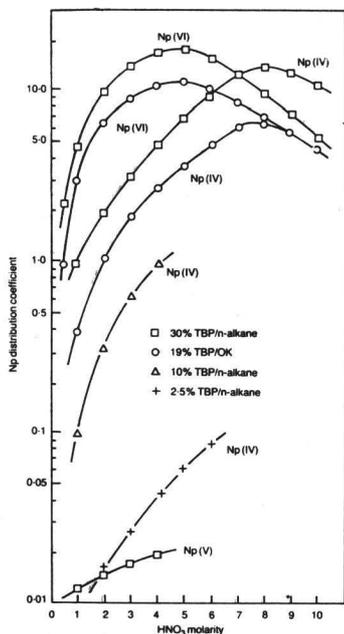


Fig. 1. Distribution of Np (IV), Np (V) and Np (VI) between nitric acid and TBP/n-alkane solutions of varying composition ($T = 20-30^{\circ}\text{C}$)

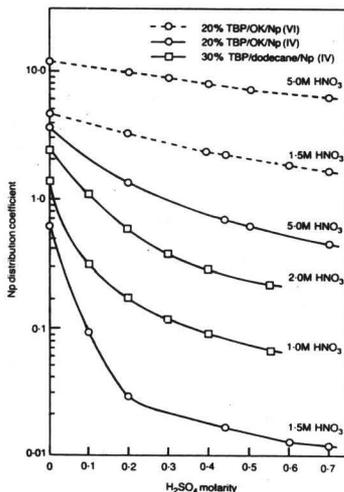


Fig. 2. Distribution of Np (IV) and Np (VI) between 20% and 30% TBP/n-alkane and mixed nitric-sulphuric acid solutions ($T = 21^{\circ}\text{C}$)

During the extraction stages of reprocessing, Np(V) will tend to be continually oxidised to Np(VI) and extracted as it moves towards the aqueous raffinate end of the contactor in an attempt to re-establish equilibrium (equation 1).

The rate of Np(V) oxidation has been measured by Moulin (5). He found:

$$\frac{-d [\text{Np(V)}]}{dt} = 1.8 \times 10^{-3} [\text{H}^+]^{1.3} [\text{NO}_3^-]^2 [\text{Np(V)}] \left(\frac{1 + [\text{Np(V)}]^{-1}}{[\text{HNO}_2]} \right) \text{M} \cdot \text{min}^{-1} \quad (3)$$

at 25°C , $E = 62.79 \text{ KJmol}^{-1}$.

Since the extent of oxidation is governed by the aqueous phase residence time in the extract contactor, the proportion of Np(VI) derived by oxidation of Np(V) can be deduced;

(iv) the effect on neptunium of U-Pu partitioning reagents.

Reagents to reduce Pu(IV) to inextractable Pu(III) are tetravalent uranium ions (usually stabilised by hydrazine) hydroxylamine and ferrous ions. Np(VI) is rapidly reduced to Np(V) by all three reagents. Further reduction to Np(IV) by U(IV) and ferrous ions is slower and by hydroxylamine is negligible. In reductive partitioning, the reduced plutonium may also participate in the reduction of neptunium.

Comparison of Predicted Neptunium Behaviour with Plant Measurement. Measurements of neptunium in fast reactor fuel reprocessing have been reported in the UK for fuel from the Dounreay PFR reactor (6), and in France for fuel from the PHENIX reactor (7).

At Dounreay the fuel is reprocessed using mixer-settler contactors. The flowsheet

uses sulphate and small concentrations of ferrous ions in most of the stripping steps. The equilibrium ratio of Np(VI) and Np(V) in the feed can be predicted from equation (2), shown as a plot in Figure 3. Figure 4 shows the oxidation of Np(V) to Np(VI) for the first extraction cycle, plotted using equation (3). Essentially complete oxidation and therefore low loss of neptunium to the cycle I aqueous raffinate would be expected in the long residence times of mixer-settlers. The use of ferrous ions in the stripping stages ensures complete reduction to Np(IV), while the presence of sulphate renders it virtually inextractable (see Figure 2). In the second and third cycles, Np(IV) is the predominant

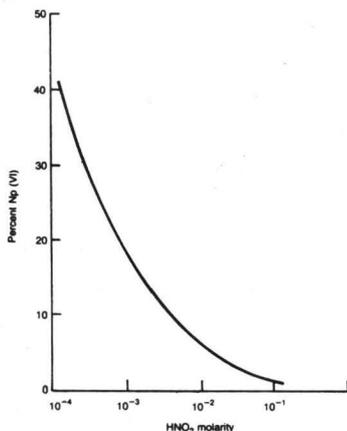


Fig. 3. Percentage Np (VI) at equilibrium in conditioned feed ($[H^+] = 3.0-4.5M$, $[NO_2^-] = 4.0-5.4M$)

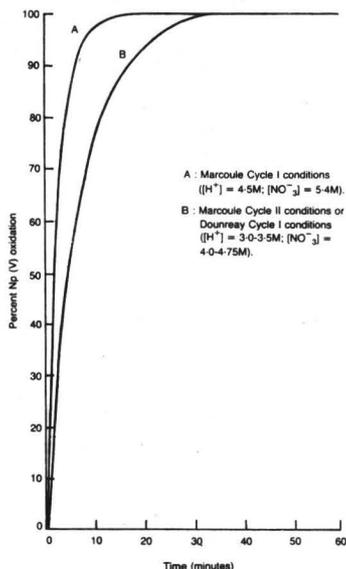


Fig. 4. Oxidation of Np (V) to Np (VI) in the presence of excess nitrous acid

neptunium species, however, the particular nitric-sulphuric acid conditions used result in partial extraction in both cycles. A summary of predicted neptunium behaviour and actual plant measurements is presented in Table 1 and shows reasonable agreement.

At Marcoule fuel has been reprocessed in a pulsed column pilot plant which uses a mixture of hydroxylamine, hydrazine and U(IV) in the U-Pu partitioning step. Again, Figure 3 can be used to estimate the Np(VI) at equilibrium in the feeds: using a 'best guess' estimate of 10^{-3} M HNO_2 , then $\sim 20\%$ of the total neptunium in the feed will be as extractable Np(VI) and $\sim 80\%$ as inextractable Np(V). However, because of the short residence times in pulsed columns oxidation of Np(V) to Np(VI) in the extraction stages will be incomplete. For a cycle I residence time of 5.5 mins,[†] Figure 4 shows that $\sim 87\%$ of the Np(V) will be oxidised to Np(VI) and for a cycle II residence time of 2 mins,[†] only $\sim 25\%$ of Np(V) to this cycle will be oxidised. The predicted and actual neptunium distribution is summarised in Table. These are in good agreement.

[†] estimated from reference (7)

Experimental and predicted Np distribution for the process plant streams

	²³⁷ Np: %			
	Dounreay Plant		Marcoule Plant	
	Measured	Predicted	Measured	Predicted
Feed	100	100	100	100
Cycle I aqueous raffinate	10.3	~0	10	10
Cycle I solvent raffinate	<5.1	2.0	-	-
Cycle II aqueous raffinate	51.2	57.0	18-58	54
Cycle II solvent raffinate	<4.2	1.0	-	-
Cycle III (Pu) purification:	-	-	32-72	36
aqueous raffinate	12.5	22.0	-	-
Pu product	20.5	18.0	-	-
Cycle III (U) purification	-	-	0.1	-

Conclusions. On the basis of the analysis described, it is possible to predict the route followed by neptunium in a specific process and also to explore the likely effects of changes in process variables.

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The degree of Tc recovery into uranium and plutonium coextract in PUREX process is by several times greater than that determined by its static distribution coefficients in the system tributyl phosphate (TBP) - uranium - nitric acid [1, 2]. The results of recent investigations have shown that the Tc distribution coefficient depends not only on uranium and plutonium concentrations but also on the concentration of zirconium [3, 4]. Tc and Zr coextraction mechanism is rather complex and imperfectly understood.

In this connection we have studied the influence of Zr, nitric acid and U on the extraction of Tc with 30 % TBP in dodecane at $(20 \pm 1)^\circ\text{C}$.

The dependence of Tc distribution coefficient on Zr concentration in the organic phase at constant concentration of nitric acid in the aqueous phase (3.1 M) in logarithmic coordinates represents a straight line with the slope equal to 1, which points to the possibility of a mixed solvate formation with components ratio equal to 1.

Nitric acid has a strong effect on extraction both of Zr and Tc. Logarithmic dependence of the Zr distribution coefficient on the activity of nitric acid represents a straight line. For a given TBP concentration its value can be calculated from the formula:

$$\alpha_{\text{Zr}} = \bar{K}_1 [\text{HNO}_3]^{1,7} y_s^{1,7}, (1)$$
 where \bar{K}_1 - effective extraction constant of Zr; y_s - stoichiometric activity coefficient of nitric acid [5].

In this case the variation of Zr activity coefficient can be neglected since according to the results of [6] its value rather weakly depends on the ionic strength ($\mu > 1$).

Tc extraction in the presence of Zr is described by a more complex dependence (Fig. 1, curve 1). At nitric acid concentration within the range 0.5 to 2.0 M the Tc distribution coefficient decreases in accordance with hydrate-solvate extraction mechanism. Most of investigators believe that in the absence of Zr, Tc is extracted in the form of trisolvate or tetrasolvate [2, 7, 8].

From the results shown in Table 1 it follows that the effective extraction constant of Tc in the form of tetrasolvate does not vary in a wide range of nitric acid concentrations. This confirms the supposition that Tc is extracted as tetrasolvate. The Tc distribution coefficient in this case is determined from the formula:

$$\alpha_1 = \frac{\bar{K}_2 [\text{HNO}_3] \cdot y_s^2 \cdot S_0^4}{(1 + \bar{K}_3 [\text{HNO}_3]^2)^4},$$
 where \bar{K}_3 - concentration extraction constant of nitric acid [9]; $S_0 = 1.08 \text{ M}$ - initial TBP concentration.

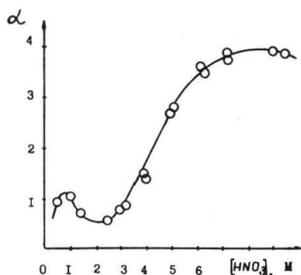


Fig. 1. Dependence of Tc distribution coefficient on nitric acid concentration. Initial Zr concentration 1.6 g/l. Curve - calculation; points - experiment

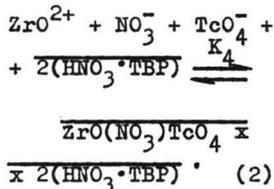
For nitric acid concentration above 2.0 M the Tc distribution coefficient sharply increases which seems to be explained by co-extraction with Zr.

Logarithmic dependence of Tc distribution coefficient on TBP concentration in organic phase is nonlinear, which is likely to be connected with the variation of the solvent activity coefficient and with the formation of solvates having different Tc to TBP ratios. However, at TBP concentration about 30 % the slope is close to 2.

Table 1. Tc extraction in the absence of Zr

Nitric acid concentration, M	Tc distribution coefficient, (α_1)	Concentration extraction constant (\bar{K}_2)	Effective extraction constant (\bar{K}_2)
0.50	1.29	0.97	1.82
0.83	1.07	1.05	1.97
1.61	0.54	1.12	1.75
2.37	0.35	1.91	2.23
4.89	0.025	5.13	2.07
			Average 1.96±0.17

Based on the results obtained the following mechanism of Tc and Zr co-extraction can be proposed:



Taking into account that Zr extraction is described by the

formula (1), we derive the expression for Tc distribution coefficient:

$$\alpha_2 = \frac{\bar{K}_4 \cdot [\text{Zr}_{\text{init}}] \cdot [\text{HNO}_3] \cdot y_s^2 (S_0 - S)^2}{1 + \bar{K}_1 [\text{HNO}_3]^{1,7} \cdot y_s^{1,7}} \quad (3)$$

where \bar{K}_4 - effective constant of Tc and Zr co-extraction; $[\text{Zr}_{\text{init}}]$ - zirconium initial concentration, M; S - concentration of free TBP, M.

The formula (3) describes well Tc extraction at high concentrations of nitric acid. It is evident that in a wide interval of nitric acid concentrations the Tc distribution coefficient can be calculated taking into account combined effect of the hydrate-solvate mechanism and

the coextraction mechanism, i. e. $d_{Tc} = d_1 + d_2$ (4). It is seen from Fig. 1 that the calculated curve agrees well with experimental points.

Uranium, as would be expected, displaces Zr from the organic phase, and Tc distribution coefficient decreases to the value determined by the mechanism of its coextraction with U (Table 2).

It should be noted that the logarithmic dependence of Zr distribution coefficient on free TBP concentration represents a straight line with the slope equal to 2. This fact confirms the supposition of Tc and Zr coextraction in the form of disolvate.

The studies performed allowed to calculate the degree of Tc recovery in

Table 2. Influence of U on the extraction of Tc and Zr, ($Zr_{init} = 0.8$ g/l; $HNO_3 = 4.6$ M)

U concentration in organic phase, g/l	Zr concentration in organic phase, g/l	Tc distribution coefficient	Zr distribution coefficient
0	0.33	0.75	0.70
10	0.32	0.73	0.70
20	0.25	0.69	0.45
38	0.20	0.67	0.33
76	0.10	0.52	0.13
108	0.06	0.35	0.07
108	0	0.36	-

PUREX process at U and Pu coextraction and its distribution on the stages of extraction battery for steady-state conditions. The calculation was made using formulae derived in [10], assuming that the value of Tc distribution coefficient in the extraction section is determined by simultaneous action of hydrate-solvate mechanism and that of Tc and Zr coextraction (formula 4), whereas in the scrubbing section it is determined by mechanism of coextraction with U, studied in detail by F. Macásek [2]. Initial data for calculation - the concentrations and flow ratios - were taken from [1]. The Zr concentration was evaluated based on the average burn-up of the fuel reprocessed (~ 30 kg/t U).

Fig. 2 shows the distribution of Tc through the stages of battery. The agreement between calculated curves and experimental points confirms the correctness of the proposed model. The degree of Tc recovery in coextract is about 90 % which also agrees with experimental data [1].

Our results show that it is possible to control the degree of Tc recovery. In order to increase Tc recovery it is necessary to keep

the acid concentration in the extraction section within the range 4-6 M, and to remove most part of Tc in raffinate the Zr content

should be minimized using, for example, a complexing agent for Zr.

The experiments have shown that for equivalent content of Zr and fluoride ions ($\sim 10^{-2}$ M) the Tc distribution coefficient decreases almost by a factor of 10. Such a suppression of co-extraction effect reduces, according to calculations, the degree of Tc recovery in PUREX process to 30 %.

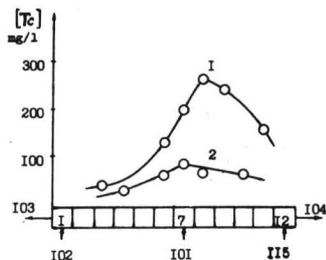


Fig. 2. Tc distribution in aqueous (1) and in organic (2) phases of coextraction battery. Curves - calculation; points - experiment

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A procedure is described for the solvent extraction of enriched uranium (35 % ^{235}U) from the waste solution of fission molybdenum production. The large scale production of molybdenum-99 is characterized by the use of ordinary fuel elements of a research reactor as starting material /1/. After the separation of fission molybdenum the fuel element solution is deposited in a storage for 4 years.

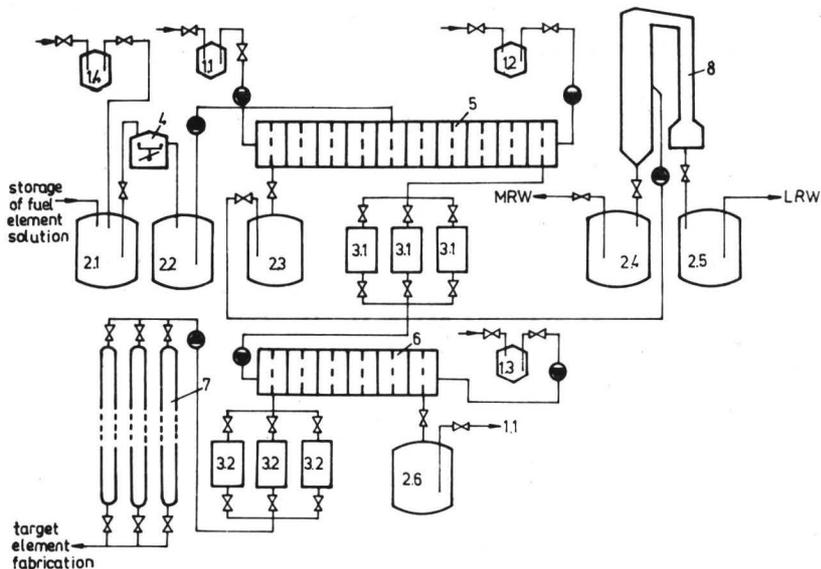
Owing to the special composition of the feed solution, presented in the Table, and the technological conditions the well-known PUREX-process had to be modified. The activity of the solution is about 0.3 Ci/L.

The schematic flowsheet of this separation process is shown in Fig. The main steps are: storage of fuel element solution in special tanks, feed adjustment, solvent extraction of uranium with tri-n-butylphosphate (TBP) diluted in tetrachloroethen and scrubbing of the extract, backextraction of uranium, storage of the $\text{UO}_2(\text{NO}_3)_2$ -solution and waste treatment.

Composition of the feed
solution

Substance	Concentration (g/L)
$\text{Al}(\text{NO}_3)_3$	163.3
$\text{UO}_2(\text{NO}_3)_2$	4.3
$\text{Hg}(\text{NO}_3)_2$	0.15
$\text{Cd}(\text{NO}_3)_2$	8.4
HNO_3	7.5
Si/SiO ₂	0.5
Fission products	0.015
Pu	0.0005

The extraction process takes place in counter-current extraction. The organic solvent is the heavy phase. The extraction and the backextraction are carried out in a new mixer-settler-unit. Flow conditions are regulated in such a way that uranium is extracted almost quantitatively, leaving most of the fission products and other impurities in the aqueous phase. The recovered uranium is well suited for fabrication of new target elements using in fission molybdenum production. The facility was put into operation in 1985.



Schematic flowsheet: 1.1 - inlet solvent; 1-2 - inlet scrub solution; 1.3 - inlet backextraction solution; 1.4 - inlet reducing agent; 2.1 - 2.6 - storage tanks; 3.1 - slab vessel for $\text{UO}_2(\text{NO}_3)_2$ org.; 3.2 - slab vessel for $\text{UO}_2(\text{NO}_3)_2$ aq.; 4 - centrifuge; 5 - extractor; 6 - backextractor; 7 - storage for $\text{UO}_2(\text{NO}_3)_2$ aq.; 8 - evaporator

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In the Purex process tributylphosphate undergoes chemical and radiolytic attack leading to the formation of acidic degradation products, mainly dibutylphosphate (DBP) and to a lesser extent monobutylphosphate (MBP). These alkylphosphoric compounds are extractants and may also give insoluble complexes with several cations of fission products. Thus their elimination from the organic phase by alkaline scrubbing of the solvent is necessary. The alkaline solution is generally made of carbonate, in order to keep uranium and plutonium, which can be present in small quantities, under a soluble form. The destination of this aqueous solution is usually the high or the medium activity wastes. Recycling actinide values from these effluent solutions in the process is to be considered to lower α -activity in the wastes (figure 1). Horwitz and coworkers [1] described a solvent extraction process (Aralex) to recover actinides from these solutions after their acidification and a subsequent phosphorous compounds extraction by 2 ethyl 1 hexanol.

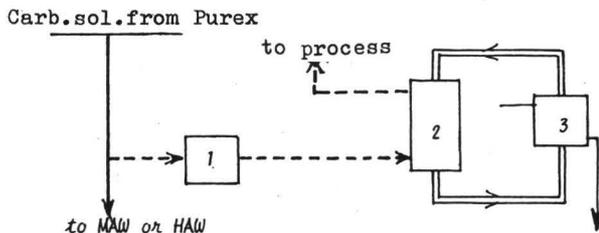


Fig.1. DBP clean up cycle. 1 - pH adjustment;
2 - DBP extraction; 3 - amine solvent treatment

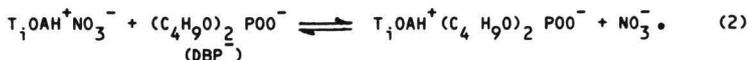
Another way to handle this problem consists of selectively extracting the disturbing organophosphorous compounds from neutral or alkaline solutions where they are under an anionic form. The actinides will stay in these aqueous solutions which can be concentrated and recycled without any risk of precipitation. Amine type extractants are known to be powerful anion exchangers and they have consequently been studied.

Tertiary amines usually display a better chemical and radiolytic stability compared to other types of amines. So we first choose the tri-iso-octylamine ; it is diluted in a mixture of dodecane and octanol to prevent third phase formation during the neutralization by an acid.

The extractant is used under the form of tri-iso-octylammonium nitrate, which is obtained by the reaction.



The extraction of dibutylphosphate by the alkylammonium nitrate is supposed to obey the following anion exchange reaction :



The formation of the tri-iso-octylammonium dibutylphosphate obviously depends on :

- the pH of the aqueous solution;
- the aqueous concentration of the nitrate ions;
- the dibutylphosphate anion concentration;

All the experiments were carried out at room temperature.

Influence of the aqueous phase pH .

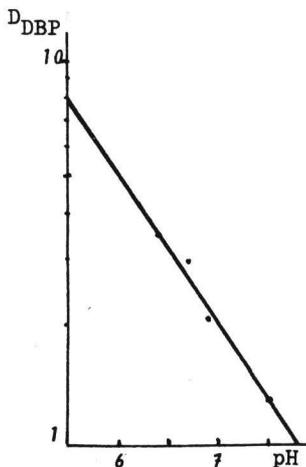


Fig. 2. DBP partition coefficient versus pH

In these experiments trioctylamine nitrate ($0,43 \text{ mol l}^{-1}$) in a mixture of dodecane (82 %) and octanol (18 % by volume) is contacted with various aqueous solutions. pH is measured at equilibrium. The results are shown on figure 2. A very sharp decrease of the DBP partition coefficient (D) around the neutrality is noted. This is consistent with equations (1 and 2) the concentration of the "anion exchanger" sharply decreasing. Influence of the nitrate concentration . We used the same solvent than above. No measurable influence on DBP extraction has been observed when increasing the NO_3^- concentration from 0 to $0,4 \text{ mol.l}^{-1}$ at pH 3,7. Combining equations (1) and (2) leads to the following relationships $D_{DBP} = K_1 K_2 [T_iOAH^+]$ where K_1 and K_2 are the equilibrium constants of the two reactions. The experimental results are consistent with this relationship.

Influence of DBP⁻ concentration . The aqueous phase is a mixture of hydrazine carbonate and hydrazinium nitrate in which the DBP concentration varies from 0.5 to $5.4 \cdot 10^{-3}$ mol·l⁻¹.

The aqueous solutions are contacted with the tri-iso-octylammonium nitrate in dodecane-octanol ; the pH at equilibrium is always 7. No variation of D_{DBP} has been noted ; its value is 2 ± 0.2 .

Optimization of the organic solution . The preliminary results show that amines may be efficient extractants for DBP in neutral or slightly alkaline solutions. An optimization of the organic system was however undertaken, namely by studying the influence of the nature of the amine, its concentration and the nature of the diluent, the purpose being to find a possibility of cleaning up alkaline solutions from DBP at higher pH.

For sake of comparison several alkylammonium nitrate have been tested in the following conditions : extractant concentration $0.1 \text{ mol} \cdot \text{l}^{-1}$ in dodecane-octanol, pH of the carbonate aqueous phase 8.1, DBP concentration $5 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$. Extraction is performed with a volume ratio of 1. The DBP partition coefficient is equal to : 0.41 for tri-laurylammonium nitrate, 4 for Aliquat 336 (commercial tri-laurylmethylammonium) nitrate, 17.5 for Primene JMT (18 to 22 carbon atoms primary amine) nitrate. The primary amine nitrate looks very favourable compared to others. So we focused our studies on this extractant.

The nature of diluent plays an important role in the extraction by ion pair formation. For similar conditions (pH 8.2, DBP $5 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$, extractant $0.1 \text{ mol} \cdot \text{l}^{-1}$) diluents of various polarity were compared :

Table I . Influence of diluent on DBP partition coefficient

Diluent	Xylene	Chloroforme	n-Dodécane	HTP	HTP-octanol mixtures %octanol			
					1	5	10	20
D_{DBP}	0,43	0,37	0,44	0,43	0.85	3.9	7.2	15.1

A diluent of relatively high polarity is needed to give a good extraction and to prevent third phase formation.

The variations of D_{DBP} versus the extractant concentration were determined at pH 8. D_{DBP} is roughly linear, the slope depending on the diluent. This is consistent with the supposed 1 : 1 stoichiometry.

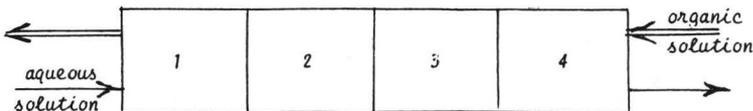
Counter current operation . A counter current test was worked out on aqueous solutions corresponding to the alkaline scrubbing of TBP leaving a plutonium purification cycle. The general conditions were the following :

aqueous phase : hydrazinium carbonate $0.7 \text{ mol} \cdot \text{l}^{-1}$
 " nitrate $0.36 \text{ mol} \cdot \text{l}^{-1}$
 hydrazine $0.96 \text{ mol} \cdot \text{l}^{-1}$
 DBP⁻ $5.6 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$

the pH was adjusted to 8.1 by addition of nitric acid.

organic phase : Primene JMT (NO_3^- form) 0.12 M
 dodecane - 2 octanol (18 % by volume)

The extraction was performed in four stages of a laboratory mixer settler bank.
 The flow rate ratio was $O/A = 1/5$.



The DBP distribution between the two phases is given on the following table :

Table II . DBP distribution between phases in each stage

Stage	1	2	3	4
DBP _{org} $10^{-3} \text{ mol} \cdot \text{l}^{-1}$	32	16	7,4	1,3
DBP _{aq} $10^{-3} \text{ mol} \cdot \text{l}^{-1}$	2	1	0,54	0,13
D _{DBP}	16	16	13,7	14,6

In these conditions the measured distribution coefficient is of the order of 10^{-2} for Pu(IV) and 0.4 for Ruthenium. Pu can be completely removed from the solvent by a one stage scrub. Amine solvent can be reused after an alkaline scrubbing to eliminate DBP (and Ru if present). The resulting aqueous effluent will be actinide free and be sent to medium activity waste.

Reference

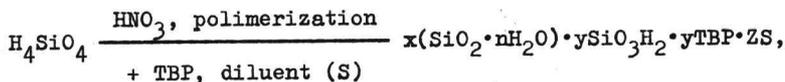
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Appearance of interphase films, stabilized emulsions and precipitates (often termed as "crud") in the extraction processes of nuclear fuel reprocessing causes a number of difficulties: incomplete phase separation, worsening of hydrodynamic conditions in extractors etc. Occurrence of crud is commonly related to the formation of stabilized emulsions which accumulate during demulsification of emulsified two-phase system in the region of phase boundary and subsequently change to interphase gelatinous precipitates. It is known that silicic acid can be one main components of interphase precipitates [1-3]. Dissolved silicic acid has the property of forming, especially in the presence of tri-n-butyl phosphate (TBP), stable interphase films significantly reducing the velocity of demulsification [4-6]. However, the mechanism of formation and the nature of interphase precipitates containing silicium have not yet been studied enough.

We have investigated the conditions of appearance and the nature of interphase precipitates formed in the extraction systems with participation of dissolved silicic acid. Most detailed investigation has been made of conditions leading to the production of stable practically undestroyable in time emulsions formed at emulsification of the phases as a result of interaction of TBP molecules with intermediate species of polysilicic acid insoluble in organic phase, which appear in aqueous solution of nitric acid in the process of polymerization of monomeric silicic acid or its low-polymerized forms. With the nitric acid concentration of 1-3 M and silicic acid concentration of 1.0 g/l such intermediate species can exist in solution for a long time - over 40-50 days. As it was found, polysilicic acid particles with different degree of polymerization participate in the formation of stabilized emulsions. During initial period of aqueous silicic acid aging the stabilized emulsion contains mainly β -form of silicic acid. As the time of aging increases the particles of γ -form take ever growing part in production of the stabilized emulsion. At the same time the volume of the stabilized emulsion decreases. Later, the transition of polysilicic acids to highly polymerized forms leads to a complete cessation of stabilized emulsion formation (Fig. 1).

Based on our data the formation of particles entering into the composition of stabilized emulsions may be written as:



where $x/y = 30-1000$, and $Z = 2-6$.

According to IR-spectrometric study in the above species a relatively strong hydrogen bond exists between the phosphoryl group of the extractant and hydroxyl groups of polysilicic acid. It has been also found that the presence in the aqueous phase together with silicic acid of hydrolyzed forms of zirconium, ferrum and aluminium intensifies the process of stabilized emulsion production. The ability of aqueous solutions of silicic acid to form stabilized emulsions especially grows in the presence of zirconium hydrolyzed forms and radiation-chemical degradation products of TBP - alkyl phosphoric acids and H_3PO_4 . Formed in this case finely dispersed precipitates of zirconium alkyl phosphates together with polysilicic acid particles concentrate after emulsification at the phase boundary in the form of voluminous stabilized emulsion.

It should be noted that the life time of the polysilicic acid active forms responsible for the generation of stabilized emulsions essentially grows in the presence of hydrolyzed zirconium species, so that the formation of stabilized emulsion at emulsification of two-phase system is observed even in some months of aqueous solution aging. It is believed that this phenomenon is connected with the formation in the aqueous solution of stable polymeric heteronuclear compounds of silicium with zirconium. The determination of silicium to zirconium molar ratio in samples of stabilized emulsion obtained from aqueous solutions with different time of aging shows that

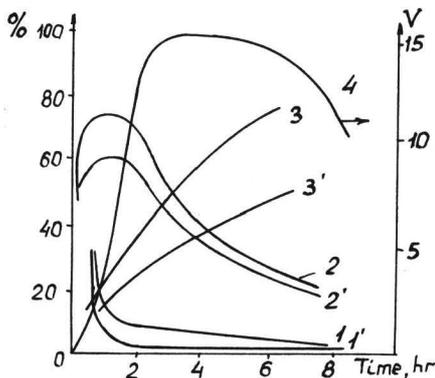


Fig. 1. Kinetic curves of silicic acid α -, β - and γ -forms variation in solutions before and after the formation of stabilized emulsions in the system: 30 % TBP + 70 % $\text{C}_{12}\text{H}_{26}$ - 3.0 M HNO_3 + 0.7 g/l H_4SiO_4 . Curves: 1, 1' - α -form; 2, 2' - β -form; 3, 3' - γ -form; 4 - time variation of stabilized emulsion volume; 1, 2, 3 - before the formation of stabilized emulsion; 1', 2', 3' - after the formation of stabilized emulsion

the initial Si/Zr value of 4-5 gradually increases to 10-15. This is likely to be explained by the increase of fraction of more polymerized forms of silicic acid in the emulsion composition.

It is interesting to note that the additions of small amounts of hydrogen fluoride (0.01-0.1 g/l) to aqueous solution cause an intensive formation of the stabilized emulsion with a volume much greater than that of stabilized emulsion formed in the absence of hydrogen fluoride. But the period during which the initial solution of silicic acid preserves its ability for stabilized emulsion production sharply decreases. Additions of hydrogen fluoride in great quantities (>1 g/l) can prevent from formation of stabilized emulsions (Fig. 2). Thus, the results obtained indicate that the formation intensity of interphase stabilized emulsions based on silicic acid is primarily determined by the factors affecting the generation of active species of polysilicic acid responsible for appearance of stabilized emulsions. As it has been found in our work these factors include the total content of silicic acid in aqueous solution, the conditions of preparation and the time of solution aging before extraction, the concentrations of nitric acid, uranyl nitrate and nitrates of other metals, temperature as well as the type of emulsion formed at mixing and the time of phase contact. In addition to these factors the intensity of stabilized emulsion formation depends on the nature of diluent and extractant. The character of stabilized emulsion volume variation depending on TBP content in extraction mixture essentially changes when benzene, chloroform or carbon tetrachloride are used instead of n-pareffines as diluents. In the

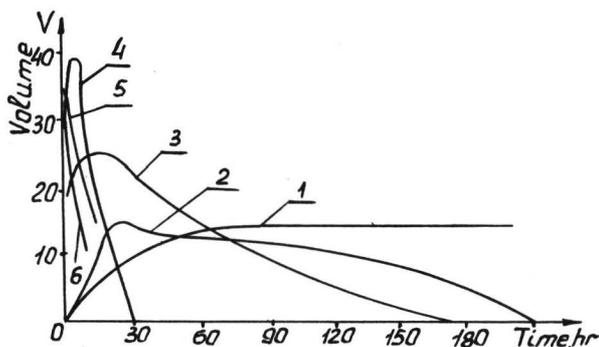


Fig. 2. Effect of H_2F_2 on the formation of stabilized emulsions in the system: 30 % TBP + 70 % $C_{12}H_{26}$ + 3.0 M HNO_3 + 1.0 g/l H_4SiO_4 . Curves: 1 - without addition; 2 - 0.001 g/l; 3 - 0.01 g/l; 4 - 0.1 g/l; 5 - 1.0 g/l; 6 - 2.0 g/l

case of carbon tetrachloride the onset of stabilized emulsion formation corresponds to the TBP volume fraction of 60-70 % [7]. The substitution of triisooamyl phosphine oxide for TBP at the same experimental conditions increases markedly the volume of stabilized emulsion which seems to be connected with the increase hydrogen bond strength between the extractant molecules and the particles of polysilicic acid.

The effect of γ -radiation with absorbed doses up to ~ 2 MGy on extraction mixtures TBP + diluent has small influence on the ability of extraction system to form stabilized emulsions. On exposure of an interphase stabilized emulsion to γ -radiation the greatest emulsion drops are destroyed, and the stabilized emulsion gradually transforms into a more compact interphase precipitate consisting of polysilicic acid gel and organic phase microemulsion. As a whole, the examination of the results obtained allows us to conclude that the problems of reducing or avoiding crud formation are connected not only with the degree of purity of solutions fed to extraction. Along with the selection of an extractant and a diluent much importance is attached to the development of optimum extraction conditions taking into account all factors affecting the formation of stabilized emulsions.

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Introduction MINKA, a small scale pulsed column facility has been installed at the "Institut für Heisse Chemie" at the Nuclear Research Center Karlsruhe, in order to study the behavior of Pu, U and HNO_3 at the Purex process under standard and off-standard conditions. Decreased HNO_3 concentration in the scrub solution and increased feed flow or decreased extractant flow were chosen as parameters to establish off-standard conditions.

The influence of decreasing HNO_3 concentration in the scrub solution has been studied in [1,2]; this plus simultaneously changed hold up of the dispersed aqueous phase on extraction behavior were reported in [2]. First results showing the influence of lowering the extractant flow on the extraction behavior of Pu and U were given in [3].

This paper presents the transient extraction behavior of Pu and U in a strongly disturbed Purex-codecontamination cycle.

Experimental. Three pulsed sieve plate columns were connected in series for the demonstration of a codecontamination cycle. The data of the columns and the conditions of the flowsheet are summarized in Table 1. A detailed description of the MINKA facility is given in [3].

Results. The extraction behavior of U and Pu at the conditions of an off-standard flowsheet was studied in the extraction and scrub-column only. The backextraction column was used as service unit.

The maximum of the concentration of U and Pu appears in the aqueous phase. Therefore in the following figures the metal concentration of the aqueous phase is plotted only.

The concentration profiles of U and Pu for the two flowsheet are shown in Fig.1. The solid line represents the extraction behavior for the flowsheet given in Table, AX:AF=2.66. The dashed line shows the data of the codecontamination cycle after additional reduction of the flow ratio AX:AF=2.52. In the first experiment the flowsheet has reached the equilibrium after a period of 62 hours. The maximum of the accumulation of U was located at the middle of the S-column, whereas the maximum of the Pu accumulation was placed at the bottom of the S-column. This value was measured to 21.3 g Pu/l which is equal to 8 times of the Pu concentration in the feed solution. The Pu mass recycled with the raffinate stream of the S-column into the A-column amounts 350% of the Pu mass supplied with the feed.

The recycled amount of the metal does not influence the

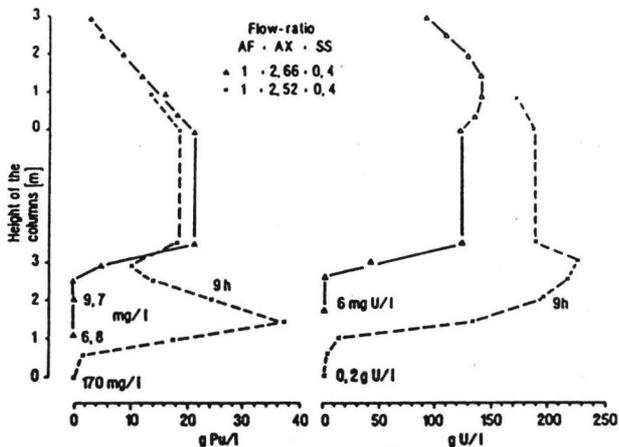
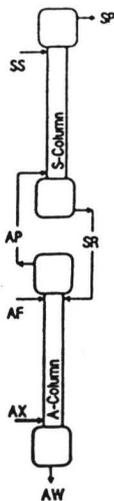


Fig.1. U, Pu concentration profiles

extraction behavior of the A-column significantly. In the AW stream the loss of Pu was determined to 5 mg Pu/l comparing with about 3 mg Pu/l AW in earlier experiments with a flow ratio of AX:AF=2.80.

The decrease of the flowrate AX:AF=2.66 to the ratio 2.52 initiated a major change in the concentration profile of U and Pu (dashed line in Fig.1). In this experiment the Pu loss in the AW stream increased to 170 mg Pu/l within a period of 9 hours. Therefore this experiment was discontinued. At the end of the experiment the U and Pu accumulation took place in both the A and S-column. For both elements the maximum concentration in the S-

Flowsheet of the Codecontamination Cycle

column	A	S	C
function	extraction	scrub	strip
conti phase	organic	organic	aqueous
diameter			
/cm/	2.6	2.6	3.6
pulsation			
amplitude			
/cm/	1.5	1.5	2.5
frequency			
/Hz/	1.2	1.2	1.0
sieve plats (23% free area)			
space /cm/	3	3	5
holes /cm/	0.15	0.15	0.32
<u>flowsheet</u>			
stream	relative flow	composition	
AF	1	M HNO ₃	
SS	0.4	2.96	g U/l 256
AX	2.66	0.2	g Pu/l 2.31
		0.4	30% TBP/Alkane

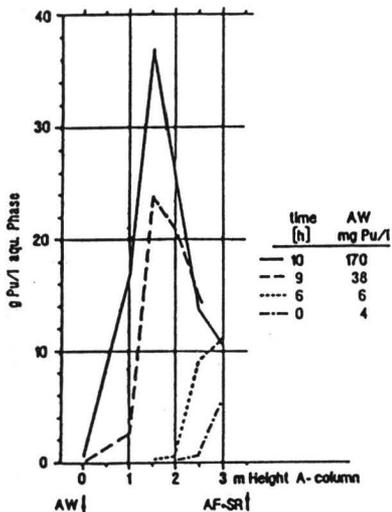


Fig. 2. A-column, Pu-break through

column was measured at the bottom of the column. Still bigger accumulations of the metals appeared in the A-column. The Pu accumulation was established at the 1-1.5 m level of the A-column (37.1 g Pu/l together with 135 g U/l). The concentration of U increased with the length of the column. Its maximum value of 226 g U/l was reached at a height of 3.5 m.

The transient behavior of Pu in the A-column is given in Fig. 2. Fig. 3 shows the corresponding data for U. The maximum of the U accumulation was located at the top of the A-column at every time in the experiment. With increasing concentrations the U extraction zone was broadened downward.

In front of the U extraction zone the Pu accumulation took place. Its extraction behavior initiated the formation of the Pu peak.

The Pu loss did not rise in the first 6 hours of the experiment, but later the losses increased rapidly.

The displacement of the U and Pu extraction front in the A-column can be clearly followed by the change of the temperature profile. The maximum of the temperature was found in the section of the column containing 80 - 100 g U/l in the aqueous phase.

The evaluation of the experiment is still under way so that no statement can be made concerning the maximum Pu accumulation.

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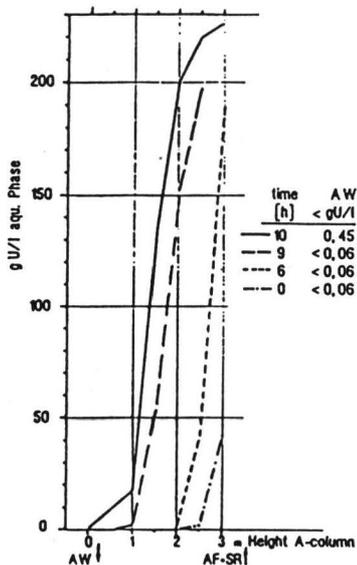


Fig. 3. A-column, U-break through

The reductive plutonium stripping operations carried out in the Purex process, such as uranium/plutonium splitting, are sometimes difficult to get under control. When these operations are performed in pulsed columns, added to the complexity of the chemical reactions involved, are the specific features of this type of contactor, whose performance is governed by a set of equally complex factors.

The perfect mastery of this process, both in the design phase and in the operating phase, requires the availability of a simulation tool incorporating the various aspects of the operation. The French Commissariat à l'Energie Atomique accordingly set up a research programme aiming to develop a mathematical model simulating the behaviour of the different species concerned in unsteady state conditions. This modelling was carried out in several steps :

- elaboration of a preliminary model, simulating uranium/plutonium splitting in mixers/settlers (already reported elsewhere <1>) ;
- elaboration of a model for simulating simple extraction operations in a pulsed column, accounting for the specific features of this contactor ;
- build-up of the final complete model.

The modelling of the uranium/plutonium splitting operation in mixers/settlers required the following in succession :

- the inventory of the chemical species to be taken into account (nine were selected : U(IV), U(VI), Pu(III), Pu(IV), HNO_3 , HNO_2 , N_2H_5^+ , Tc(ox), Tc(red)) ;
- the compilation of data concerning the partition of each of these species between the aqueous nitric phase and the solvent (30% TBP, diluent) (interdependent partition, described by a semi-empirical formula for the extraction mechanisms) ;
- the inventory of the chemical redox reactions ('functional', 'interfering' or 'useful' reactions) involving the various components, in both phases ;
- the formulation of the kinetic aspects relative to the interfacial transfer of the species and the main chemical redox reactions involved.

These details were obtained either from the compilation of published results, or, above all, from experimental determinations made in the CEA laboratories. They hence provide the basis for a model simulating a partition operation with uranium nitrate in a compartmented extractor. This model was validated successfully by comparing the results of its operation :

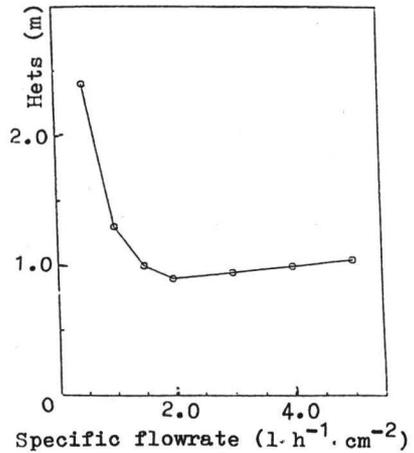
- with results of specific experiments performed in a suitable alpha installation (laboratory mixers/settlers) ;
- with operating results of industrial units.

The modelling of simple extraction operations (not involving chemical redox reactions) in a pulsed column required consideration of :

- Data relating to partition and to the transfer kinetics for the species concerned (U(VI), Pu(IV), HNO_3), previously obtained.

Fig.1 . Mean HETS(*) versus total specific flow rate (uranium extraction)

(*)HETS : Height Equivalent to Theoretical Stage



• Mechanisms specific to liquid/liquid extraction columns which are reflected on the whole by axial mixing effects in both phases.

We thus developed a multi-component dispersion model which, after the determination of the axial dispersion coefficients, allows the calculation of simple extraction operations encountered in nuclear fuel reprocessing.

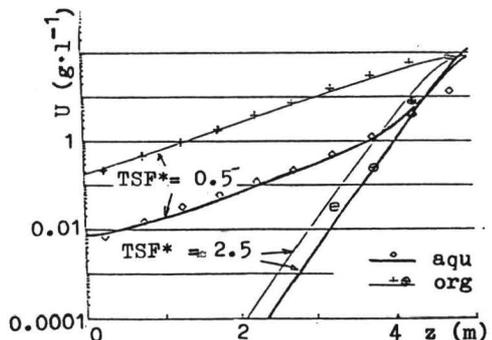
The validation of the model required the use of extensive experimental facilities, ranging from laboratory pilot plants to prototype industrial installations. The conducted tests consisted in the simultaneous determination of :

- concentration profiles in both phases, for different extraction operations ;
- axial dispersion coefficients by injection of tracers into each phase.

The lower performance observed at low flow rate is well simulated by the model. Figure 1 shows the variation in the mean HETS as a function of total specific flow rate, calculated for the same set of parameters. The comparison of the experimental and calculated concentration profiles (Figure 2) is also satisfactory.

Fig.2 . Calculated and on) experimental U(VI) profiles (extracti

(*) TSF : Total Specific Flow rate (l.h⁻¹.cm⁻²)



The completion of the foregoing two developments served to undertake the construction of a model able to simulate the metabolism of the different chemical species involved in a reductive stripping operation on plutonium in a pulsed column. The use of this apparatus as compared with mixers/settlers leads to significant differences in the operation of uranium/plutonium splitting. The competition between the various chemical reactions is intensified, both phases remaining in permanent contact. A number of relatively negligible mechanisms in mixers/settlers assume greater importance here. This meant that the corresponding kinetic data used in the first model had to be adjusted.

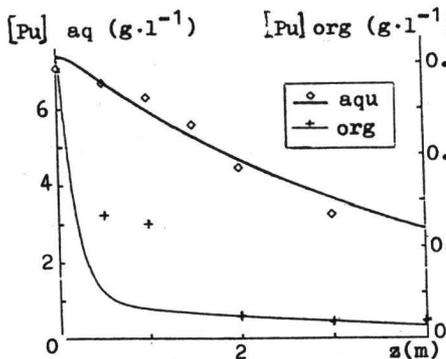


Fig. 3 : Calculated and experimental Pu profiles (U/Pu splitting)

able mechanisms in mixers/settlers assume greater importance here. This meant that the corresponding kinetic data used in the first model had to be adjusted.

The model thus obtained served to reproduce the behaviour described above, and yields very satisfactory results, as shown by the successful comparisons of the computer code with the reference experiments performed in a suitable test facility (Figure 3).

Hence we now have an qualified tool for calculating the most complex extraction operations conducted in the Purex process. Its field of application extends to :

- The optimized definition of process flow sheets as well as equipment.
- The simulation of incidental operations in order to predict possible developments, the means for detecting them (optimization of control systems), and the measures required to return to the normal state : for example, the model helps to carry out the safety analysis which may be required to guarantee the safe operation of the facility concerned.

Finally, it provides a solid basis of knowledge that could be exploited advantageously, both for training operators and for the elaboration of efficient tools for aid in facility control (expert system).

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Introduction. Operation of liquid-liquid extraction equipment can give rise to the entrainment of very small drops of one phase dispersed in the other phase, which adversely affects product purity. For example, in the reprocessing of spent nuclear fuel uranium (U) and plutonium (Pu) are extracted from highly active aqueous feed. Entrainment of aqueous phase in the organic product could result in carry-over of 'non-extractable' fission products with the U and Pu, which would put an undesirable burden on downstream purification and waste treatment processes.

This paper describes experiments with a pulsed plate column to study;

- the mechanisms which produce aqueous phase entrainment;
- the size characteristics of the entrained drops;
- their effect on the carry-over of a 'non-extractable' impurity.

The system studied was uranyl nitrate (UN)/nitric acid - 20% tributyl phosphate in odourless kerosene (TBP/OK) which is used to simulate Purex type flowsheets. Approximately 2 g/l of non-radioactive Cs were added to the UN feed as a tracer for 'non-extractable' fission products.

Experiment. The column was operated on a compound extract/scrub process and had a 10 m high and 50 mm diameter section fitted with stainless steel nozzle plates, with approximately 6 m height for extraction, and 4 m height for scrubbing. A settler for phase disengagement at the top of the column was approximately 1 m high and 100 mm diameter.

The size distribution of aqueous drops entrained in the organic phase was measured by a Malvern laser spectrometer. A sample of the organic phase from the column was placed in the path of a parallel beam of monochromatic laser light and the diffraction pattern produced by the sample was measured by a diode plate and modelled automatically by the spectrometer using scattering theory [1].

Mechanisms which produce entrained aqueous drops. Experiments show that two mechanisms arise in the Purex system;

1. Column pulsation - which produces a small volume fraction of fine drops at the bottom end of the drop size distribution;
2. Precipitation of water from the organic phase - which occurs when U, or U and Pu, is extracted into the organic phase.

Figure 1 shows how the concentrations of dissolved and entrained water in the organic phase varied with distance along the column. The dissolved water concentration is constant along most of the extract section but decreases sharply at the U feed point, where most of the U is extracted. Consequently, the entrained water concentration, which was constant and <0.1 vol % along most of the extract section where the first mechanism predominates, increased to ≈ 0.7 vol % at the U feed point because of the second mechanism. However, most of the precipitated water is removed in the scrub section of the column and the organic product from the column contained <0.1 vol % entrained water.

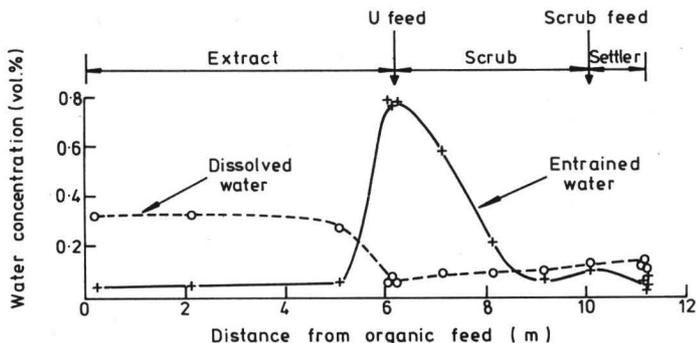


Fig.1. Variation of water concentrations along extract/scrub column

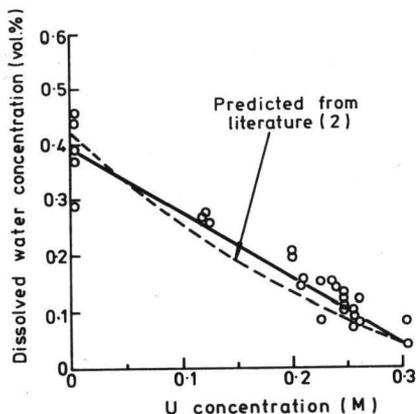


Fig. 2. Variation of dissolved water concentration with U concentration.

Figure 2 shows how the dissolved water concentration in the organic phase varied with U concentration. The data show a good correlation, dissolved water concentration varying from <0.1 vol % when the organic phase was almost saturated with U to ≈ 0.4 vol % when no U was present. The experimental data agree well with values calculated from the literature[2] assuming that the concentration of "free" TBP is equal to the total concentration of TBP less that bound to U as the disolvate ($UO_2(NO_3)_2 \cdot 2TBP$).

Size characteristics of entrained drops. Measurements with the laser spectrometer indicate that the precipitated drops are much smaller than those produced by column pulsation. As Figure 3 shows, the entrained drops near the U feed point vary from approximately 2 to 10 μ m diameter with a mean of 3 μ m. This is in contrast to the entrained drops 1 m below the U feed point, where little U was still present in the aqueous phase and the mechanism of column pulsation therefore predominated, whose diameter varied from 2 to 190 μ m with an average of 50 μ m.

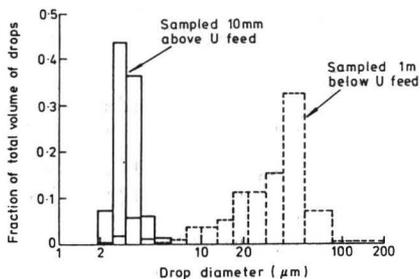


Fig. 3. Size distribution of drops entrained in organic phase near U feed

Samples of the organic product leaving the settler at the top of the column contained entrained drops with a broad size distribution but, as Figure 4 shows, there were two peaks in diameter of approximately 7 μm and 130 μm.

Comparison of Figures 3 and 4 suggest that the drops entrained in the organic product have the characteristics of both mechanisms of drop formation and therefore comprise;

- (a) a small fraction of precipitated drops which have passed through the scrub section of the column without either coalescing with large drops of scrub acid or coalescing with each other sufficiently to attain a size (~ 200 μm) able to sediment down the column against the flow of organic phase;
- (b) drops formed by column pulsation.

In both cases some coalescence of the entrained drops during passage through the column and top settler is evident because the peaks in the drop diameters in the organic product are a factor of 2 - 3 greater than they are near the U feed point i.e. 7 μm compared with 3 μm for precipitated drops and 130 μm compared with 50 μm for mechanically formed drops.

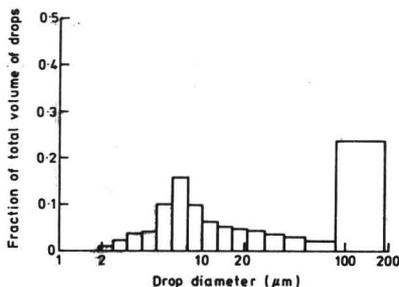


Fig. 4. Size distribution of drops entrained in organic product from top settler.

Dependence of Cs carry-over on aqueous phase entrainment. Cs can be carried over in the organic product because it is dissolved in the organic phase and/or dissolved in the aqueous phase entrained in the organic phase. Samples of the organic phase from the scrub section of the column were analysed therefore for their total and dissolved Cs concentrations, the difference between the two values being that due to entrainment of aqueous phase.

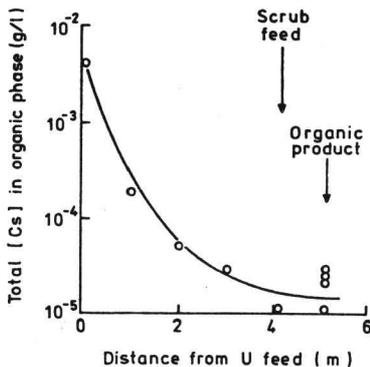


Fig.5. Cs concentration profile in scrub section.

As Figure 5 shows, the total concentration of Cs in the organic phase decreased from 4×10^{-3} g/l near the U feed point to, on average, 2.3×10^{-5} g/l in the organic product from the top of the column. The concentration of dissolved Cs in the samples was below the limit of detection of 1.1×10^{-5} g/l. The carry-over of Cs in the organic product due to aqueous phase entrainment therefore appears to be, on average, between 1.2 and

2.3×10^{-5} g/l (the latter value if it is assumed that there is no Cs dissolved in the organic phase). As Table shows, a sample of organic product which did not contain a detectable amount of total Cs had an entrained water concentration which was an order of magnitude less than the other samples.

Concentrations of entrained water and Cs in samples of organic product

Sample N°	Entrained water (vol %)	Total Cs (g/l)
1	0.002	$<1.1 \times 10^{-5}$
2	0.02	3.1×10^{-5}
3	0.07	2.2×10^{-5}
4	0.04	2.6×10^{-5}

Conclusions. There are two mechanisms which produce entrained aqueous drops in the extraction stages of the Purex process; drop shear during mixing and chemical precipitation of dissolved water during uranium extraction. Entrained drops formed by water precipitation are much smaller than those formed mechanically (typical mean diameters being 3 μ m and 50 μ m respectively).

In pulsed column tests most of the drops formed by chemical precipitation were removed by the scrub process. The concentration of Cs in the organic product after scrubbing was very low ($\approx 10^{-5}$ of the concentration in the U feed) but appeared to depend on the concentration of entrained aqueous phase.

Experiments are in hand to study how the two mechanisms of entrained drop formation determine carry-over of non-extractable impurities and to develop methods by which entrainment can be reduced.

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Introduction. A dynamic model of pulsed plate column operation, BRADSIM, has been developed jointly by BNFL and the UKAEA, to enable designers and operators of pulsed columns for reprocessing irradiated nuclear fuel to predict column performance during transient operation. The model takes into account the changes in the hydraulic behaviour and mass transfer performance of a column from the beginning of an operational transient until steady-state is reached.

The pulsed plate column is a differential contactor in which mechanical energy is applied via liquid pulsing to enhance its extraction performance. It can be used for a wide range of processes, but probably its best known use has been in the nuclear industry.

The pulsed column comprises a vertical, cylindrical column containing a series of equally spaced horizontal perforated plates arranged over its length. The liquids are fed countercurrently to the column and a pulsing action applied to the base of the column. If the light phase is to be dispersed it is forced through the plate perforations on the upstroke and the continuous phase flows downwards on the downstroke.

This paper, which is the first of several to be published, describes the BRADSIM model of column operation and gives examples of simulations for a PUREX-type system for reprocessing reactor fuels. Predicted profiles of solute concentration and liquid physical properties are presented and compared with experimental data from a 50 mm diameter column in the Harwell Solvent Extraction Pilot Plant⁽¹⁾ and a 300 mm diameter column in the Sellafield Pulsed Column Test Rig⁽²⁾. The extraction systems studied were uranyl nitrate (UN) - nitric acid/20% and 30% tributyl phosphate/odourless kerosene (TBP/OK).

Description of the model. The model simulates the dynamic response of a pulsed plate column to perturbations in operating parameters and variables. It takes account of the column hydraulic behaviour, multi-solute mass-transfer, non-linear equilibrium relationships for the solutes and volume changes resulting from solute transfer.

The model divides a column into a cascade of non-equilibrium well-mixed elements, with additional end elements for the introduction and withdrawal of the appropriate feed, product and raffinate streams. (An element does not necessarily coincide with those formed by two adjacent plates). A system of dynamic mass balance equations for all the elements of the cascade is developed in which backmixing is accounted for by the inclusion of a backflow fraction of each phase between elements.

The equations take into account the interdependence of hydraulic behaviour and mass transfer performance. For example, they take into account:

the effect of changes in the physical properties of the solutions, due to solute transfer, on the volumetric flowrates of the phases and the dispersed phase hold-up (DPHU), and the effect of changes in the concentration and flowrates of the feeds, and hence the DPHU, on solute concentration profiles.

The rates of solute transfer in each element are described in terms of the film mass-transfer coefficient for both phases, the interfacial area per unit volume in each element and the solute overall concentration driving force across the films.

The ability to predict temperature profiles is important with respect to monitoring column response to transients. Temperature has been included in the model as an integration variable and is treated in a similar way to DPHU and solute concentrations so that temperature profiles can be calculated during transient behaviour.

An essential requirement for the design of pulsed columns is a knowledge of the physical properties of the solutions. These will vary significantly along the column as the solutes are transferred from one phase to the other. Thus, equations have been included in the model for calculating profiles of phase densities, viscosities and the interfacial tension.

Comparison of predictions with experimental data

(i) Harwell Solvent Extraction Pilot Plant - Experimental and predicted uranium concentrations in the solvent product stream under start-up conditions for uranium extraction using 20% TBP/OK are shown in Figure 1. These show good agreement between predicted and experimental values, and in both cases the time to steady-state from start-up is approximately 0.5 h.

Experimental and predicted uranium concentration profiles at steady-state in both solvent and aqueous streams are shown in Figures 2 and 3

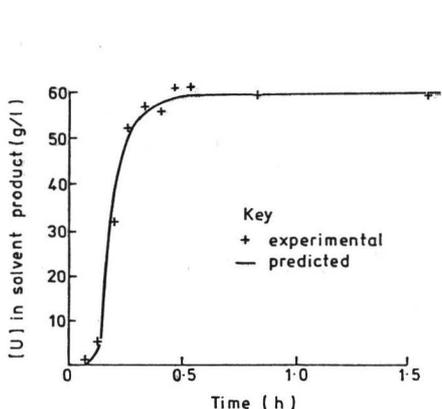


Fig. 1. U concentration in solvent product vs time.

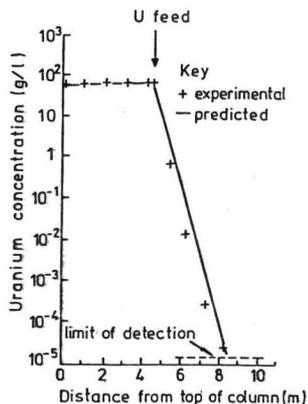


Fig. 2. U concentration profiles in solvent phase.

respectively. The model correctly predicts a concentration of $<10^{-4}$ g U/l in the aqueous raffinate 4 m from the U feed point and a concentration of ~ 60 g U/l in the solvent in the scrub section of the column. However, the rate of mass transfer in the extract section appears to be slightly under-predicted (because the predicted U concentrations in both phases occur on average 0.2 m further from the U feed point than they did experimentally) and the U concentration in the aqueous phase in the scrub section is rather over-predicted.

The profiles of density, viscosity and interfacial tension in the solvent and aqueous phases at steady-state are shown in Figure 4. Good agreement with the experimental data is evident, which confirms the accuracy of the correlations used in the model.

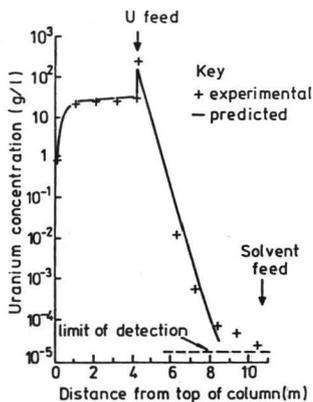
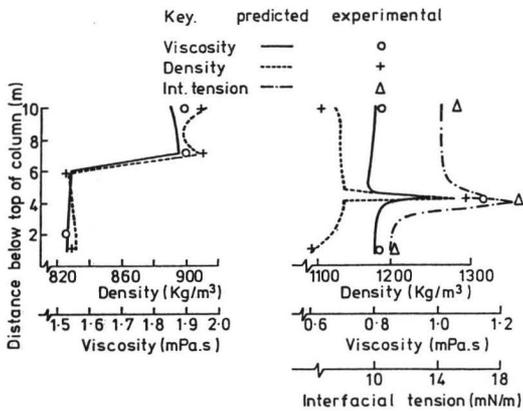


Fig. 3. U concentration profiles in aqueous phase.



(a) Solvent phase.

(b) Aqueous phase.

Fig. 4. Predicted and experimental physical property profiles.

(ii) Sellafield Pulsed Column Test Rig (PCTR) - Good agreement is evident between the experimental and predicted concentration profiles for uranium and nitric acid at steady-state using 30% TBP/OK shown in Figures 5 and 6. It should be noted that at the time of acquiring these experimental data the PCTR used a side-entry feed-pipe which gave inefficient feed distribution. However, by adjustment of the model it was possible to match the observed profiles and thus highlight the use of BRADSIM as a means of identifying non-ideal hydraulic behaviour. Currently such large scale columns are fitted with feed distributors to alleviate this effect.

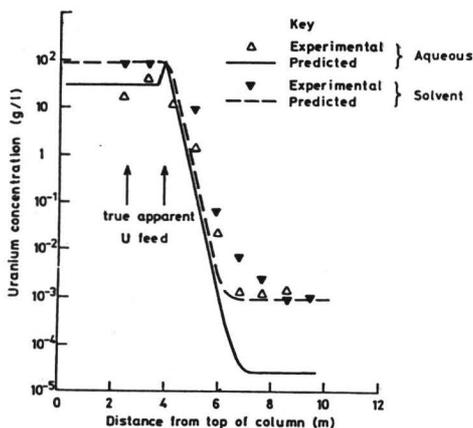


FIG. 5. U CONCENTRATION PROFILES

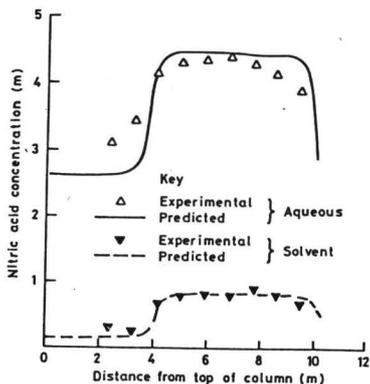


FIG. 6. NITRIC ACID CONCENTRATION PROFILES

Conclusions. A model, BRADSIM, has been developed which predicts the dynamic response of a pulsed plate column, from the onset of an operational transient to steady-state.

Overall, the agreement of the model predictions with experimental data for U extraction by 20% and 30% TBP/OK is good in both pilot plant and large industrial contactors.

Additionally it should be noted that, since the correlations for the mass transfer coefficients used in the model are fundamental in nature and not specific to the Purex flowsheet conditions, the model can be applied to a wide range of flowsheet conditions and other systems.

Experimental and industrial columns will exhibit non-ideal flow behaviour which will depend on the column geometry. BRADSIM can be used to diagnose this behaviour and predict its effect on column performance.

Acknowledgements. BRADSIM is based on initial work at the University of Bradford by Professor W.L. Wilkinson and Dr. J. Ingham. The experimental work was undertaken by teams led by Mr. C. Phillips at Sellafield and Mr. J.A. Jenkins at Harwell. A valuable contribution has been made by Mr. D.A. Houlton (Bradford University Research Ltd). Long-term support has been given by Mr. A.L. Mills (Harwell) and, Dr. W. Batey and Dr. P.J. Thompson (Dounreay).

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The need for processing of liquid highly radioactive wastes (HAW) arising from radiochemical technology is determined by the requirements for long-term safe storage of these wastes and by the demand for some radionuclides.

HAW contain the following main radioactive elements: ^{90}Sr , ^{137}Cs , TPE (^{241}Am , ^{243}Am , ^{244}Cm), RE (^{144}Ce , ^{144}Pr , ^{147}Pm , ^{151}Sm , ^{154}Eu , ^{155}Eu).

The present report concerns the summary results of the systematic investigation on extracting properties of cobalt dicarbolyde $\left\{ \left[\text{C}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co} \right]^- \right\}$ solution in nitrobenzene. The dicarbolyde polyhedral complexes of some transition metals are known to possess strong hydrophobic features. Complex anion salts are readily soluble in polar organic solvents of nitrobenzene type and largely dissociated in the organic phase. This is due to inert shell of the anion which interacts rather weakly with positive ions. Carborane complex anion form is synthesized from ortocarborane by -BH-group elimination on boiling in methanol in the presence of NaOH and as a result of reaction between the formed acid and cobalt dichloride in strongly alkaline medium.

Metal cations in the presence of cobalt dicarbolyde in anion form (D^-) are extracted into nitrobenzene as dissociated ion pairs according to the following reaction:



The extraction proceeds by substitution of M^+ for H^+ between the aqueous and organic phases:



In the case $C_{\text{M}^{+n}} \ll C_{\text{H}^+_{\text{D}^-}}$, $[\text{H}^+]_{\text{org}} = [\text{D}^-]_{\text{org}} = C_{\text{H}^+_{\text{D}^-}}$, the distribution coefficients are

$$D_{\text{M}} = K_{\text{nH}}^{\text{M}} \frac{C_{\text{H}^+_{\text{D}^-}}^{\text{n}}}{C_{\text{H}^+_{\text{aq}}}^{\text{n}}}, \quad (3)$$

where K_{nH}^{M} is an equilibrium constant of extraction exchange.

For $\log K_{\text{H}}^{\text{Cs}} \sim 10^2$, i.e. for effective extraction of cesium from acidic solutions (up to 4-6 M HNO_3), the extractant concentration should be within 0,01-0,1 M. The alkali-earth elements are extracted rather weaker. In order to extract strontium from 0,5 M HNO_3 at the distribution coefficient ~ 2 , the extractant concentration should be relatively high ($\sim 0,5$ M).

Constants of extraction of cations from the aqueous phase into nitrobenzene are defined by hydrate number of a specific cation in nitrobenzene; the greater the hydrate number of cation is, the lower is the constant of its extraction. This dependence explains the great difference in recovery of alkaline, alkali-earth and rare-earth elements in the presence of cobalt dicarbolyde in nitrobenzene, as the equilibrium constants of extraction exchange differ markedly for these element groups. So, in contrast to cesium, for the exchange reaction



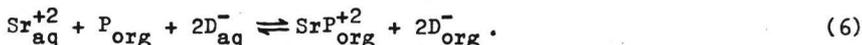
the value of $\log K_{2\text{H}}^{\text{Ba}}$ is 0,69+0,94 (hydrate number $h_{\text{Ba}^{+2}}=11,5 \pm 1$) even at $C_{\text{HNO}_3} \leq 1$ M.

For the exchange reaction



the value of $\log K_{3\text{H}}^{\text{Ce}} = 0,51+1,31$ (hydrate number $h_{\text{Ce}^{+3}}=16,2 \pm 2$) at $C_{\text{H}^+\text{D}} -$ within 0,04-0,3 M and C_{HNO_3} within 0,3-0,5 M.

Further investigation disclosed a synergetic effect resulting in complex formation of strontium, barium and trivalent elements with compounds of linear polyether type as for example polyethylene glycols (P). These complexes pass into the organic phase more effectively than free ions according to the following reaction:



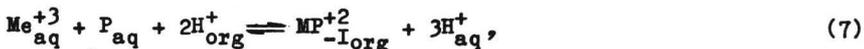
The presence of polyethylene glycols increases significantly the distribution coefficients of strontium, barium and trivalent elements and affects slightly the extraction of cesium.

The extraction of trivalent elements is characterized as follows:

- the relations between $\log D_{\text{Eu}}$ and $\log C_{\text{H}^+}$ may be expressed as a line with a slope -3;

- the relations between $\log D_{\text{Eu}}$ and concentration of extractant are expressed also as straight lines with slope +2.

These results should be accounted for by the following proposed extraction mechanism:



where MP_{-1}^{+2} is a complex in which one hydrogen atom is cleaved from polyethylene glycol or hydrate sphere of metal cation.

The composition of complexes in the organic phase was not estimated and could be fairly complicated. The complexes EuP^{+3}_{-3} and EuP^{+2}_{-1} prevail at lower concentrations of polyethylene glycol in the organic phase. At higher concentrations of polyethylene glycol these complexes react with next 1-2 molecules and give rise to some other compounds with probable composition EuP^{+3}_2 , EuP^{+2}_{-1} , EuP^{+3}_3 .

Extraction equilibria in the case of trivalent elements are more complicated as compared with extraction of mono- and divalent cations.

In studies of radiation stability of dicarbolyde complexes the high γ -radiation resistance of extractant was revealed and an interesting phenomenon of radiation synthesis was detected which resulted in conversion of the main anion in irradiated organic phase to halogen-derivative compound with higher chemical stability.

In the last few years the extensive investigations have been undertaken with the aim of examination of the properties and possible use of chlorinated cobalt dicarbolyde for technological recovery of cesium, strontium, lanthanoids and actinoids from the liquid HAW.

The data obtained suggest that this extractant offers many advantages over the known extractants for cesium and strontium. It can be used in strongly acidic media, it is chemically and radiation resistant and provides good efficiency for recovery and separation of Cs, Sr, TPE and RE.

On this basis a technological flowsheet for cesium and strontium recovery was elaborated and tested with actual HAW solutions in a laboratory installation mounted in hot cells. The flowsheet envisaged the recovery of cesium by extractant containing 0,06 M chlorinated cobalt dicarbolyde in mixture with nitrobenzene and carbon tetrachloride, extract washing and stripping of cesium by nitric acid. Strontium was recovered from raffinate by similar extractant with addition of 1 vol. % of "Slovafol 909". The test of strontium and cesium recovery flowsheet was performed by using the raffinates arising from the first cycle of VVER spent fuel reprocessing without any preliminary adjustment. The recovery of Cs and Sr in extract was 99,8 %, the total losses did not exceed 0,3 %. The decontamination factors for accompanying γ -nuclides were over 500. An essential drawback of the flowsheet consists in the use of two extractants for Cs and Sr recovery.

The further improvement of Sr and Cs recovery with chlorinated cobalt dicarbolyde leads to development of a technological flowsheet with one extractant.

The test data on simulated solutions indicated that cesium recovery was about 98 % and the decontamination factors for main radionuclides (^{144}Ce , ^{106}Rh , ^{154}Eu) were $\sim 10^3$. The strontium recovery degree was

more than 95 %, the decontamination factor for cesium was $\sim 10^3$, for fission products ~ 500 . The 4-fold concentration of strontium as compared with the feed simulated solutions was achieved; experiments with cesium concentration failed.

The positive test results for the simulated solutions enabled to proceed to laboratory experiments on real raffinate from spent fuel reprocessing. The recovery of cesium and strontium was about 98 % with rather high decontamination from accompanying radionuclides.

The concentrations of main macroimpurities in cesium and strontium reextracts did not exceed their content in feed solutions. The recovery and decontamination characteristics were not subjected to significant changes under the process conditions and this is sufficient demonstration of steady operation of the extraction flowsheet.

Along with the development of the processes for cesium and strontium recovery, the recovery of trivalent elements by the same extractant was investigated. As a result, a complex flowsheet was proposed which made it possible to recover Sr, Cs, RE and TPE from HAW. The laboratory experiments provide data on the main extraction and technological parameters of the flowsheet.

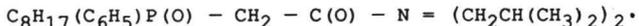
Thus, the use of chlorinated cobalt dicarbolyde as extractant permitted to develop a technological flowsheet with one extractant which afforded the fractional recovery of Sr, Cs and RE-TPE sum.

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At the Energy Research Center Casaccia (Roma) ten cubic meters of alpha contaminated liquid wastes, originated by the U-Pu mixed fuel fabrication at the Plutonium Laboratory, are stored. As their Pu-Am content is too high to be considered a LLLW, a simple process permitting the total elimination of alpha emitters is under investigation.

The process, named **TESEO**, based on the liquid-liquid extraction technique, will utilize a new neutral bifunctional extractant, the octyl(phenyl)-N,N'-diisobutylcarbamoylmethylphosphin oxide (CMPO):



This compound, developed at the Chemistry Division of Argonne National Laboratories (ANL), Chicago (USA), extracts all actinides in different valence states from acidic media. The TRUEX process, developed at ANL for the treatment of TRU containing wastes [1], is based on the use of CMPO.

Aim of this activity has been to develop a TRUEX-like process for the:

- selective separation of alpha emitters (mainly U, Pu, Am), in order to decrease the alpha activity of the liquid wastes at less than 370 Bq/g (10 nanocuries/g) of disposed form;
- recovery of Pu (and in some case of U^{235}) in a form suitable to allow its use in the fabrication plant;
- separation of the alpha emitters in a small volume.

The items investigated have been the:

- classification of waste solutions with regard to their chemical composition in four types: nitric, oxalic, alkaline, analytical waste solutions [2] (Table);
- verification, with simulated solutions of the possibility of mixing these different waste solutions without formation of solids or third phases. The mixing of the wastes has the aim to avoid the study of four different flowsheets, one for each single waste [3];
- purification of commercial CMPO produced by M&T Chemicals Inc., Rohway, (N.J.) 07095, with different methods (crystallization and ion-exchange) and study of its impurities [2];
- choice of the organic solvent composition (0.25M CMPO, 1M TBP in tetrachloroethylene (TCE) [3];

ALPHA LIQUID WASTES TO BE TREATED

acidic waste	oxalic waste	alkal. waste	analytical wastes		
Type 1	Type 2	Type 3	Type 4a	Type 4b	
HNO ₃ 3-7 M	Oxalic Ac. 0.6 M	NH ₄ OH 11M	HSCN 0.02M	AgNO ₃ 20g/l	
Pu 24	HNO ₃ 1M	NH ₄ NO ₃ 0.5M	Fe(SO ₄) ₃ 0.03M	Fe(SO ₄) ₃ 0.01M	
U 43.3 g	Pu 50.1g	CCl ₄ traces	H ₂ SO ₄ 0.7M	U 1017 g	
	U 9.14g	THFA(*) 0.5M	H ₃ PO ₄ 2M	Pu 12.56 g	
		Pu 14g	HNO ₃ 0.06M	others(°) traces	
			U 815g		
			Pu 20g		
			others(**) traces		
Volume 934 L	Volume 153 L	Volume 15.1 L	Volume 50 L	Volume 36 L	

(*) tetrahydrofurfurylic alcohol; (**) (NH₄)₆Mo₇O₂₄·24H₂O, (C₆H₅NHC₆H₄SO₃)₂Ba, K₂CrO₇
 (°) Al(NO₃)₃, HSCN, Ce₂(SO₄)₃

- selection of seven samples of real waste solutions with different chemical composition; determination of their radiochemical and chemical composition[3];
- extraction (Fig.1)and stripping(Fig.2)tests in batch with suitable mixtures of these real waste solutions[3];
- modelling of a reference flowsheet obtained by means of the SOLVEX computer code[3] (Fig.3);
- experiments in mini mixer settlers with mixtures of real waste solutions;
- definition of the parameters of the TESEO Process.

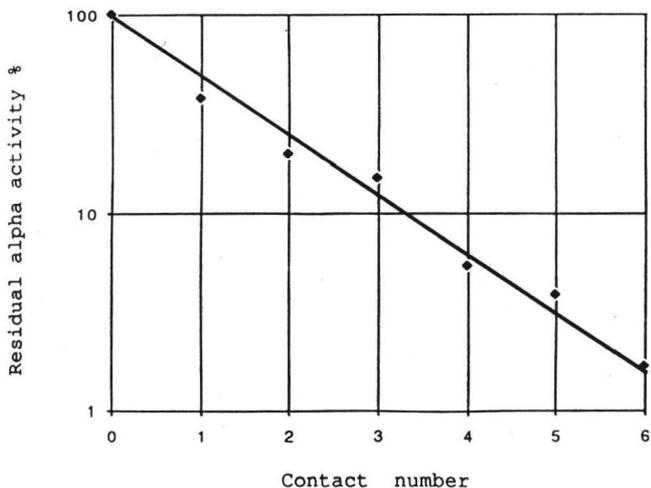


Fig.1. EXTRACTION TEST FOR A TYPICAL MIXTURE OF REAL WASTE SOLUTIONS

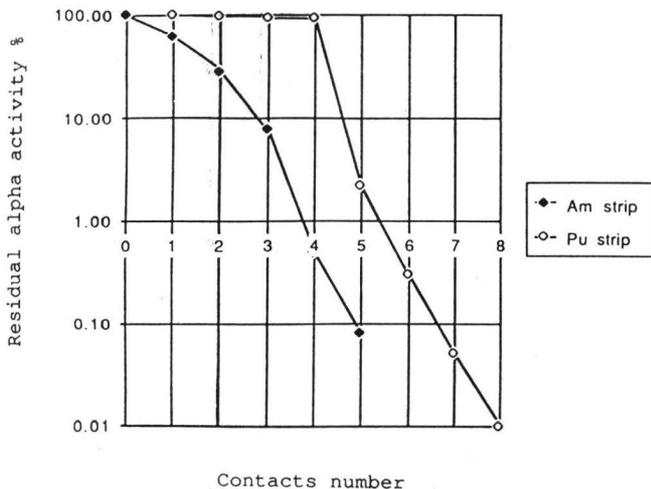


Fig. 2. SELECTIVE STRIPPING TEST

Stripping solution: 0.04M HNO₃ for Am(III) and 0.04M HNO₃ + 0.05M HF for Pu(IV)

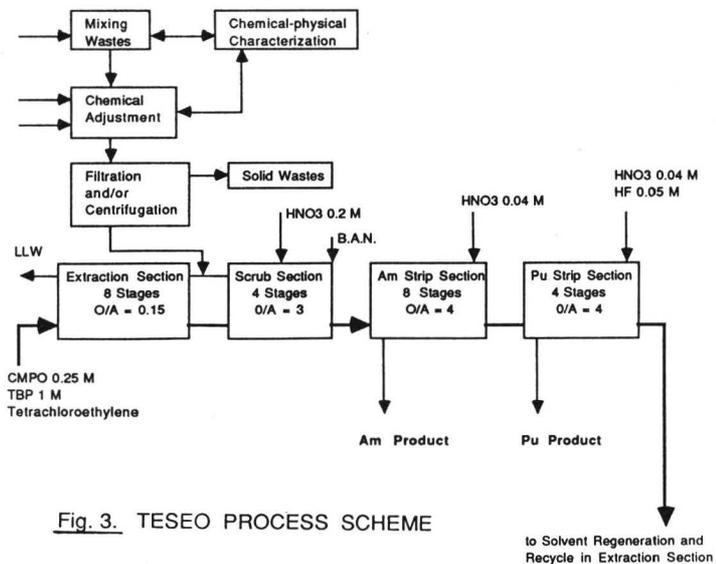


Fig. 3. TESEO PROCESS SCHEME

The basic TESEO process flowsheet involves the following operations: waste solutions of different type in 2 liter plastic containers are introduced in a first glove box, where the feed mixture is prepared. To this purpose calculated amounts of solutions with appropriate chemical compositions are mixed at predetermined ratios. After chemical adjustment and filtration, the feed solution is transferred into a second glove box, where the extraction is carried out. An 8+4 stages mixer-settler battery (efficiency 90%) is utilized for the extraction and for the scrubbing sections. The scrub solutions are 0.2M HNO_3 and 0.5M basic aluminum nitrate. In laboratory experiments a volume reduction factor of 6.25 was reached in the extraction-scrub section and 4 in the stripping section. It is possible to obtain a total Pu+Am stripping in a 4 stage mixer-settler or a selective stripping of Am (with 0.04M HNO_3 ; 4 stages) and Pu (with 0.04M HNO_3 + 0.05M HF; 4 stages) as shown in Fig.3. Uranium is recovered during the solvent regeneration with a Na_2CO_3 solution. The decontaminated solutions can directly be transferred to a cementation unity.

The planning, the installation and the operation of a small scale plant are foreseen during the years 1988-1989.

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Introduction. In processes for uranium recovery from phosphoric acid liquors the improvement of extraction equipment is still a wide development area. The majority of uranium solvent extraction plants use banks of mixer - settlers which take up much space especially for the separation of phases after mixing.

To reduce the volume of equipment, centrifugal extractors and some types of columns have been used from time to time but there occurred some difficulties with emulsification of phases. A tendency to create stable dispersions is characteristic for uranium extraction systems and results from low coalescence rate of drops. On the other hand this disadvantageous feature can be utilized purposeful when operating the extraction process in a spray column in which a densely packed dispersion is maintained. Such mode of process operation is also called extraction with dense packing of drops and it is suitable to liquid systems just with low coalescence rate.

The experimental investigations of spray columns working with dense packing of drops showed that high holdup values, up to about 70% could be obtained [1,2,3] with resultant high interfacial area. Furthermore, low backmixing [4] or even absence of backmixing [5] in both phases had also been found. Therefore, the use of densely packed dispersions seems to be an interesting proposal for the extraction of uranium. The aim of this work was to test this experimentally.

Apparatus. The densely packed dispersions were obtained in two experimental columns of the same diameter but different heights, as shown in Fig. 1. The first column was a standard spray column of Elgin design. It was constructed from glass and the only materials in contact with the liquids were glass, stainless steel and teflon. The height of the column proper was 1,0 m and the diameter was 0.04 m. The distributor was placed in the upper expanded part, being a set of nozzles with diameter of openings equal to 1,0 mm.

For the conventional operation with loosely packed dispersions and lower hold-up the coalescence interface was kept constant in the expanded bottom vessel. To form a densely packed dispersion the interface level was raised into the extended lower part of the column proper. The interface area available for coalescence was thus decreased and the drops began to form a dense dispersion.

The column of type II was of the same diameter but its height was 4,0 m. In that column the conventional distributor was replaced

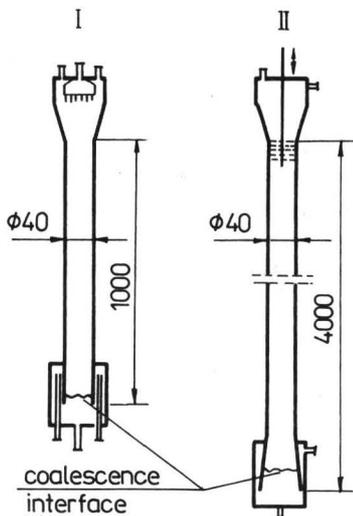


Fig.1. Extraction columns used in investigations

I - a standard spray column of Elgin type;

II - a modified column

with a mechanical dispersing device to avoid crusting and clogging of the smallest cross sections, which is a well known phenomenon in the phosphoric acid industry. The droplet dispersion was produced by means of a set of 5 reciprocated sieve plates with diameter of holes equal to 8 mm. The lower part of the column was modified using a conical section, within the coalescence interface was maintained. This design is an improved concept of Kehat's and Letan's [6] recommendation.

Results. In this work U(IV) was extracted from phosphoric acid with nonylphenylphosphoric acid (NPPA) dissolved in kerosene. The concentration of the extractant in the organic phase was 0,25 mol/l.

For both columns uranium extraction efficiency φ as well as the basic hydrodynamic parameters, i.e. holdup ϵ and the height of densely packed dispersion bed H , had been determined. Exemplary results for a constant organic to water phase ratio $O/W = 1:5$ are presented in Figs. 2 and 3 for columns I and II respectively. On the diagrams the total column loadings ($u_c + u_d$) were plotted on the abscissa axis against the parameters φ , H and ϵ successively.

The uranium extraction degree had been calculated from the following equation:

$$\varphi = \frac{c_F - c_R}{c_F - c_R^*}, \quad (1)$$

where c_F , c_R are uranium concentrations in the water feed phase and in raffinate phase, whereas c_R^* is the equilibrium concentration in raffinate phase related to the organic phase entering the column.

Fig. 2 a presents a comparison of uranium extraction efficiencies when first the organic and next the water phase were dispersed in the column of type I. When the organic phase was dispersed in the water phase a constant extraction degree of ca. 13% was obtained, independently of the column loading (line 1). In that case the column worked

with lessely packed dispersions. The efficiency of uranium extraction could be increased by about 4 to 6 times while working with densely packed dispersions (curve 2). This was possible when the water phase was the dispersed one. As is seen in Fig. 2a, the extraction efficiency in column I increased with increased total flow rates ($u_c + u_d$), whereas in column II this dependence is reversed, as shown in Fig. 3a.

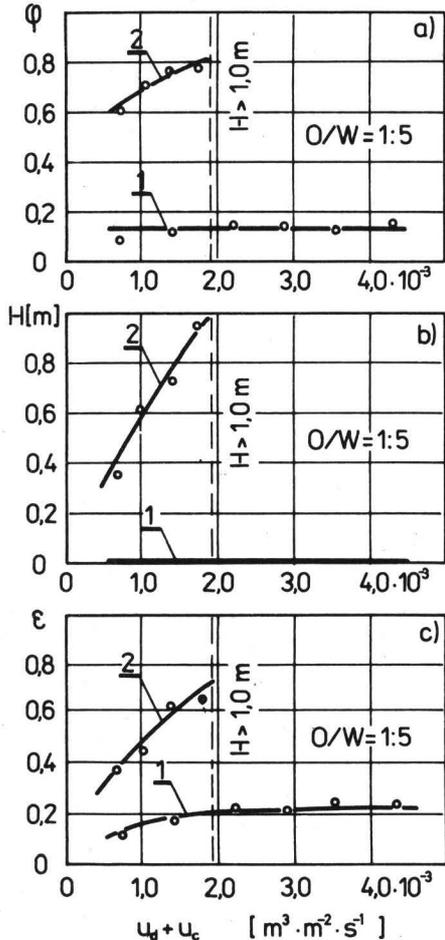


Fig. 2. Comparison of

- a - uranium extraction efficiency φ ,
- b - densely packed bed height H and
- c - holdup ε

for loosely and densely packed dispersion in column of type I.

- curve 1 - dense dispersions
- curve 2 - loose dispersions

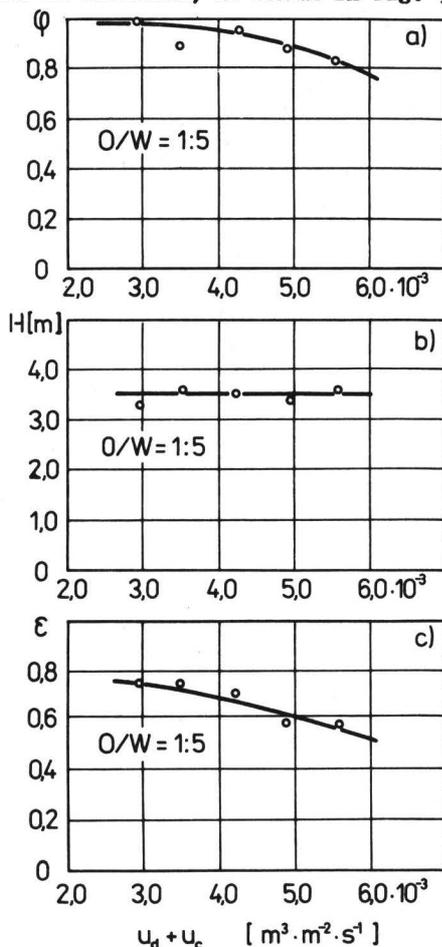


Fig. 3. Effect of total column loading ($u_d + u_c$) on

- a - uranium extraction efficiency φ ,
- b - height of the densely packed bed H and
- c - holdup ε ,

for densely packed dispersions in column of type II

This may be easily explained by the fact that in the smaller column the height of the dispersion bed increased (Fig. 2b) which caused also an increase in holdup values (Fig. 2c). On the other hand, the second column was operated with constant height of dispersion bed (Fig. 3b) and holdup values decreased under these conditions (Fig. 3c). Such a holdup dependence is characteristic for the operation with dense dispersions [1,3,4].

In the column of type I the bed of densely packed dispersion became established at a certain height for each pair of flow rates u_o and u_d , however the height could not be maintained constant for a long time. The gradual accumulation of impurities at the interface caused the rate of coalescence to change and thus, the height of dispersion bed to decrease with time. This inconvenience was eliminated in the bigger column, in which a conical bottom section was used. Such a construction made possible the easy control of coalescence rate at the interface and therefore, the easy maintenance of the dispersion bed at a constant height. This design was tested and worked extremely well.

Conclusions. A small coalescence ability, characteristic for uranium extraction systems may be utilized purposeful to create densely packed dispersions, which are characterized by low backmixing and high hold-ups of the dispersed phase. The results of mass transfer investigations showed that the uranium extraction efficiency could be increased by 4 to 6 times by applying the dense dispersions, in relation to the conventional extraction with loose dispersions. In columns of 1,0 and 4,0 m height which had been used in experiments the values of uranium extraction efficiency varied in the range 55-80% and 75-99% for the smaller and the bigger column respectively. High uranium extraction efficiency obtained in experiments may be interesting practically although columns of greater diameter should be tested before such an operation can be used industrially. It is planned to be done as soon as the corresponding equipment is obtained.

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A long termed research programm is in progres to ascertain the reduction of entrainment losses and capital costs. The separation of entrained organic phase was examined in the pilot plant with organic phase loop presented in Fig.1.

The extraction of uranium was performed in four stages countercurrent "pump-mix" mixer-settler. Continuous organic phase was synergistic mixture DEHPA (0,5 M) - TOPO (0,125 M) in kerosene and aqueous dispersed phase was phosphoric acid (30% P_2O_5).

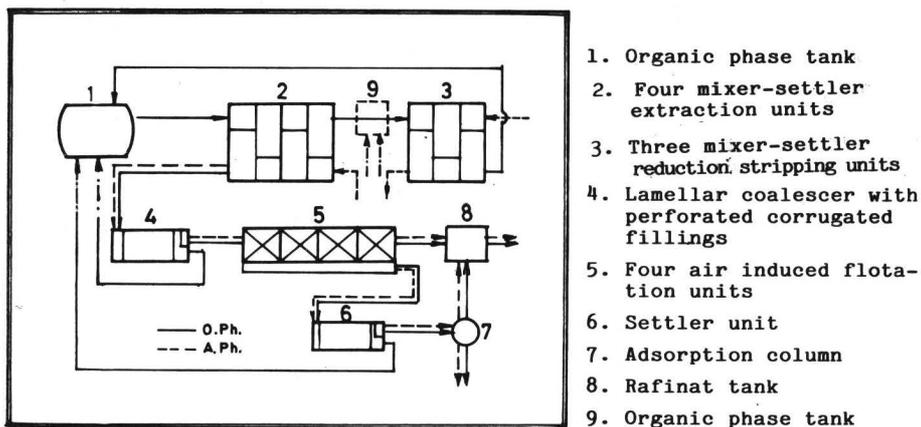


Fig. 1. Organic phase loop

The aqueous phase entraine, at 90% confidence, 533 ± 103 ppm of organic phase in mixer-settler units. The aqueous phase was lead in the lamellar coalescer which was chosen and designed (1,2,3,4,5) for the reasons of simplicity and possibility of direct scale up. Thereafter,, decrease of the organic phase content in the rafinat was effected in four air induced flotation units. The flotation overflow was split in the "settler" and aqueous phase part was lead in the adsorption column.

The separated organic phase contain some uranium and was lead back in the mixer-settler units for reductive stripping.

Determination of the entrained organic phase content was realised by following methods: gas chromatography (x) and centrifugal separation in the bottles with capillary tubes (y), (6). By gas chromatography beside the entrained organic phase the dissolved DEHPA and TOPO in the aqueous phase were determined. As their solubility is neglectible the correlation of these methods is possible. Regression analysis of 17 parallel measures give the following relation:

$$y = 0,75 X + 49,70$$

with correlation coefficient $r = 0,959$ what does mean that the confidence of the find relation is higher than 99,9%. The method of centrifugal separation (y) was used for the contents of organic phase in the range of 50-800 ppm (vol/vol) and the method of gas chromatography (x) for the contents of organic phase in the range of 20-70 ppm (vol/vol).

On the basis of the obtained results material balance for the raffinat and entrained organic phase is evaluated and presented in Table 1.

The efficiency of the lamellar coalescer unit was 62%. Thereafter, efficiency of the flotation units was 77%. Feed content in adsorption column was small; about 100 ppm (vol/vol) and it's efficiency was 63%. The overall efficiency of the examined conception for the separation of entrained organic phase was 91%.

The Fig.2. presents cross sections of designed lamellar coalescer as well as corrugated perforated filling plate. The air induced flotation units where of "Denver sub A N°5" type and the adsorption column was filled with activated carbon.

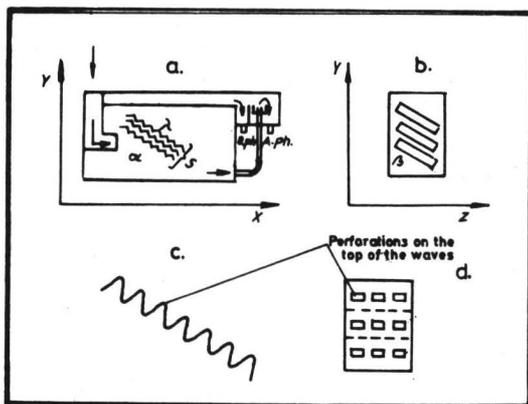


Fig. 2. Cross-sections of lamellar coalescer a,b and corrugated perforated filling plate c,d.

Table 1. The material balance for the rafinat and the organic phase

Equipment and place	Position on the Figure 1	Volume of the rafinate V(dm ³)	Distribution of the rafinate R%(vol)	Content of the organic phase in the rafinate OF%(vol/vol)	Volume of the organic phase V(dm ³)	Distribution of the organic phase R%(vol)
	(1)					
Coalescer	4	-	-	-	-	-
input	2.1.	111,0000	100,0000	0,0533	0,059163	100,00
underflow	4.1	110,9636	99,9672	0,0205	0,022755	38,46
overflow	4.2.	0,0364	0,0328	99,9999	0,036408	61,54
Four flota- tion cells	5	-	-	-	-	-
input	4.1.	110,9636	99,9672	0,0205	0,022755	38,46
underflow	5.1.	99,8672	89,9704	0,0040	0,003994	6,75
overflow	5.2.	11,0963	9,9967	0,1690	0,018760	31,71
Secondary coalescer	6	-	-	-	-	-
input	5.2.	11,0963	9,9967	0,1690	0,018760	31,71
underflow	6.1.	11,0887	9,8808	0,0100	0,001109	1,88
overflow	6.2.	0,0176	0,0159	99,9999	0,017650	29,83
Column with activated carbon	7	-	-	-	-	-
input	6.1.	11,0787	9,9808	0,0100	0,001109	1,88
output 1	7.1.	11,0780	9,9801	0,0037	0,000410	0,70
output 2	7.2.	0,0007	0,0007	99,9999	0,000699	1,18

According to the results obtained from such pilot plant the residual content of entrained organic phase, at 90% confidence, was 53±16 ppm (vol/vol), therefore the losses of organic phase were 8,63% (vol).

The challenge from the technical and economical point of view could be investigation of the new conception of organic phase loop. The substitution of the flotation units by densely packed coalescer could be examined. This question have to be realised with respect of specific characteristics of the (DEHPA-TOPO-kerosene) - phoshoric acid system.

The brife comparative analysis of this two methods will be discussed. The considerations affecting the choice of the method and equipment from the process, operation, design and economic points of view are presented in Table 2.

Table 2. Comparative analysis of selected methods

Methods for secondary separation	Flotation	Coalescence (densly packed)
Proces considerations		
- efficiency	- 75%	-90%
- residual content of entrained org.ph.	- 25-50ppm (vol/vol)	-20ppm (vol/vol)
Operation considerations		
- different characteristics	- requirement of stable feed content (one safety settler)	- sensitive to the temperature changes
	- separation of the flotation overflow (one "settler")	- sensitive on the occurance of stable third phase
	- sensitive to the temperature changes	- requirement of frequent regenerations
- throughput	- big	- small
- maintenance	- easy	- uneasy
Design considerations		
- information status	- lot of patents	- not enough
- improvements	- limited	- possible
Economic considerations		
- capital costs	- very high	- high

The answer which method is more convenient have to be searched on pilot-plant scale under consideration of all specific problems which could appear within the scale up.

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Introduction. We have recently studied the mutual influence of extraction of uranium (VI) and iron (III) and the effect of removal of iron from the organic phase before reextraction of uranium (VI) with ammonium carbonate solution in the process of uranium recovery from wet phosphoric acid (1).

The purpose of this investigation is to determine the conditions of uranium (VI) reextraction with ammonium carbonate from the organic phase obtained by the extraction of wet process H_3PO_4 , without previous removing of iron (III).

Experimental. Crystalline uranyl nitrate was used for all uranium solutions. Di-2-ethyl-hexyl phosphoric acid (D2EHPA) and trioctyl-phosphineoxide (TOPO) were provided as a high purity product by Mobil Oil Co. Organic solutions were prepared with D2EHPA and TOPO in nonaromatic hydrocarbon diluent Mobil 190/210 and by dissolving uranyl nitrate and Fe (III) chloride, and the solution was purified by multiple water washes. Aqueous solutions of selected concentration were prepared from the $(NH_4)_2CO_3$ analytical grade "Kemika" and carbamate solution from industrial plant Kutina (intermediate of urea). The measurements of distribution ratios were performed in the thermostated bath. Equal volumes of aqueous and organic solutions were mixed mechanically 10 minutes at $50^\circ C$. It has been previously established that the temperature does not effect the efficiency of reextraction, but influences only on the speed of phase separation. The concentration of U(VI) and Fe(III) in the aqueous and organic phases were determined by spectrophotometry (2).

Results and discussion. The dependence of distribution ratios on the concentration of ammonium carbonate is shown in the figure 1. Increasing ammonium carbo-

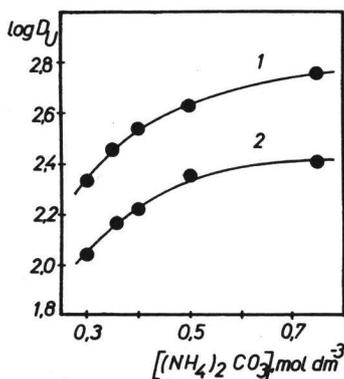


Fig.1. Distribution ratios of U(VI) vs. initial concentration of $(NH_4)_2CO_3$:
 1 "Kutina" and 2 anal. grade,
 $c_{U(VI)}^i = 3,4 \cdot 10^{-2} mol \cdot dm^{-3}$

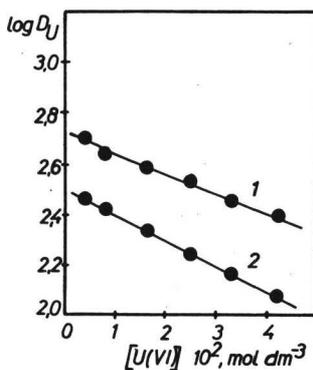


Fig.2. Distribution ratios of U(VI) vs. initial concentration of U(VI):
 $0,4M (NH_4)_2CO_3$; $c_{U(VI)}^i = 3,4 \cdot 10^{-2} mol \cdot dm^{-3}$

nate concentration results in the increase of distribution ratios in all cases. The effect of carbonate composition on the efficiency of reextraction is also presented. The values of distribution ratios of uranium are higher if the reextraction is performed with carbonate 1. The typical curves of dependance on the uranium concentration are shown in figure 2. The increase of value of distribution ratios of U(VI) at lower initial uranium concentrations is more expressed with carbonate 1.

Considering the results of previous investigations of U(VI) and Fe(III)coextraction (1) the dependence of uranium reextraction on the concentration of extractant has been tested. The values of U(VI) distribution ratios decrease with the increase of extractant concentration in both cases. (Figure 3).

The dependence of the distribution ratios of U(VI) on the phase volume ratio at various concentrations of ammonium carbonate are shown in figure 4. Further results have shown that with the phase volume ratio $aq = 2/1$ the efficiency of reextraction is $> 99\%$, if in organic phases Fe(III) is present or not. However, the Fe(III) which is present in organic phase causes the precipitation of $Fe(OH)_3$ in solutions of ammonium uranyl tricarbonate in the second or in the third stage. The precipitation depends on the concentration of Fe(III) in organic phase, concentration of aqueous phase and initial and equilibrated pH values.

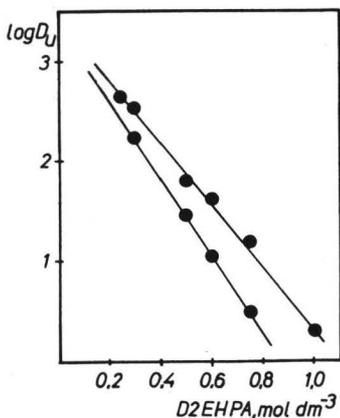


Fig.3. Distribution ratios of U(VI) vs. concentration of extractant: $0,4M(NH_4)_2CO_3$; $c_{U(VI)}^i = 3,4 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

The results show that for the optimal uranium reextraction it is necessary to control the pH values and to maintain them within the limits 8,0-8,4(3). The efficiency of reextraction is not satisfactory, below the value $pH=8$ and above $pH=8,4$ $Fe(OH)_3$ is being precipitated in the solution of ammonium uranyl tricarbonate (Figure 5, Table). In the figure 5 the slight decreasing of U(VI) distribution ratio caused by the presence of Fe(III) in organic phase is also visible.

The concentration profile of stationary state after twelve hours of continuous counter current extraction from $0,3M$ D2EHPA + $0,075M$ TOPO with $0,38M$ $(NH_4)_2CO_3$ in mixer settler units is shown in figure 6. The phase volume ratio is $o/aq=2,5/1$ and the reaction temperature (working temperature)

Multistage reextraction of U(VI) from 0,3M D2EHPA + 0,075M TOPO
 with 0,4M(NH₄)₂CO₃: o/aq=2/1, $c_{U(VI)}^i = 3,4 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$;
 $c_{Fe(III)}^i = 9,5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

Stage	D _U	D _{Fe}	pH init.	pHeq.	% reex. (I-III)
I	x _{0,040}	-	9,76	7,77	
	0,030	0,0004	9,76	7,76	
	0,003	0,0005	8,30	6,29	
II	x _{5,24}			8,15	
	4,16			8,12	
	0,08			7,53	
III	x _{314,0}	Fe(OH) ₃		8,56	99,95
	152,0			8,53	99,87
	5,2			8,01	83,39

x without Fe(III) in organic phase

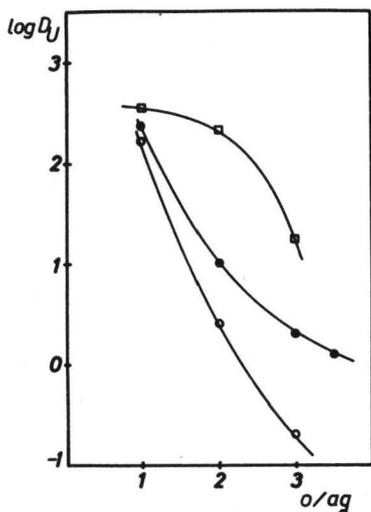


Fig. 4. Distribution ratios of U(VI) vs. phase volume ratio o/aq:

(NH₄)₂CO₃: ○ 0,4M; ● 0,5M; □ 0,75M

$c_{U(VI)}^i = 3,4 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

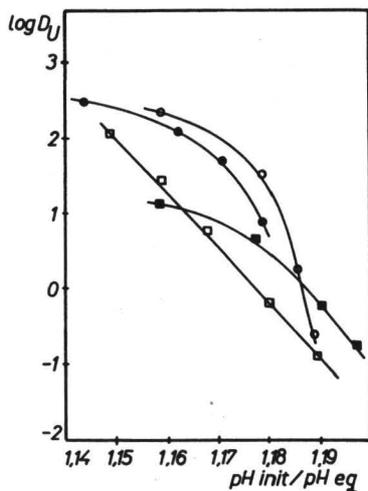


Fig. 5. Distribution ratios of U(VI) vs. pH init./pH eq. ratios:

0,4M(NH₄)₂CO₃: ● □ Kutina; ○ ■ anal. grade;

□ ■ $c_{Fe(III)}^i = 9,5 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$

○ ■ $c_{U(VI)}^i = 3,4 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

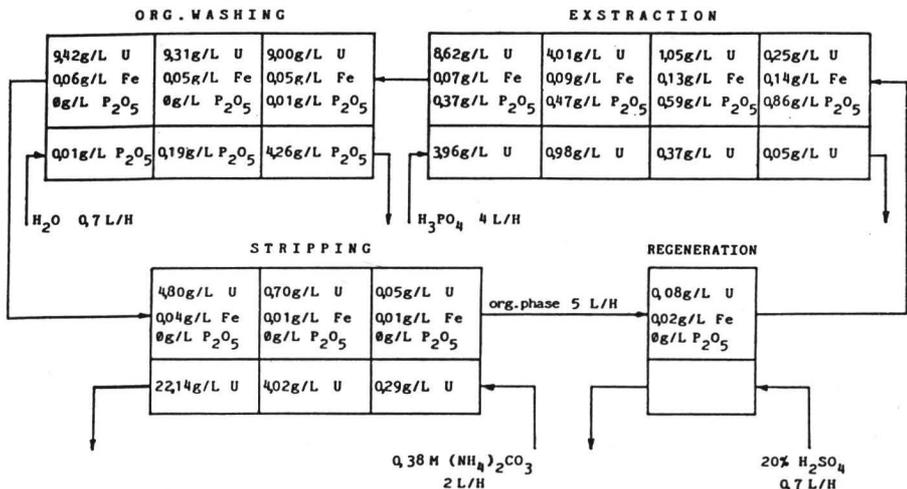


Fig.6. The concentration profile of secondary extraction/strip system

has been 49 to 50°C, and the pH values in the course of process have been maintained within the limits from 8 to 8,45. This has been achieved by adding 20% NH₄OH and HCl (1:1). The efficiency of reextraction has been 99% and the precipitation of Fe(OH)₃ in the solutions of ammonium uranyl tricarbonate has not been observed.

Uranium peroxidhydrate which has been precipitated from such obtained solutions has been of high purity.

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HYDROMETALLURGY

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INTRODUCTION. In this contribution the results of the experimental work on some liquid-liquid extraction processes for the recovery of gold from HNO_3/HCl leaching solutions of Au minerals are summarized.

The solvent extraction of gold from HNO_3/HCl solutions represents an alternative process when the cyanoalkaline leaching and the carbon-in-pulp adsorption cannot be employed. Some Cu, As and Sb containing pyritic minerals and some carbonious rocks need expensive roasting pretreatments and sometime do not allow an economic gold recovery [1] [2]. On the contrary, the aqua regia attack of these minerals permits good gold recoveries. Unfortunately selectivity problems, due to the presence of many dissolved chloroanionic complexes, can arise.

As gold extractants we have chosen a trialkylaliphatic amine, the TriOctylAmine (TOA) and a di-substituted aliphatic amide, the N,N-Di-n-ButylOctanamide (DBOA). Both extractants have been examined in batch and in mini mixer-settlers experiments using leachates of peruvian and bolivian concentrates. With these minerals, very rich in sulfur (pyrites, stybine), a 90-95% gold recovery in 12-24 hours has been reached, by leaching with 4M aqua regia (HCl 3M / HNO_3 1M) at room temperature and with a 1/3 solid/liquid ratio. On these leachate solutions (2-3M total acidity, 10-60 ppm of Au) the two processes with TOA (GAMEX PROCESS) [3] and with DBOA (AUMIDEX PROCESS) [4] have been tested and compared.

THE GAMEX PROCESS. This process, utilizes as solvent for gold extraction a solution of TOA in a commercial mixture of aromatic diluents. A 0.14 M (0.5%w) extractant concentration assures high separation factors from Fe(III), Sb(V), Zn, Cu, Pb, Sn and alkaline earths, and high Au loadings ($\approx 10\text{g/l}$). Tertiary amines are typical liquid anion exchangers [5]. Their selectivity can be attributed to the presence into the organic phase of $\text{TOA}\cdot\text{HNO}_3$, the predominant species in equilibrium with the 1:3 HNO_3/HCl leaching solutions. This species exhibits a high affinity for Au chlorocomplexes and a low extracting ability for chlorocomplexes of other metal ions.

Co-extracted metals are easily scrubbed from the organic phase with 0.5M HNO_3 . A 0.25M thiourea in 0.5M HCl stripping solution

allows a very good Au recovery in aqueous phase, followed by electrolytical precipitation to obtain a metal of high purity. With the flowsheet shown in Fig. 1, tested in laboratory scale mixer-settlers, a 99% Au recovery from very diluted feed solutions and elevated concentration factors have been reached.

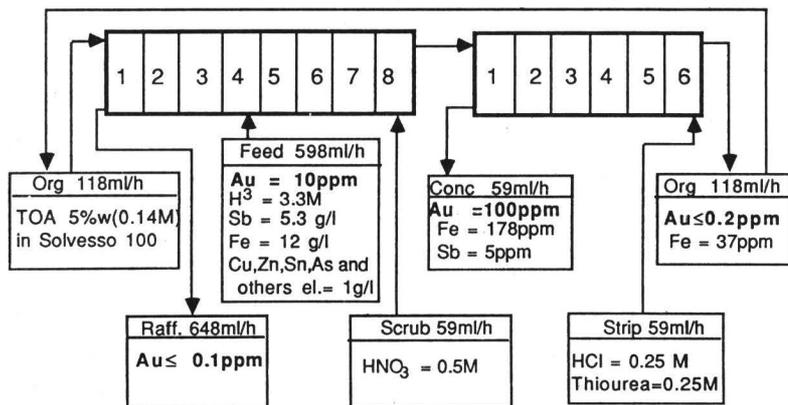


Fig. 1. THE GAMEX PROCESS WITH TRI-n-OCTYL AMINE

THE AUMIDEX PROCESS. This process is based on the use, as solvent, of a 0.2M (5%w) solution of N,N'-di-n-Butyloctanamide (DBOA) in mesitylene. This compound, also employed in U-Pu separations [6], is a powerful gold extractant from aqua regia solutions. The physical-chemical characteristics of DBOA are reported in Table. The

Physical-chemical characteristics of DBOA

N,N'-di-n-butyl octanamide has the following structure:

$$\text{CH}_3(\text{CH}_2)_6\text{-C(O)-N}(\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3)_2$$

It is a colorless mobile liquid with these characteristics:

Molecular Weight	255.45
Boiling Point	100-120°C (1mmHg)
Density	0.861g/l
Refractive index n_D^{20}	1.452

Solubility (moles/l at 21°C) in water: $2.3 \cdot 10^{-5}$; in n-dodecane: ∞ ; in mesitylene: ∞ .

It is prepared by reaction of octanoyl chloride and dibutyl amine (yield > 80%), but other preparation methods are available [6].

Chemical stability: N,N'-di-n-butyloctanamide is a very stable compound with regard to light, temperature and action of acidic or basic, oxidising or reducing agents.

The principal hydrolysis products are octanoic acid and dibutyl amine.

extraction ability of these substances is attributed to a solvation process similarly to other "oxygen donors" ligands like TBP. DBOA exhibits a good selectivity as shown by its extraction behavior with leachate solutions of gold containing minerals. Concentrated solutions of Fe(III), Hg(II), Sn(II), Zn, Cu are easily separated from gold in HNO₃/HCl solutions. As with tertiary amines the only troublesome ions are Bi(III) and Sb(III). In Fig.2 the flowsheet of the process is reported.

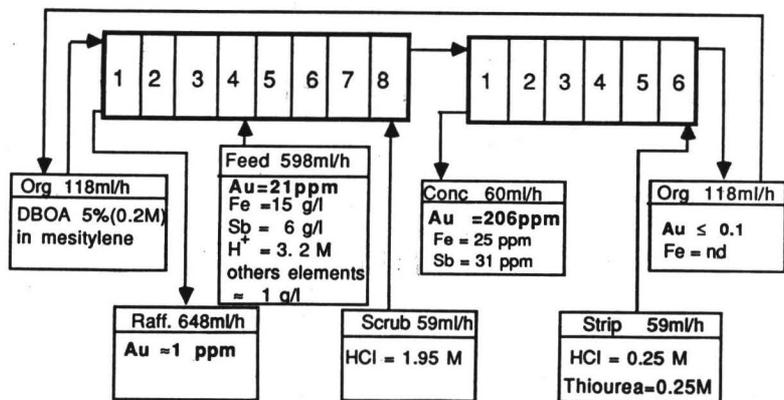


Fig.2. THE AUMIDEX PROCESS WITH N,N' DI n-BUTYL OCTANAMIDE

CONCLUSIONS. The results of the experimental work with TOA or DBOA as extracting agents of gold from acidic leachates, strongly support the possibility of using these extractants on an industrial scale. At laboratory scale both processes, tested with various leachates solutions obtained from different minerals gave at least a 98% gold recovery and concentration factors > 10. The tests were run with mini mixer-settlers and without reflux of the organic phase. With an appropriate "in stage" or "in battery" reflux the concentration factor may increase of one or two orders of magnitude.

Both extractants exhibit good stability toward chemical degradation. The introduction of 1-2 g/l of urea into the feed solution assures an even higher stability of the extractants and prevents the chemical attack of the diluent.

The main differences between the two flowsheets lies in the scrubbing sections. In the AUMIDEX process, the necessity to scrub with HCl solutions in order to keep the Au distribution ratio

sufficiently high, favorably affects the removal of the coextracted metals from the organic phase.

Fe(III) at high concentrations interfere with the gold separation process. However the different stability of the chlorocomplexes in aqueous phase allows high Au/Fe separation factors.

The presence of high concentrations of Bi(III) can also originate problems. A small amounts of EDTA in the scrub solution is effective in removing Bi(III) from the organic phase, thus reducing its interference.

The efficiency of gold reextraction from the organic phase with thiourea was excellent in both processes. The stripping kinetics was also adequate to obtain more than 98% of gold recovery in few stages.

The good hydrodynamic behavior of the phases in the mixer-settler experiments (fast transfer kinetics, no cruds at the interphase, no losses of organic phase for solubilization or entrainment) permits the organic phase recycling after a suitable solvent regeneration section. The use of mesitylene as diluent of the amide reduces the coalescence time of the phases.

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As part of a project to recover valuable materials from the residues arising from the chlorination of titaniferous ores, Warren Spring Laboratory was commissioned to study the feasibility of using solvent extraction for zirconium and niobium separation and recovery. The feed material for this study was a crude pulp produced by HCl dissolution of the chlorination residue followed by selective precipitation of the zirconium and niobium as sulphates. These pulps contained on a wet basis up to 10% Zr and 3% Nb; varying quantities of Ti, V, Fe, Cr as impurities; 3-5% sulphate and 0.15-0.25% chloride. The pulps were soluble in both HCl and H₂SO₄. Thus solvent extraction from both chloride and sulphate solutions had to be considered.

The Chloride System

From the literature [1] it was known that from HCl-HF mixtures niobium was readily separated from zirconium and titanium with a secondary amine, LAl. However for the current project the introduction of HF into the flowsheet caused problems because of the need for complete HF recovery and recycle. Consequently this approach was not examined in any detail. Preliminary testwork on the extraction of zirconium and niobium from chloride solution with amines, Table, showed that high extraction could only be achieved at high chloride concentrations with tertiary and quaternary amines

Extraction of Zirconium and Niobium from Chloride Solution with Amines

Feed Solution: Approx 13 g l⁻¹ Zr and 4.9 g l⁻¹ Nb as Cl⁻ (HCl + MgCl₂)

Extractant : 30% amine in Solvesso 150; Modifier - Isodecanol, 10%

Amine	Cl ⁻ in Feed soln.	Extraction %		Separation Factor, Zr/Nb
	M	Zr	Nb	
Primene JMT	8.6	0.0	0.0	-
	10.5	1.9	16.9	0.098
	12.0	14.5	38.9	0.266
LA-2	8.6	0.0	0.0	-
	10.5	8.9	16.0	0.51
	12.0	33.7	34.9	0.95
Alamine 336	8.6	19.7	6.7	3.1
	10.5	68.3	22.6	7.3
	12.0	87.4	46.7	7.9
Aliquat 336	8.6	13.9	5.9	2.4
	10.5	78.4	20.0	13.1
	12.0	93.1	39.5	20.7

which showed moderate selectivities for zirconium which increased with increasing chloride concentration. No vanadium or chromium were coextracted but iron was strongly coextracted. Although the results of this work looked promising HCl/Cl⁻

would need to be recycled to minimise process costs. To do this Nb must first be removed and it is not clear how this can be done effectively and completely from the zirconium extraction raffinate. Furthermore, the feed liquor contains appreciable amounts of SO_4^{2-} which will build up on recycle and would have to be removed by precipitation to maintain the chloride system. Thus this approach was also abandoned.

While the literature [2-4] reports favourably on the use of alkyl phosphorous acids for selective zirconium extraction, preliminary testwork with both chloride and sulphate pulp leaches showed considerable crud formation and very poor phase breaks. Consequently this approach was not pursued.

Tributyl phosphate on the other hand gave excellent and selective extraction of zirconium from niobium from chloride solutions but because of the reported rapid degradation of TBP to n-butyl chloride in the presence of HCl solutions containing zirconium [5] this approach, too, was abandoned.

The Sulphate System

Unlike the extraction behaviour found in the chloride system, amines were found to extract both zirconium and niobium from low strength sulphuric acid solutions. Comparative tests on liquors produced by H_2SO_4 leaching of the pulps showed that Primene JMT gave the best performance, closely followed by Alamine 336. Both the secondary amine LA-2 and the quaternary amine Aliquat 336 gave inferior performances, Fig 1. The separation factor for Zr from Nb at leach acid concentrations of 2M and 3M H_2SO_4 was ~ 31 with a Zr extraction of $\sim 70\%$ for Primene JMT. Thus this reagent was selected for further study. Distribution isotherms were developed for zirconium using both the acid treated and free base forms of the extractant. The feed liquor for this work contained 21.9 g l^{-1} Zr, 6.7 g l^{-1} Nb, 5.6 g l^{-1}

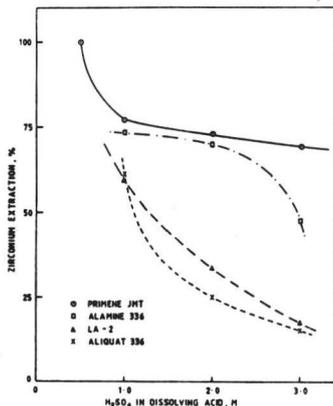


Fig.1. Extraction of zirconium from sulphuric acid solutions of a mixed Zr/Nb feedstock with amines. Extractant: 30% amine in solvesso 150; modifier, isodecanol, 10%

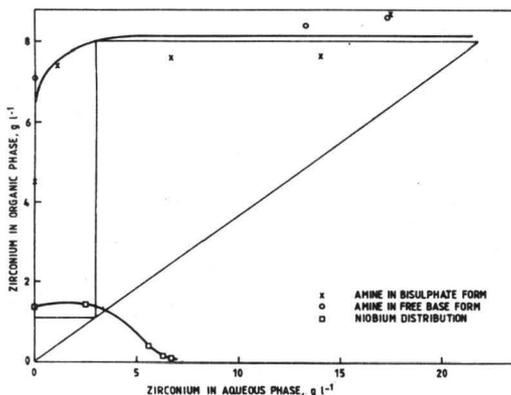


Fig.2. Zirconium and niobium extraction isotherms from sulphate solution with Primene JMT. Extractant: 30% Primene JMT in solvesso 150; modifier: 10% isodecanol; feed Zr 21.9; Nb 6.7 g l^{-1}

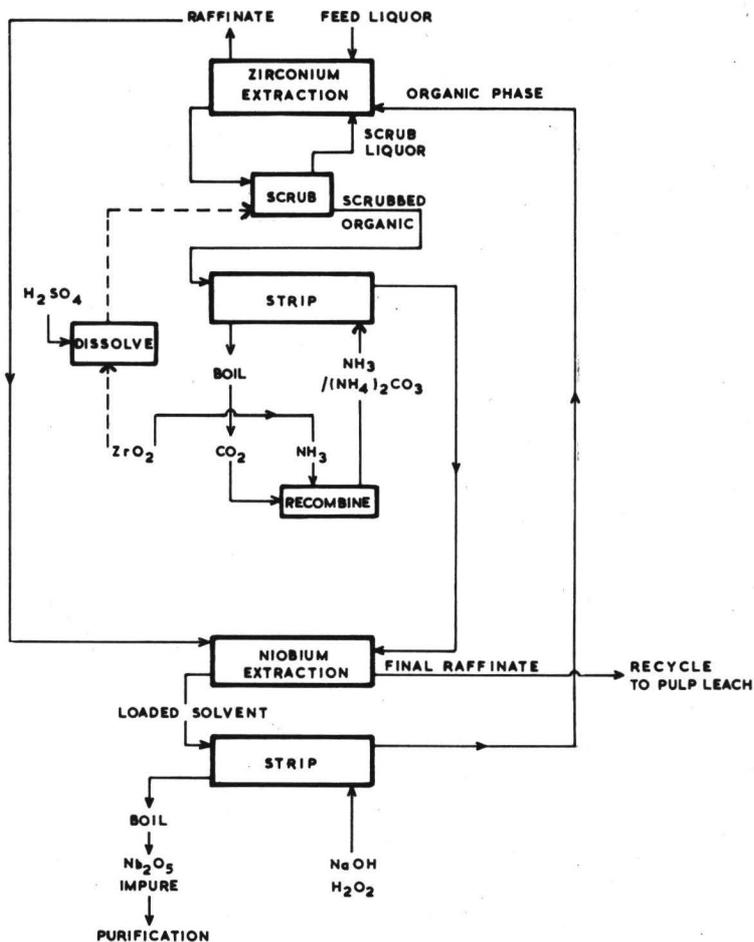


Fig. 3. Suggested flowheet for the separation and recovery of zirconium and niobium

Ti, 0.3 g⁻¹ Fe, 0.5 g⁻¹ Cr. Both modes of operation gave organic phase loadings of > 8 g⁻¹ Zr for 30^{v/o} Primene JMT in Solvesso 150 with 10^{v/o} isodecanol as modifier, Fig 2. No significant difference in separation factors between the two systems was noted. In presence of a large excess of organic phase, titanium, iron and chromium were all extracted with the zirconium. On increasing the ratio of aqueous to organic phase (A/O), however, these metal ions could be effectively crowded out of the organic phase. A McCabe Thiele construction on Fig 2. shows effectively 100% Zr removed in 2 stages. Coextracted niobium could be effectively scrubbed from the organic phase with a scrub feed containing 16.3 g⁻¹ Zr in 2M H₂SO₄ at an A/O ratio of 0.1 in two crosscurrent stages.

Stripping of the zirconium from the loaded organic phase could be carried out in several ways. Sodium carbonate (2M) gave 95% recovery in a single stage while 3M HCl gave 98% recovery in a single stage also. In practice an ammoniacal/ammonium carbonate strip would be favoured as the ammonia and carbon dioxide could be thermally released, collected and recombined for recycle thus precipitating a ZrO_2 product, a small portion of which could be redissolved in H_2SO_4 for scrubbing purposes.

Although little work was carried out on this aspect, niobium was readily extracted with Primene JMT from the raffinate from zirconium extraction. From other work [6] niobium can be readily stripped from the loaded organic phase using a $NaOH/H_2O_2$ strip. Thermal decomposition of the peroxy complex will yield an impure Nb_2O_5 product which can be further purified by conventional means.

Thus a tentative flowsheet for processing the Zr/Nb pulps produced from the liquor obtained from leaching the residues from chlorination of titaniferous ores can be envisaged as in Fig 3. From the available data about two extract stages, two or three scrub stages and two strip stages would be required for the zirconium circuit and the proposed flowsheet is considered to be technically feasible. The authors acknowledge the financial support of Tioxide (UK) Ltd for this work.

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The separation process of counter current extraction is an effective method for separating and purifying substances, and it is widely used for the separation of rare earths. However, for a given process, only two components can be separated. When it is used for multi-component systems of rare earths, more separation processes will be needed, and the separating circle must be very long. Literature [1] reported a three-exit method in which three components can be separated simultaneously, and the separation results of La-Pr-Nd were published. During the same time, we put forward another kind of three-exit extraction separation technique [2], and with this technique, the separation experiment in the system of (Gd-Tb-Dy)Cl₃-HCl-HEH(EHP)-Kerosene was carried out.

1. Experiments

Extractant: ammoniated HEH(EHP)-Kerosene

Aqueous feed: mixed rare earths chloride solution, Tb₄O₇ 5%

Scrubbing solution: HCl, 1.0-3.0 mol/l

The separation experiment of Gd-Tb-Dy was carried out in separatory funnels. The rare earth concentrations were analysed by EDTA capacity method. The compositions of rare earths both in feed and in stages were analysed with VF-320 X-ray fluorescence spectrometer. The purities of the outlet products were determined by GPS-2 emission spectrometer.

2. The process of three-exit extraction separation technique

In order to improve the separation efficiency for rare earths, a three-exit extraction separation technique, based on experiments and computer simulation, has been developed (Fig.1).

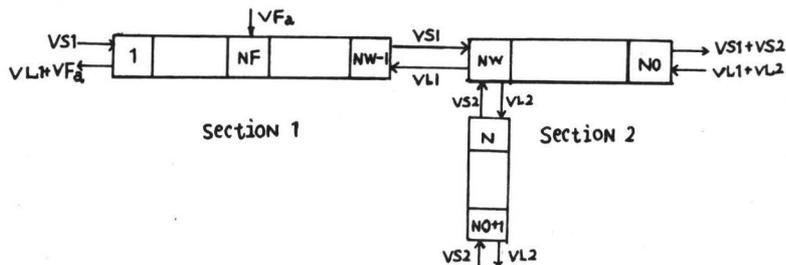


Fig.1. The scheme of three-exit extraction separation

NF, N - the feeding stage number and the total stage number
 1, NO+1, NO - the first, second, and third exit stage numbers
 NW, VF_a - the back flowing stage number and the volume of aqueous feed
 VS₁, VS₂ - the volumes of extractant
 VL₁, VL₂ - the volumes of scrubbing solution

3. Separation of Gd-Tb-Dy with the three-exit technique

Stage numbers: N=38, NF=11, NW=19, NO=30

Flow ratios: VF:VS1:VS2:VL1:VL2=6.6:18.4:5.4:4.0:4.5

The separation results are shown in Table 1 and Fig.2-3

Table 1. The purities of the three outlet products

Exit	(La-Gd)%	Tb%	(Dy-Lu)%
1	99.99	0.01	/
2	3.34	68.90	27.76
3	/	0.20	99.80

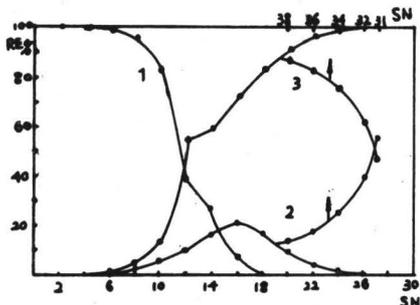


Fig.3. The compositions of rare earths in organic phase
1 - (La-Gd)%; 2-Tb%; 3 - (Dy-Lu)%

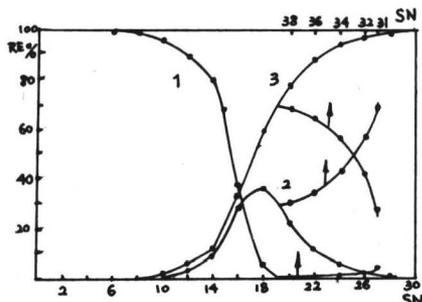


Fig.2. The compositions of rare earths in aqueous phase
SN - stage number; 1 - (La-Gd)%;
2 - Tb%; 3 - (Dy-Lu)%

4. The advantages of the three-exit technique

From Fig.1-3, it is seen that stage 1-18 (section 1) functions as a process of Gd-Tb separation, stage 19-38 (section 2) acts as a process of Tb-Dy separation. But the three-exit process is not simple combination of the two processes. There are two main differences between them. The first is that, the scrubbing solution for section 2 includes the solution for section 1, thus the rescrubbing ratio of section 2 is larger than that of commonly used Tb-Dy separation process, and the number of stages can be reduced. The second difference is that in stage NW-1, the scrubbing solution for section 1 contains rare earths. This results that the concentrations of rare earths in scrubbing section for section 1 are larger than that of general Gd-Tb separation process, so the number of stages can be further reduced.

Acknowledgement

We are indebted to Chunfu He, Hongxing Ren, Yulan Tong and Xuedong Liu for providing X-ray fluorescence analysis.

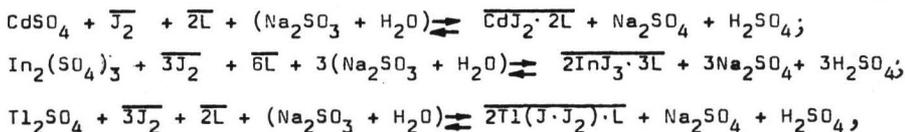
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The use of extraction methods has resulted in effective evolution of rare and dispersed elements from the complex salt solutions of lead-zinc production. Indium, thallium and cadmium obtained after hydrometallurgical treatment of lead powders were suggested to be extracted with tributyl phosphate containing molecular iodine /1,2/. To form extracted complexes reactant-reductant of iodine, e.g. sodium sulfite, is introduced into the extraction system. Then the extraction process is described by the following reaction equations:



where: L - (RO)₃P(O)R_{3-n}; R = C₄H₉ + C₈H₁₇; n = 0 + 3.

In organic phase mononuclear nonhydrated complexes of nonelectrolytes (CdJ₂L₂), (InJ₃L₃) and (TlJ₃L) are formed. Tautomeric equilibrium exists in organic phase /1/:



Extraction by 1,8 M solution of tributyl phosphate, containing 0,35 M J₂, in kerosene allows during 6-8 countercurrent stages to extract in organic phase more than 99,9% of thallium, 99,5-99,9% of cadmium and 92-96% of indium. To avoid the formation of thallium precipitation the equilibrium organic phase must contain not less than 0,1 M of free molecular iodine. Separation coefficients of Cd-Zn, Cd-Cu are at the level of 50, and Cd-Fe(II), Cd-As(III) and Cd-Sb(III) at the level of 10³. Separation coefficient for Tl-Zn is more than 10⁴.

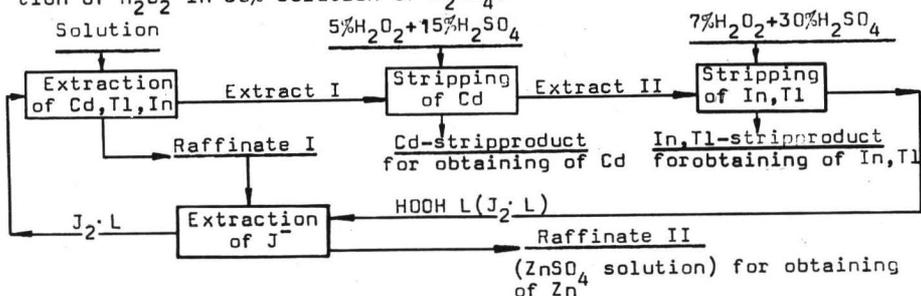
The stripping of elements may be carried out using sulphate hydrogen peroxide solution. For example, stripping of cadmium may be described by the equation:



Table 1. Effective extraction constants (LgK) of $(MeL)_q J_n$ complexes at 25° C (diluent - n-octane, R = C₄H₉)

L	lgK		
	TlLJ ₃	CdL ₂ J ₂	InL ₃ J ₃
(RO) ₃ PO	8,7·10 ⁷	3,9·10 ⁴	1,9·10 ³
(RO) ₂ P(O)R	1,3·10 ⁸	9,5·10 ⁴	8,3·10 ³
(RO)P(O)R ₂	1,7·10 ⁸	2,5·10 ⁵	4,9·10 ⁴
R ₃ PO	2,3·10 ⁸	6,6·10 ⁵	3,4·10 ⁵

Varying H₂SO₄ and H₂O₂ concentration the selectivity at stripping may be achieved. Values 95-97% of cadmium is stripped with 5% solution of H₂O₂ in 15% solution of H₂SO₄, and then values 98-99% of indium and thallium are hollowed out from organic phase with 7% solution of H₂O₂ in 30% solution of H₂SO₄.



Technological diagram of the extraction of cadmium, thallium and indium.

Table 2. Compositions of products in Cd, Tl, and In-extraction from zinc sulphate solutions

Product	Concentration, g/dm ³								
	Zn	Cd	Tl	In	Fe(II)	As(III)	Sb(III)	J ⁻	H ₂ SO ₄
Solution	60-80	1-15	0,3	0,1	2-10	1-5	0,25	0,01	15-25
Raffinate I	60-80	0,2	0,01	0,005	2-10	1-5	0,25	0,01	20-35
Raffinate II	60-80	0,1	0,005	0,005	2-10	1-5	0,25	0,01	25-40
Cd-strippingproduct	2-3	120-150	0,02	0,005	0,1	0,1	0,01	0,01	15-20
Tl, In-strippingproduct	1-2	1,0	8-20	2-6	0,1	0,05	0,01	0,01	280-320

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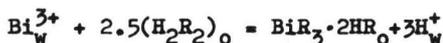
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Hydrometallurgic methods of bismuth extraction are based on the nitrate and chloride solution processing [17]. Nitric acid is the best solvent for metallic bismuth, its alloys and compounds. For leaching of bismuth bearing ores and concentrates one generally uses hydrochloric acid, mixtures of HCl and CaCl₂ or H₂SO₄ and NaCl. Thus obtained nitrate solutions contain (g/l): 1-10 Bi, 4-40 Pb, 0.2-1 Ag, 0.15-0.4 Cu, 0.01-0.05 Zn, 0.0005-0.002 Fe, 5-40 HNO₃, and chloride solutions contain: 1-3 Bi, 1-2 Cu, 1-2 Pb, 0.5-1 Zn, 3-6 Fe, 0.02-0.05 As, 60-80 Cl.

These solutions should be treated by the liquid-liquid extraction technique to obtain better concentration and purification degree.

The comparison of cation exchange, neutral and anion exchange extractants capacity has shown that the first ones are of practical interest while treating nitrate bismuth bearing solutions. These extractants provide bismuth concentration and purification and allow quantitative reextraction with diluted solutions of mineral acids. Bismuth distribution coefficients are reduced in series of dialkyldithiophosphoric > dialkylthiophosphoric > thionaphtenic > alkylphosphoric > dialkylphosphoric acids > alkylmercaptanes > naphtenic > carbonic acids. To increase sharply the extractant capacity it is necessary to substitute sulphur for oxygen in it. Thus, on di-2-ethylhexylphosphoric acid (D2EHFA) transition to di-2-ethylhexyldithiophosphoric acid (D2EHDTPA) the bismuth extraction constant increases 16 orders ($\lg K_{D2EHFA} = 3.4$, $\lg K_{D2EHDTPA} = 19.5$) when using octane as a diluent.

The D2EHFA solution in kerosene was taken as an extractant to treat bismuth containing nitrate solutions. Bismuth extraction from HNO₃ solutions with D2EHFA may be expressed as:



with constant $K = \frac{D}{F} \frac{[\text{H}_w^+]^3}{[\text{H}_2\text{R}_2]_o^{2.5}}$, where F accounts for Bi and

nitrate ions complex formation. In technological solutions nitrate-ion concentration is 3-4 M and for extraction of Bi

with $D_{Bi} \sim 10$ one should take an extractant with lg K equal to 3. For dialkylphosphoric acids if heptane acts as a diluent, Lg K is equal to 3.3 (D2EHPA), 4.3 (DBPA), 4.7 (IDAPA), 4.8 (DAPA), 4.9 (DHPA), 5.1 (DDPA).

The advantage of D2EHPA over extractants of other classes is Bi reextraction by relatively diluted HNO_3 solutions, as well as a possibility of its effective purification from impure metals (Pb, Cu, Ag, AZn, Ca, Mg, Na, etc.) both during Bi extraction and organic phase washing with diluted (0.2-1.0 M) HNO_3 solutions [27]. The 3-5% TBP addition to the D2EHPA solutions in kerosene has accelerated the process of phase separation and slightly increased D_{Bi} . That is why the given mixture may be used for bismuth extraction from HNO_3 solutions with a higher (to 4 M) concentration.

Bi may be reextracted from organic phase with 2.5-5.0 M HNO_3 or 1-3 M HCl solutions. Since Bi forms stable water phase complexes with nitrate and chloride ions, it is advisable to carry out Bi reextraction from the cation exchange reagents with a mixture of an acid and its ammonium salt [37].

This decreases acid and alkaline reagent consumption during the reextract processing.

Industrial tests has showed the possibility of complex processing of bismuth-, lead- and silver-containing nitrate solutions. In this case bismuth was extracted by the mixture of di-2-ethylhexylphosphoric acid and 3-butylphosphate, while silver was extracted by di-2-ethylhexeldithiophosphoric acid.

Comparison of extractants of different classes has shown that neutral extractants may be effectively used to treat chloride solutions that were obtained during the copper-bismuth concentrate leaching. In this case bismuth distribution coefficients are reduced in series of: threooctylphosphin oxide > dioctylsulfoxide > oilsulfoxide > threobutylphosphate > hexacyclic > methylisobutylketone > dioctylsulphide > n-octanoic n-hexanoic > isoamilic alcohols > dibutyl ether. TBP was used to extract bismuth from chloride solutions [47]. D_{Bi} is high (10) in the 10-80 g/l acid concentration range; D_{Bi} reduces when HCl content increases (Fig.2).

Bi purification can be carried out on its extraction from diluted (5-10 g/l) HCl solutions as at these conditions Cu, Fe, Zn, Pb and As distribution coefficients are 10^{-1} . At Bi reextraction by hydrochloric solutions of ammonium chloride it is possible to concentrate it and purify from Fe and Zn impurities since D_{Fe} and D_{Zn} are higher then D_{Bi} in this case. Bi can be

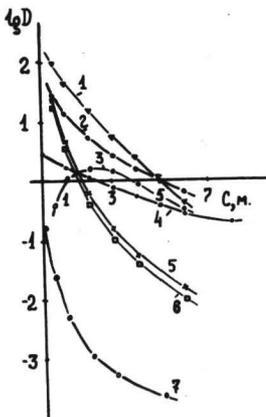


Fig. 1

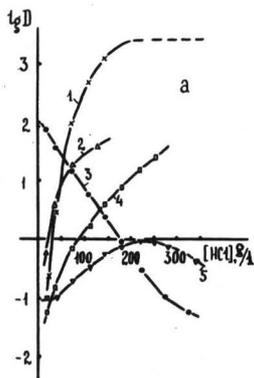


Fig. 2

Fig. 1. Bi extraction from HNO_3 solutions with D2EHPA, TBP and their mixtures, and its reextraction by ammonium salt (4,7), E, M.; 2,0 D2EHPA, 33% TBP (1); 1,0 D2EHPA 67% TBP (2), 100% TBP (3); 1,0 D2EHPA, 5% TBP (4,7); 1,0 D2EHPA, 7% TBP (5); 1,0 D2EHPA (6); (4-7)-dilution - kerosene. 3 g/l Bi_w (1-3,5,6), 24 g/l Bi_o (4,7), 4 - NH_4NO_3 (1,1 M HNO_3), 7 - NH_4Cl (0,8 M HCl)

Fig. 2. Extraction of Fe (III) (1); Zn (2); Bi (3); As (III) (4); Cu (5); Pb (6) with TBP from solutions of HCl (a) and NH_4Cl (70 g/l HCl) (b); $[\text{Me}]$ 1 g/l

obtained as a hydroxide on processing the organic phase with the equivalent volume of sodium hydrate solution (40 g/l).

The method of bismuth oxide production from Cu-Bi concentrates (0.4-0.6% Bi) based on Bi leaching with the hydrochloric acid at L:S = 2:1 and temperature $90 \pm 3^\circ\text{C}$ followed with its concentration and purification by TBP extraction has been industrially tested [5].

Extraction can be used to determine Bi in different materials and technological solutions, while Bi extraction with diluted cation exchange reagent D_{Bi} comes to 10^3 and this allows to avoid impurity influence on Bi determination. Bismuth is extracted quantitatively ($D_{\text{Bi}} \geq 10^3$) by the 0,05 N D2EHDTPA solution from 0,1-8,7 M HClO_4 , 0,1-10 M H_2SO_4 , 0,1-6 M HNO_3 , as well as from 0,1-6 M HCl and 0,1-4 M HBr solutions, in which Bi forms stable halogenide complexes. During extraction by D2EHDTPA or its salt (indium, plumbate) Bi can be separated from alkaline, alkaline-earth, rare-earth elements, Al, Ga, Ti (IV), Zr, Cr (III), Mn (II), Fe (II), Fe (III), As (V), As (III),

Zn, Cu, Cd, Tl (I), Sn (II), Co, Ni, Ag, Au (I), Hg (II). In this case Bi may be determined directly in the organic phase by adsorption of its dialkyldithiophosphate (as 330 nm $Bi_{0} \geq 1$ mkg/ml and 400 nm $Bi_{0} \geq 5$ mkg/ml). At the D2EHPA extraction from diluted (0,1-1 M) acid solutions Bi can be quantitatively separated from alkaline, alkaline-earth elements, Zn, Cd, Ni, Co, Cu, Fe (II), Cr (III), Mn (II), As (III), As (V), Pb and during reextraction it may be separated from In, Ga, Tl (III), Fe (III), Sn (IV), Sb (III), which are extracted together with Bi. At D2EHPA extraction Bi may be defined in reextracts (4-6 N HNO_3 or 7-8 M H_2SO_4) by the iodate method directly in the organic phase adding dithizone, catechold violet, 1-2-pyridylazo-2-naphtol, methyltymol blue and thiourea to Bi-containing extract. Besides the extraction - photometric method Bi determination at D2EHPA and D2EHDTPA extraction is possible by the atomic absorption method, and by spraying an extract in the air-acetylene flame.

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For the last years, low-grade ores and ores that are more difficult to be upgraded have been involved in copper processing which affects the quality of cathode copper. One of the most harmful impurities accumulated in the electrolyte is arsenic, and one of the most effective methods of its removal is solvent extraction [1, 2]. The method is already used in industry [3, 4]. When copper is electrolytically processed, arsenic occurs in the sulphuric acid solutions in the form of arsenic acid and is only quite effectively extracted by undiluted TBP.

When using such extractant, one has to deal with a very slow emulsion separation process during the extraction and stripping stages. The utilization of centrifugal extractors in this case is superior to any other type of extractors. The high capacity, low extractant volume and its minimum losses, characterize the centrifugal extractor.

The present paper considers the results of semi-industrial testing of copper electrolyte purification in centrifugal extractors. Design features and technical characteristics of a single-stage extractor, which has a rotor diameter of 125 mm (CE-125), used in the study are described previously [5]. The extractor (Fig.1), consists of a fixed body 1, in which a rotor unit 6 with drive 5 and bearing-support 4 are placed. The feed solutions are fed to the mixing chamber 9 where they are mixed with a stirrer 8. The resulting emulsion is fed to the rotor by a screw pumping device 7, where it is separated under the action of centrifugal forces. The separated liquids are directed into the circular collectors 2. Then they gravitate from the collectors to the adjacent extractor. The location of the interface in the separation chamber is provided by the selection of diameter of the overflow ring 3, installed at the heavy phase outlet. It was preliminarily determined that arsenic extraction with 100% TBP and stripping with water are proceeding very rapidly: one second phase contact is sufficient to reach equilibrium. The extraction is increased with the growth of aqueous phase acidity (Fig.2) and with the decreasing of temperature (Fig.3). The conditions of purification processing were established on the basis of enlarged laboratory study with a CE-33 [6].

The semi-industrial testing was carried out on an installation comprising six CE-125: 4 - on extraction and 2 - on stripping. The electrolyte after filtration is corrected with a view to reach a sulphuric acid contents up to 170 - 180 g/l and is fed to the fourth stage of the extraction cascade. The extractant is fed to the first stage. Stripping is carried out with water of a temperature of 40 - 50°C which is fed to stage 6. The batchwise washing of extractant from acid products of its hydrolysis is done by a 1-2% soda solution in two CE-125. On the basis of phase entrainment, the capacity of the whole installation is approximately equal to 0.5m³/hour and is determined

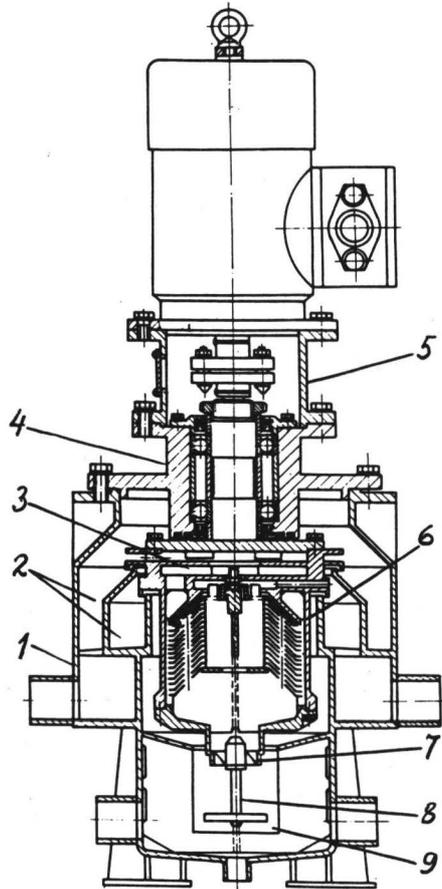


Fig.1. Centrifugal Extractor

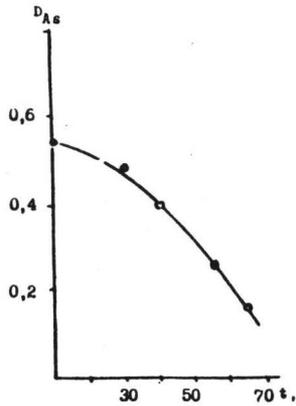
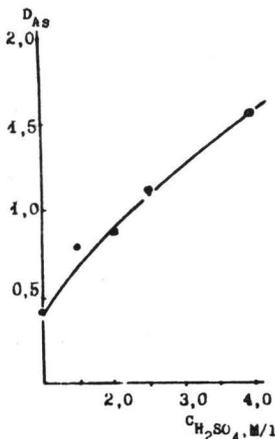


Fig.2. Effect of copper electrolyte acidity on arsenic extraction by TBP

Fig.3. Effect of temperature of arsenic extraction by TBP

by the operation of extraction. The phase entrainment on each stage was not higher than 0.05% when the ratio O:A = 1 and the temperature of the solution equals to 30 - 45°C. Increasing O:A up to 3 and simultaneously decreasing the temperature to 23 - 25°C leads to a rise of extractant entrainment into the electrolyte up to 0.5%. This is the result of temperature decrease, as well as the inversion of emulsion-type in the mixing chamber [7].

The characteristics of the feed solutions and the distribution of arsenic on process flow are presented in the table. One can see that increasing the electrolyte acidity from 95 - 110 g/l to 170 g/l, leads to an increase of arsenic extraction from 45 - 56% to 70 - 75% (when the ratio O:A equals 1.5). Increasing the flow ratio up to 2 leads to a higher extraction of 80%. The contents of arsenic in purified electrolyte - when the sulphuric acid concentration is 170 g/l - is in average 2.6 g/l which corresponds to a separation factor of 3.7. Its contents in the recirculated extractant reaches 0.15 g/l or 2.3% from a total contents in the feed solution. Copper and sulphuric acid contents in the arsenic strip solution are 1.1 g/l and 31.3 g/l corresponding 3.0 and 18.4% accordingly and can be returned into the process by the additional operation of extractant scrubbing.

A long-time operation of this installation shows reliable work of the centrifugal extractors and good purification of copper electrolyte from arsenic.

Characteristics of Feed Electrolyte and Distribution of Arsenic Among Flows

Feed electrolyte			Raffinate	Strip	Recirculated Extractant	Volumetric flow ratio O:A		
Concentration g/l			As	As	As	extraction	stripping	
H ₂ SO ₄	Cu	Ni	As	As	As	As	As	
110,3	-	-	11.4	6.2	4.8	0.01	1.5	1.5
95,6	-	-	13.0	5.3	7.7	0.5	2.0	2.0
97,0	-	-	11.3	7.7	8.3	0.8	1.0	2.0
136,2	33.7	15.5	8.1	4.5	3.2	0.04	1.5	1.0
169,0	38.1	16.2	9.3	2.8	5.6	0.2	1.5	1.5
170,0	33.7	14.6	8.2	1.7	7.0	0.4	2.0	2.0
172,0	41.1	20.3	9.8	3.1	7.0	0.05	1.5	1.5
170,0	-	-	9.3	2.3	6.5	0.1	1.5	1.5
173,0	34.3	-	9.0	2.2	6.6	0.2	1.5	1.5

Note: The temperature of all flows is 25-33°C, except arsenic strip which is 37 - 46°C.

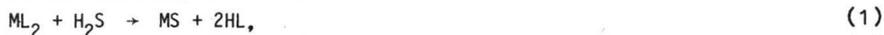
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Summary. It is possible in some solvent extraction systems to strip loaded organic with hydrogen sulphide giving a sulphide precipitate and regenerated extractant. Situations in which this technique could be considered are briefly discussed. Data are presented showing the response of several chelates of KELEX 100 to sulphide stripping using hydrogen sulphide at elevated temperatures.

Introduction. Many solvent extraction circuits incorporate acid stripping of loaded organic followed by metal electrowinning. Alternatively, it is sometimes possible to precipitate metal sulphide powder from loaded organic using hydrogen sulphide [1], or metal powder directly using hydrogen [2,3,4]. Examples of the relevant reactions for metal M loaded into extractant HL are:



The circumstances in which reactions 1 and 2 might be technically and economically feasible involve many factors. The stripping reaction must simultaneously produce powder and regenerated extractant at acceptable rates and yields. Also, the organic structure must be stable under the stripping conditions, while the powder product should be readily filterable.

Assuming the above criteria are satisfied, sulphide stripping in particular could be a viable option when the loaded organic contains small concentrations of a high value metal with a redox potential at which hydrogen reduction is not possible. Dissolution of the sulphide product in a small volume of acid would give higher metal concentrations for subsequent purification and electrowinning than obtainable by acid stripping. In addition, some metal separations may be possible through selective precipitation as sulphide.

The work described below concerns the sulphide stripping of gallium, aluminum and sodium loaded separately into an alkylated 8-hydroxyquinoline (KELEX 100 - Schering Aktiengesellschaft). These systems were chosen because, firstly, KELEX 100 has good thermal stability at the elevated temperatures needed for reactions 1 and 2 [5]. Also, this extractant loads gallium with high recovery from Bayer solutions containing small amounts of gallium but with a large excess of sodium and aluminum [6]. However, when contacted with Bayer solution, co-extraction of these latter two metals uses most of the extractant's loading capacity. Thus the objectives of the present work were to determine if gallium, aluminum and sodium are sulphide stripped using hydrogen sulphide, and if so, whether relative reaction rates indicate that gallium could be selectively recovered when loaded from gallium, aluminum, sodium mixtures.

Experimental. Unloaded organic phase comprised (vol.%) 8.5 KELEX 100, 10.0 decanol dissolved in a low vapour pressure kerosene of aromatic content below 1%. Gallium or aluminum or sodium were loaded from nitrate solutions under conditions such that metal concentrations were similar to those obtained in the organic phase when loaded from a typical Bayer solution after alumina precipitation (about $0.20 \text{ g.l}^{-1}\text{Ga}$, $1.5 \text{ g.l}^{-1}\text{Al}$, $2.0 \text{ g.l}^{-1}\text{Na}$) [6]. Solutions were analysed using atomic absorption spectrophotometry.

Sulphide stripping tests were carried out using a standard 2 l. capacity stainless steel Parr autoclave. After flushing air from the reactor using nitrogen, loaded organic, contained in a glass liner, was heated to the reaction temperature, then hydrogen sulphide was admitted below the solvent level at a predetermined pressure. During sulphide stripping, the organic was stirred, while both temperature and pressure were held constant. Analytical samples of the organic phase were withdrawn periodically during reaction, at the end of which the reactor was cooled under hydrogen sulphide. After filtration, the solid product was retained for further examination, while the organic was recycled.

Results and Discussion. As shown in Figures 1 and 2, gallium can be sulphide stripped leaving residual solutions containing as low as 2 ppm gallium. The fastest reaction rate measured was at 170°C with 0.62 MPa hydrogen sulphide, essentially complete gallium recovery being obtained after 20 minutes. An important requirement of the system is ability to recycle sulphide stripped organic. Figure 1 includes data showing that, at least for reaction at 145°C with 0.62 MPa hydrogen sulphide, gallium loading levels and subsequent stripping kinetics are reproducible through three load-strip cycles.

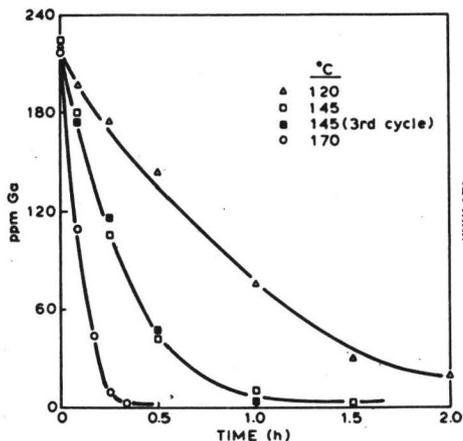


Fig. 1. Effect of temperature on sulphide stripping of gallium with 0.62 MPa H₂S

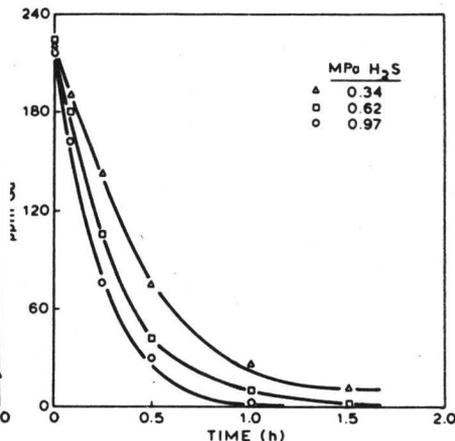


Fig. 2. Effect of hydrogen sulphide pressure on sulphide stripping of gallium at 145°C

The conditions used to sulphide strip gallium also cause the equivalent reaction for aluminum, as seen in Figures 3 and 4. At an initial aluminum concentration of 2.1 g.l⁻¹, 50% to 60% of this amount precipitates when about 2 ppm gallium is reached in the gallium/KELEX 100 system shown in Figures 1 and 2. However, in comparing gallium and aluminum stripping kinetics using the present data, it should be noted that free KELEX concentrations differ widely. When 8.5 vol.% KELEX is loaded with 0.22 g.l⁻¹ gallium or 2.10 g.l⁻¹ aluminum, about 4% or 87% respectively of the loading capacity is used. Since the presence of unloaded extractant may suppress stripping rates, gallium stripping in particular may be faster when 0.22 g.l⁻¹ gallium and 2.1 g.l⁻¹ aluminum co-exist in the same solvent.

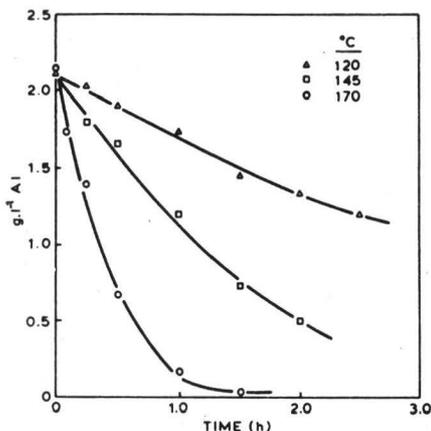


Fig. 3. Effect of temperature on sulphide stripping of aluminum with 0.62 MPa H₂S

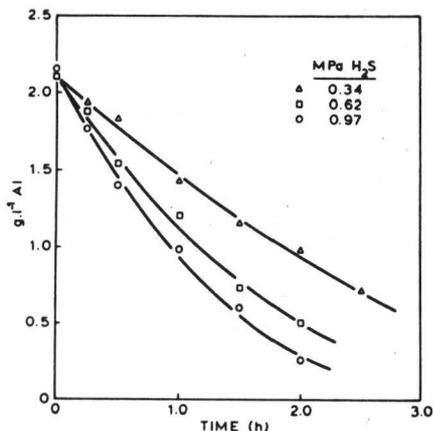


Fig. 4. Effect of hydrogen sulphide pressure on sulphide stripping of aluminum at 145°C

The behaviour of sodium at various temperatures and hydrogen sulphide pressures is shown in Figures 5 and 6. About 80% to 85% of the sodium precipitates under conditions which produce 2 ppm residual gallium, as seen in Figures 1 and 2. Based on the present results, it is therefore probable that gallium could be sulphide stripped at good yield from mixed gallium, aluminum and sodium containing extractant, and with partial selectivity over aluminum providing the reactions are immediately terminated at roughly the 2 ppm gallium level. However, most of the loaded sodium is expected to precipitate at high gallium recoveries. The sulphide stripping reactions are assumed to be:



Here, GaL₃, AlL₃ and NaL are the relevant metal chelates of KELEX (HL).

The precipitates formed as easily filterable free powder with no attachment to internal reactor surfaces. However, gelatinous products appeared when the reactions were carried out at above 170°C. X-ray diffraction analyses showed the solids to contain hydrated thiosulphates, these presumably being formed by sulphide oxidation in moist air following removal from the reactor. Powders produced in the gallium/KELEX 100/hydrogen sulphide system contained about 45 weight % gallium, which compares with 59 weight % for stoichiometric Ga₂S₃. All the precipitates were readily soluble in warm, dilute hydrochloric or sulphuric acids.

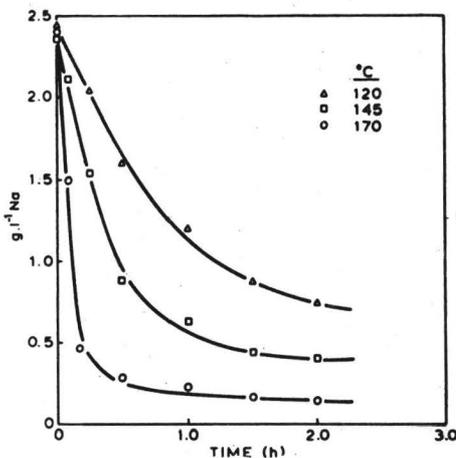


Fig. 5. Effect of temperature on sulphide stripping of sodium with 0.62 MPa. H_2S

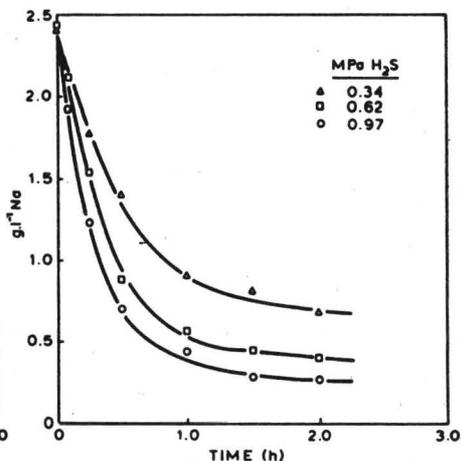


Fig. 6. Effect of hydrogen sulphide pressure on sulphide stripping of sodium at 145°C

Conclusions. This work demonstrates a potential application of sulphide stripping in which a high value metal loaded at low concentration can be recovered as an acid soluble concentrate. Specifically, gallium can be sulphide stripped at high recovery from KELEX 100 using hydrogen sulphide at elevated temperature and pressure. Tests with organic containing either gallium or aluminum or sodium suggest that, if loaded from Bayer solution, gallium could be sulphide stripped with partial selectivity over aluminum, but nearly all the sodium would coprecipitate. Further experiments using Bayer solution would determine if the expected stripping behaviour occurs. The resistance of the organic to degradation over a large number of recycles is also unknown. In addition, the possibility of replacing toxic hydrogen sulphide with an aqueous solution of sodium hydrogen sulphide or sodium sulphide should be studied.

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1. INTRODUCTION. Aluminium plants produce considerable quantities of flue dust during the process of electrolysis - for a comparatively large plant in Norway it may amount to more than a thousand metric tons a year. The dust represents both a storage and a waste problem. The main constituents of the dust are common elements such as aluminium, sodium, iron, sulphur, fluorine and carbon, the latter one accounting for about one third of the total mass. In addition to these elements others and more rare ones are also present, notably gallium and vanadium which seem to accumulate, possibly through a sublimation process, in the dust. The amounts may vary, and in the case of gallium figures in the range of 0.1 to 1% (Ga_2O_3) have been quoted. Vanadium as a rule seems to be somewhat more abundant. Table 1 gives the result of the analytical examination of the sample investigated in this work.

Table 1 Composition of flue dust sample, main elements

Introductory work [1] on this sample had as its primary goal to recover Al

Element	Al	Fe	Na	F	S	C	V	Ga
Concn., %	12.7	4.0	10.8	16.4	14.3	33	0.36	0.13

and F, preferably in the form of cryolite (Na_3AlF_6) or chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$) and pure enough to be recirculated. Hydrochloric acid was thought to be the most favourable leaching agent. It is known that GaCl_3 is easily extracted by a number of organic extractants, so the resulting solution was expected to be a suitable medium also for separating off Ga.

This initial investigation was not successful, neither with respect to the recovery of Al and F in a usable form, nor with regard to Ga extraction. The HCl solutions of Ga were shaken out with TBP (tributyl phosphate) of various concentrations but with little effect, and the expected separation from Fe did not take place. Following these negative results the project was shelved for a while. However, as interest in Ga for laser and other applications grew, it was decided to take up work again, but now with the principal objective of recovering Ga. V was included later, more or less by accident.

2. LEACHING OF FLY DUST. 2.1. Leaching with water or HCl. Initial attempts [1] to leach the dust with water at temperatures up to 100°C and contact times up to 24 hours showed that about 25% of the dust went into solution in all experiments. At 100°C the dissolved material was almost pure Na_2SO_4 , while at 20°C the Na_2SO_4 was contaminated by Al and F. No Ga dissolved.

The hydrochloric acid leachings were done in two ways. One way was to treat the dust with 6 N HCl (300 ml acid to 100 g of dust) for 2 hours at 110°C . The yield of dissolved gallium was about 70%. The other way was to calcine the dust at 700°C and leach the residue with either 3.7 N HCl (500 ml acid to 100 g

residue) or with 6 N HCl (300 ml acid to 100 g residue), both at boiling temperature for 2 hours. Leaching with 3.7 N HCl gave a yield of only 52% Ga, while leaching with 6 N HCl produced about 90% dissolved Ga.

The reason for the difficult extraction of Ga was thought to be associated with the presence of fluoride. Also chloride ions form complexes with Ga. When the investigation was resumed it was first looked at Ga leaching by other mineral acids with less tendency to form complexes with this element.

2.2. Leaching with HNO_3 or H_2SO_4 . 10 g samples were leached with 50 ml acid of desired concentration. The slurry was stirred for 4 hours at the temperature chosen. It was filtered when cold, washed with water, and the filtrate diluted to 100 ml before analysis. Only Ga, Fe, and acidity were determined. The results are shown in Table 2.

Table 2. Result of leaching experiments with HNO_3 and H_2SO_4

Sample No.	Acid	Initial concn., N	Temp., °C	Final acid concn., N	Undissolved matter, %	Concn., mg/l		% dissolved	
						Ga	Fe	Ga	Fe
1	HNO_3	1.4	22	0.45	66.4	24	600	18.5	15.0
2	HNO_3	1.4	100	0.025	48.7	45	1000	34.6	25.0
3	HNO_3	2.9	55	0.65	60.9	86	2200	66.2	55.0
4	HNO_3	2.9	100	0.40	37.7	110	2500	84.6	62.5
5	HNO_3	7.2	22	2.9	75.3	42	1000	32.3	25.0
6	HNO_3	7.2	55	2.4	61.9	90	2300	69.2	57.5
7	HNO_3	7.2	100	2.4	40.4	111	3000	85.4	75.0
8	HNO_3	14.4	55	5.6	79.9	74	2000	56.9	50.0
9	H_2SO_4	3.6	70	0.75	48.7	104	3600	80.0	91.3

To find optimum conditions for leaching Ga more work remains to be done, but the experiments above indicate that Ga yields well above 80% can readily be obtained with the mineral acids tried in this study.

3. EXTRACTION EXPERIMENTS. 3.1 Materials and conditions. For these experiments 1000 g portions of dust were leached with HNO_3 or H_2SO_4 of initial concentrations 2.9 N and 3.6 N respectively. The leachates were not diluted with water, but the acidity was adjusted in each case by addition of NH_3 .

HDEHP (hydrogen di-(2-ethylhexyl) phosphoric acid) extractions were carried out with 1 M solutions. The amine extractants Amberlite LA-1 (secondary amine from Rohm & Haas) and TIOA (tri-isooctyl amine) were 0.2 and 0.5 M respectively. All agents were diluted with Solvesso 150.

Element concentrations were determined by ICP spectroscopy and only in the aqueous phase.

3.2 Extraction of iron. Iron was thought to be the most difficult element to get rid of. HDEHP is known as a good extractant for Fe^{3+} , and extraction was tried from both HNO_3 and H_2SO_4 leachates. Equal volumes of aqueous and organic solutions were shaken for 5 min. when samples were drawn for analysis. This was

repeated also after continued shaking for 15, 30, 60 min. In addition to Fe and acidity the initial and final solutions were analysed for Al, Ga, and V. The results are shown in Tables 3 and 4.

Table 3. Extraction of Fe from a HNO_3 leachate

Shaking time, min	Concn. in aqueous phase				
	H ⁺ , N	Fe, mg/l	Al, mg/l	Ga, mg/l	V, mg/l
0	0.27	3230	12400	110	260
5	0.60	2240			
15	0.60	1540			
30	0.60	1150			
60	0.63	640	12300	110	260

Ga and V are not extracted under these conditions and very little, if any, Al. Fe is known to extract slowly in a H_2SO_4 medium, but it seems that even the HNO_3 system still is in a state of non-equilibrium after 60 min. Both aqueous phases were adjusted back to the initial acidity and reextracted with fresh portions of HDEHP for another 60 min. The rest concentration of Fe was then found to be 10 mg/l in the HNO_3 system and 230 mg/l in H_2SO_4 , which indicates that Fe may be difficult to remove completely in the latter system.

Table 4. Extraction of Fe from a H_2SO_4 leachate

Shaking time, min	Concn. in aqueous phase				
	H ⁺ , N	Fe, mg/l	Al, mg/l	Ga, mg/l	V, mg/l
0	0.24	5400	17000	175	390
5	0.36	3600			
15	0.44	2500			
30	0.51	1500			
60	0.57	620	16900	175	390

3.3. Extraction of Ga and V. Normally HDEHP will also extract Ga when conditions are suitable. Extraction experiments were carried out from both HNO_3 and H_2SO_4 media of various acidities. Contact time was 5 min. and the phase volume ratio 1:1. Tables 5 and 6 show the results of these experiments.

In experiments 3 and 4 of Table 5 and experiment 6 of Table 6 the acidity of the solutions was adjusted so as to bring the pH as close to the precipitation point as possible. It looked as if this point was higher in the H_2SO_4 system than in the other. Not surprisingly, the results indicate that lower acidity promotes extraction of both Ga and V. Both systems also extract Fe, but not to the extent that might be expected. Also a little Al is extracted at the lower acidities.

Table 5. Extraction with HDEHP from HNO₃ solutions

Expt. No.	State	Concn. in aqueous phase				
		H ⁺ , N	Fe, mg/l	Al, mg/l	Ga, mg/l	V, mg/l
1	I	0.67	2200		93	
	A	0.72	1600		93	
2	I	0.13	1540		90	
	A	0.18	300		63	
3	I	0.01	2500		92	
	A	0.08	200		48	
4	I	0.05	<5	11900	105	200
	A	0.17	<5	10500	38	95

I = Initial, A = After equilibration

3.4. Back extraction. Back extraction was tried with H₂SO₄ and HCl. Low acidity (0.05 N) strip solutions proved very inefficient for the elements under study. 3 N solutions, however, gave good recoveries of Ga and V, while Fe was only partly stripped. Al was stripped practically quantitatively by H₂SO₄, unexpectedly poorly by HCl.

In Table 7 are the results of the back extraction experiment with 3 N HCl since this is the important one with a view to the subsequent separation of Ga and V. The organic phase was stripped twice, each time with an equal volume of strip solution for 5 min. Initial concentrations (calc.) in the organic phase were: Fe: 320 mg/l. Al: 1000 mg/l. Ga: 90 mg/l. V: 310 mg/l.

Table 7. Back extraction from HDEHP with HCl

Strip No.	Concn. in aqueous phase					Total amount stripped, %			
	H ⁺ , N	Fe, mg/l	Al, mg/l	Ga, mg/l	V, mg/l	Fe	Al	Ga	V
1	3.10	180	160	100	300	56	16	100	97
2	3.10	35	210	<10	10	67	37	100	100

Strip solution No. 1 (Table 7) was shaken for 5 min. with an equal volume of the Amberlite LA-1 extractant. Afterwards the following concentrations were found in the aqueous phase:

H⁺: 3.05 N. Fe: 40 mg/l. Al: 160 mg/l. Ga <2.5 mg/l. V: 300 mg/l.

Table 6. Extraction with HDEHP from H₂SO₄ solutions

Expt. No.	State	Concn. in aqueous phase				
		H ⁺ , N	Fe, mg/l	Al, mg/l	Ga, mg/l	V, mg/l
1	I	0.17	2250		88	
	A	0.37	1200		72	
2	I	0.20	2800		96	
	A	0.24	1500		67	
3	I	pH= 3.0	2800		96	
	A	0.11	600		46	
4	I	pH= 2.0	1170		70	
	A	0.13	300		12	
5	I	pH= 2.0	<10	9400	68	
	A	0.17	<10	8800	26	
6	I	pH= 4.0	920	17500	185	370
	A	pH= 1.75	700	16500	65	55

I = Initial, A = After equilibration

3.5. Separation of Ga and V. It is known [2] that Amberlite LA-1 extracts Ga from HCl solutions. V can also be extracted, but extraction starts at a higher acidity.

Practically all the Ga has been extracted but no measurable amount of V (or Al). Also a considerable portion of the iron extracted, but that was expected since Fe^{3+} forms negative complexes with the chloride ions.

3.6. Separation of V from Fe and Al. The best way of achieving this separation was thought to be extraction of pentavalent V by TIOA from a H_2SO_4 solution. For this purpose V had to be precipitated from its chloride medium. This proved possible by oxidising the V from its tetravalent state, and adding NH_3 until precipitation occurred. V would then come out with the hydroxides of Fe^{3+} and Al^{3+} . It was found that the degree of V coprecipitation was dependent on the concentrations of these ions. An experiment was carried out in which mixtures of V of constant initial concentration and Fe^{3+} of varying concentration were precipitated. The result is shown in Table 8. Initial V concentration was 2700 mg/l, and the tabulated Fe concentrations are those that would be if precipitation did not occur. V concentrations are those measured after precipitation.

To the aqueous phase remaining after extraction of Ga (3.5) was added NaClO_3 to oxidise V. Neutralisation of the solution with NH_3 then produced a brown precipitate which was filtered off, washed with water and dissolved in a minimum of 1 N H_2SO_4 .

Table 8. Coprecipitation of V^{5+} with Fe^{3+} by NH_3

Element	Concentrations, mg/l					
	Fe	0	266	523	1246	1800
V	2700	2120	1870	980	600	325

The solution was analysed with the following result:

H^+ : 0.2 N. Fe: 190 mg/l. Al: 770 mg/l. V: 1375 mg/l.

The solution was shaken for 5 min. with an equal volume of the TIOA extractant.

Analysis of the resulting aqueous phase then showed:

Fe: 185 mg/l. Al: 780 mg/l. V: 200 mg/l

Only small amounts of Fe and Al have been extracted while over 85% of the V has been transferred to the organic phase in this single equilibration.

Amberlite LA-1 was also tried for this step, but proved far less effective.

4. PREPARATION OF CONCENTRATES OF Ga AND V. 4.1 Ga. The H_2SO_4 based leachate used for the experiment had the following composition with respect to the key elements:

H^+ : 2.1 N. Fe: 7.6 g/l. Al: 25 g/l. Ga: 200 mg/l. V: 570 mg/l with leaching recoveries of 80 and 82% for Ga and V respectively.

500 ml leachate was adjusted to an acid concentration of 0.3 N by adding conc. NH_3 . It was shaken out twice, each time with 500 ml HDEHP for 60 min. Between the shake-outs acidity was adjusted back to 0.3 N with NH_3 .

The aqueous phase after this operation was neutralised with NH_3 to the point where permanent turbidity prevailed. pH was then 3.7. The solution was equilibrated with 150 ml HDEHP by shaking for 5 min. pH was again adjusted, this time it ended up at pH 4.0. Extraction was repeated with another 150 ml portion of HDEHP

The combined organic phases (300 ml) were stripped twice, each time with 75 ml 3 N HCl by shaking for 5 min. The strip solutions were also combined,

ascorbic acid was added in slight excess of the Fe present, and Ga extracted by shaking for 5 min. with 75 ml Amberlite LA-1. The organic phase was washed with 50 ml 3 N HCl containing a little (ca. 20 mg) of ascorbic acid. Finally Ga was stripped by shaking for 5 min. with 25 ml water. The strip solution was analysed with the result listed in Table 9.

Table 9. Analysis of strip solution containing purified Ga

Element	Fe	Al	Ga	V
Concn., mg/l	25	<1	3480	<1

also the Fe. Conc. NH_3 was then added until nothing more precipitated. The precipitate was filtered off and washed with water, and then dissolved in 1 N H_2SO_4 . The solution was diluted to 100 ml (measured acidity 0.5 N) and shaken once for 5 min. with 50 ml 0.5 M TIOA. The organic phase was washed once with 25 ml 0.5 N H_2SO_4 .

Sufficient ascorbic acid to reduce all V^{5+} to V^{4+} was added to 50 ml 0.5 N HCl and the solution used to strip the vanadium from the TIOA phase by contacting the solution for 5 min. Analysis of the resulting aqueous phase gave the result listed in Table 10.

Table 10. Analysis of strip solution containing purified V

Element	Fe	Al	Ga	V
Concn., mg/l	115	40	<1	4840

The purity of Ga with respect to the other elements in the table is 99.3%. Recovery of Ga through the extraction steps was 87%, and thus the overall yield including leaching was about 69.5%.

4.2 V. To the aqueous phase remaining after extraction of Ga (4.1) was added sufficient NaClO_3 to oxidise the V and

Calculated in analogy with Ga the purity of V is 96.9% and recovery through the separating steps reckoned from the leachate is 86%, giving an overall yield of 75.5%.

5. COMMENTS AND CONCLUSIONS. The work presented above does not pretend to have found optimum conditions for recovering

Ga and V from aluminium flue dust. It shows, however, that both elements can be leached in relatively good yields from the dust, and also that they can be separated out in good purity and acceptable yields through a series of simple shake-out extraction operations. The results can probably be considerably improved by applying multistage extraction and scrub principles such as is normally done in industrial processes.

The economic implications of a process based on the separation scheme followed in this work have not been evaluated.

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The removal of impurities such as P, As and Si from alkaline leaching solutions is an important step in hydrometallurgy of W and Mo. The traditional method used in industry is by precipitation with the addition of magnesium salt. This process has many problems such as low recovery, disposal of precipitate and pollution arising from the storage of precipitate.

Solvent extraction can be considered as a better method for impurity removal in comparison with precipitation method if an effective solvent system can be developed. Work on the extraction of P, As, Si and their heteropolyacid formed with W and Mo(1-2) have been reported, which generally were carried out under acidic condition. It has been found that separation of W from Mo and Re(VII) from Mo can be carried out satisfactorily in weakly alkaline solutions by synergistic extraction with primary amine and TBP(3-4). In the present paper, the mechanism of extraction of P from weakly alkaline molybdate solution by primary amine and TBP was investigated.

EXPERIMENTAL PART

An electric shaker was used to mix aqueous and organic solutions. Primary amine(R_2CHNH_2 or simplified as RNH_2 in the following expressions) with a total carbon number of about 21 was supplied by the Institute of Organic Chemistry, Academia Sinica, Shanghai, China. The other chemicals were of analytical grade purity. Mo and P were analyzed by thiocyanate and molybdophosphate colorimetry respectively.

RESULTS AND DISCUSSIONS

The extraction of phosphorus. The extraction of P is a function of pH value of aqueous solutions, concentrations of Mo and P in the aqueous phase, temperature, phase ratio, and both type and concentration of amine and neutral donor extractants used. Experimental results show that synergism of amines with TBP decreases in the order of primary, secondary and tertiary amines. P can not be extracted without the presence of Mo in the aqueous solution. It can be proposed that P is extracted into the organic phase as molybdophosphoric acid. It was found that a mixture of 1-2% RNH_2 and 10-20% TBP(v/v) with n-heptane as diluent can be used to separate P from sodium molybdate

solution with equilibrium pH 6.4-6.6 very effectively when the initial concentration of P and Mo were in the range of about 100mg/l and higher than 40g/l respectively at 25°C or higher. The separation factor of P to Mo can be higher than 1000 and one stage extraction of P can be better than 99% under above conditions.

Determination of the extracted species The extraction equilibrium can be written as



where some of reactants and products are represented in atomic form only because their exact molecular formulae are unknown.

From equation (1) we can get

$$\text{Log}K = \text{Log}D_p + mpH - n\text{Log}(Mo) - x\text{Log}(TBP) - y\text{Log}(RNH_2), \quad (2)$$

where K is extraction equilibrium constant and D_p the distribution ratio of P. From the slopes of Fig. 1-4, n, m, y and x are estimated as 2, 3, 2 and 1, respectively and the equilibrium constant was calculated as 2.08×10^{57} . It should be pointed out that the ratio of Mo/P in the organic phase is a function of that in the aqueous phase. The ratio of Mo/P in organic phase is always about 2 when that in aqueous phase is less than about 6 which was used in the experiments. This is in agreement with the slope of Fig.1. The primary extraction reaction may be expressed as

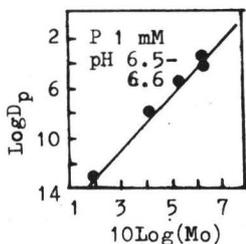
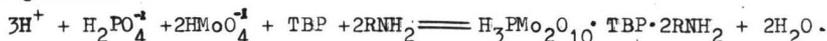


Fig. 1. Determination of n.
Initial organic phase:
1%RNH₂+15%TBP(v/v)
(30.43mM RNH₂+556mM TBP)

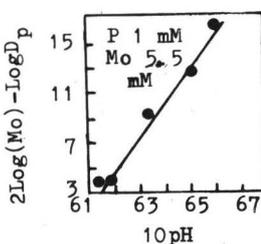


Fig. 2. Determination of m
Initial organic phase:
1%RNH₂+15%TBP(v/v)

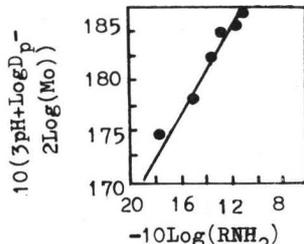


Fig. 3. Determination of y
TBP 556 mM
P 1mM, Mo 6mM
pH 6.4-6.8

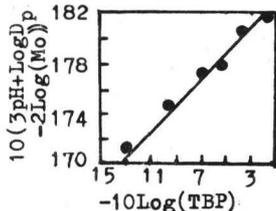


Fig. 4. Determination of x.
RNH₂ 1%(30.43mM) P 1mM Mo 5.5mM pH 6.4-6.7

All the experiments were carried out at room temperature and the mixing time was 10 minutes (the equilibrium time of the extraction was about 2 minutes).

The infrared absorption band of stretching vibration of the -NH group in a primary amine has been found to be much broader and the wave number of P=O group in TBP has been shifted from 1275 to 1260 cm⁻¹ after loaded with molybdophosphoric acid as shown in Fig. 5.

The liquid chromatography absorption peak of the extracted species has been found to be broadened after extraction which indicates that the extracted species consists of two or more substances whose polarities are very close but less than those of primary amine and TBP according to the decreasing order of polarity from right to left in the liquid chromatography spectra as shown in Fig.6.

Dependency of molar conductivity on the concentration of the extracted species. The shape of line CA in Fig.7 suggested that the extracted species was weakly dissociated in a mixture of RNH_2 , TBP and n-heptane. When n-heptane was evaporated, more extracted species was dissociated and the conductivity increased rapidly because of higher polarity of RNH_2 and TBP as solvent(see line AB in Fig.7).

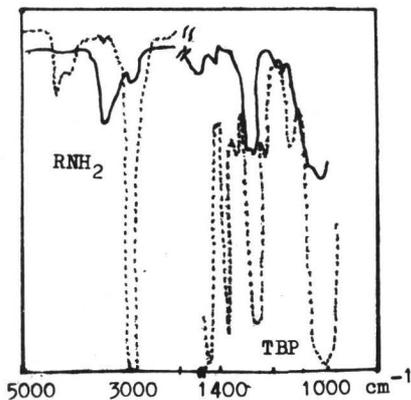


Fig.5. Infrared spectra of the extracted species. Solid Line--1% RNH_2 + 15%TBP in n-heptane; Dotted line--above organic solution loaded with P and Mo

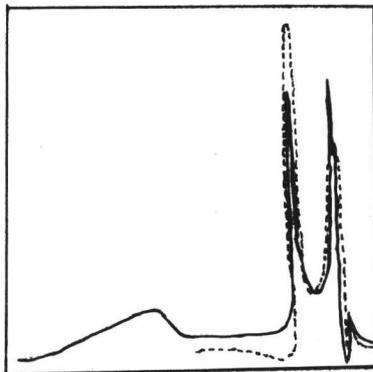


Fig.6. Liquid chromatography of the extracted species. Solid line--the spectra of organic solution with 1% RNH_2 +15%TBP(v/v) in heptane; Dotted line--above organic solution loaded with P and Mo

Discussion of mechanism of extraction and the structure of extracted species. The synergism of amines with TBP towards the extraction of P from sodium molybdate solution decreases in the order of primary, secondary and tertiary amines. It can be considered that the number of active hydrogen atoms in amines plays an important role in the synergism. It can be suggested that the hydrogen bonds were formed between TBP, active hydrogens of primary amine and molybdophosphoric acid. This is in agreement with the previous work(3-4).

The extracted species dissociated in the organic phase may come from the direct dissociation of neutral molecules or the occurrence of ionic association. It is reasonable to propose that the occurrence of ionic association contributes little to the formation of extracted species.

So the mechanism of extraction is predominantly by solvation extraction.

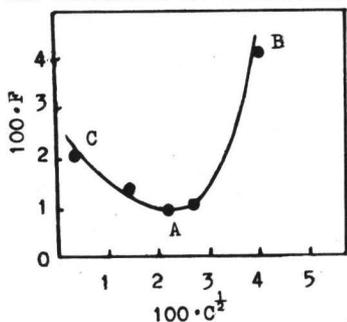


Fig. 7. Dependency of molar conductivity of the extracted species on its concentration

C: The concentration of molybdophosphoric acid
 F: Molar conductivity of molybdophosphoric acid
 Temperature: 13°C

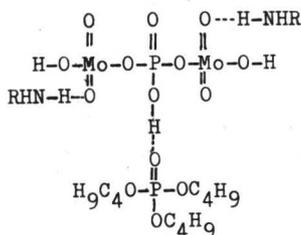


Fig. 8. Proposed structure of the extracted species

The structure of the extracted species can be expressed as shown in Fig. 8 (the most probable structure).

CONCLUSTIONS

The extraction of P from weakly alkaline sodium molybdate solutions can be carried out very effectively with a mixture of primary amine and TBP as extractants. Phosphorus is most probably extracted into the organic phase as 2-molybdophosphoric acid. The mechanism of synergistic extraction has been studied. Hydrogen bonds are considered to be formed between TBP, primary amine and molybdophosphoric acid during extraction. The composition of the extracted species has been determined and its structure suggested.

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For the purpose of recovering cobalt(II) and nickel(II) from leach liquors obtained from Yugoslav ore (the Goleš locality) the possibility of applying the commercial extractant Cyanex 272 (bis(2,4,4'-trimethylpentyl)phosphinic acid) was examined. Cyanex 272 proved to have an advantage over related organophosphoric extractants D2EHFA (di-2-ethylphosphoric acid) and PC88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester) [1,2]. Extractions were carried out from aqueous sulphate, chloride and sulphate-chloride solutions. The extractant Cyanex 272 was better at separating cobalt-nickel from a sulphuric acid medium [1,2], whereas chloride leach liquors made simple removal of iron(III) possible [3,4].

A sample of Cyanex 272 was a gift of Cyanamid Ltd. Canada. The samples extracted were leach liquors or solutions prepared from pure chemicals. Ground ore of grain size < 0.125 mm was leached in a device of own construction at room or higher temperature (85°C). In Table an average content of metals determined in ore and leach liquors is given.

Average content of cobalt, nickel and iron in the ore from the Goleš locality and in leach liquors produced by different procedures [5-8]

	Leaching agent	Temp., °C	Content of metals		
			Co	Ni	Fe
ore, %	-	-	0.06	1.3	21.3
leach liquors, g/dm ³	8 M HCl	85	0.25	3.6	68.0
	8 M HCl	room	0.23	2.6	40.0
	1 M H ₂ SO ₄	85	0.10	2.0	17.0
	1 M H ₂ SO ₄ -8M HCl	room	0.25	2.9	46.0

Extraction was carried out in graduated cuvettes (15 cm³). By absorbance measurement - concentrations of cobalt (using nitroso-R salt) and nickel (using dimethylglyoxime and K₂S₂O₈) were determined. Iron was determined by complexometric titration and larger quantities of nickel gravimetrically.

In prepared samples of composition corresponding to the metal content in ore leach liquors the effect of different diluents on cobalt extraction from aqueous sulphate solutions with Cyanex 272 was examined. The diluents were: n-hexane, benzene, 2,2',4'-trimethyl pentane (i-octane), kerosene and a mixture of benzene and 2,2',4'-trimethyl pentane. Experimental conditions (temperature, initial pH, contact time, initial phase volume ratio) were chosen on the basis of preliminary examination. Figure 1 shows the results of extraction with the above diluents at different initial phase volume ratios of organic to aqueous phase (r¹).

The histogram in Fig. 1. shows the systems with 2,2',4-trimethyl pentane as diluent to yield best results. The recovery and separation of metals strongly depend on the pH of

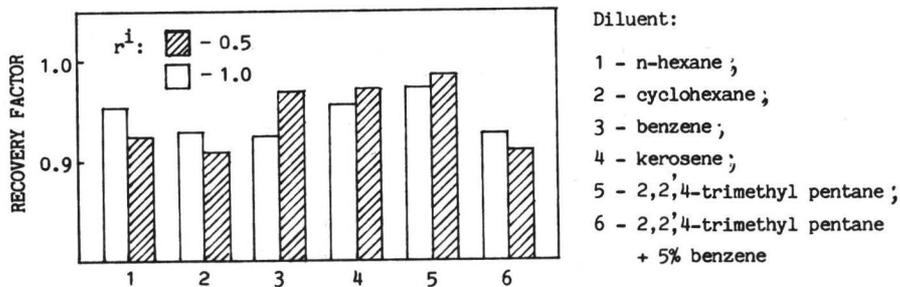


Fig. 1. Recovery factor for cobalt extracted from a sulphate medium with 10% Cyanex 272 in different diluents. Initial pH = 8.0, $c_{Co}^i = 0.08 \text{ mg/cm}^3$, $r^i = 0.5$ and 1.0

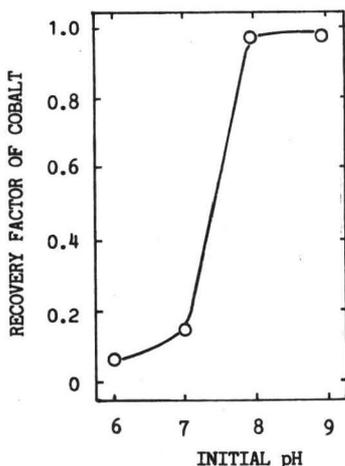


Fig. 2. The effect of initial pH value on extraction of cobalt with 10% Cyanex 272 in 2,2',4-trimethyl pentane from sulphate medium

$c_{Co}^i = 0.08 \text{ mg/cm}^3$;
 $r^i = 1.0$

the extraction systems with Cyanex 272 because of reaction mechanism. Under defined experimental conditions the most favourable initial pH value for extraction of cobalt was 8.0 (Fig. 2.) and corresponding the most favourable equilibrium pH value was 6.0 (Fig. 3.).

At the same initial value pH = 8 the change in initial phase volume ratio had no great influence on extraction, as was observed by a parallel investigation. At chosen experimental conditions (10% Cyanex 272 in 2,2',4-trimethyl pentane, initial pH = 8.0 and $r^i = 1.0$) extraction of cobalt ($c_{Co}^i = 0.08 \text{ mg/cm}^3$) and nickel ($c_{Ni}^i = 1.77 \text{ mg/cm}^3$) as well as the cobalt-nickel separation were studied.

Contrary to the results reported in literature, most of which refer to a higher temperature, these results were obtained at 25°C.

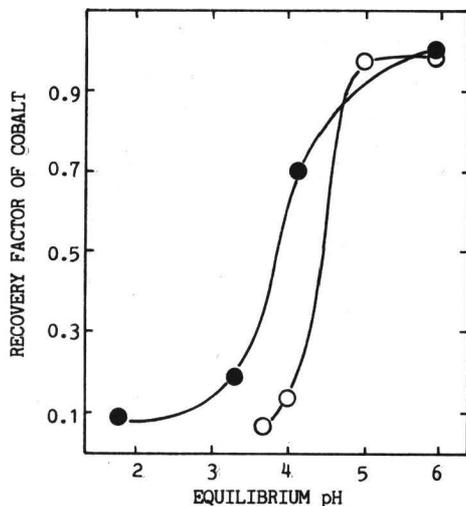
During the extraction of cobalt from leach liquors some interferences caused by the presence of other components appeared. One was due to high concentration of iron. In

Fig. 3.

The effect of equilibrium pH value on extraction of cobalt with Cyanex 272 from sulphate medium. A comparison with results reported in Ref. 2.

● - 185 g/dm³ Cyanex 272 in Kermac 470B + 10% nonyl phenol
 $c_{Co}^i = 0.015 \text{ mol/dm}^3$, $t = 50^\circ\text{C}$,
 $r^i = 1.0$ (Ref. 2.)

○ - 10% Cyanex 272 in 2,2',4-trimethyl pentane
 $c_{Co}^i = 0.08 \text{ g/dm}^3$, $t = 25^\circ\text{C}$,
 $r^i = 1.0$



order to solve the problem the possibility of extracting iron from leach liquors before cobalt and nickel was studied. For the extraction of iron from leach liquors recovered by different procedure (as given in Table 1) the solvents used were: diisopropyl ether, ethyl ether and their mixtures with n-butyl alcohol. Best results were obtained from chloride and chloride-sulphate media with the mixture of ethyl ether and n-butyl alcohol. As illustration, from a sample of chloride leach liquors with the mixed solvent ethyl ether + n-butyl alcohol (30%) in the first stage of extraction the recovery factor (R) was 0.988 and the separation factors iron-cobalt (α_{Co}^{Fe}) and iron-nickel (α_{Ni}^{Fe}) were 2000 and 1600 respectively.

Finally, it should be emphasized that efficacious application of Cyanex 272 for the recovery of cobalt from the investigated ore from the Goleš locality depends, in addition to the above, also on effective removal of other components present in leach liquors, in the first place on effective removal of aluminium. Investigations are in progress.

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The three-exit extraction technology has been reported [1,2] for the separation of rare earths recently, but has not been reported in non-rare earth separation. In many cases, there are multi-component system, such as in the work of nickel electrolyte purification Cu, Co, Ni may coexist. Usually Cu and Co are treated as one component, and separated from nickel. Here a new technology, by which the three elements can be separated simultaneously, is proposed.

1. The extraction and separation ability

From the effect of pH on the distribution ratio of each element in individual component system (Fig.1), it is determined that

$$pH_{\frac{1}{2}}^{Cu} = 3.3; \quad pH_{\frac{1}{2}}^{Co} = 3.8; \quad pH_{\frac{1}{2}}^{Ni} = 4.7.$$

The order of extraction ability can then be formulated as Cu > Co > Ni. And the slopes have the same order. These determine the relation between the exits and elements in the technology.

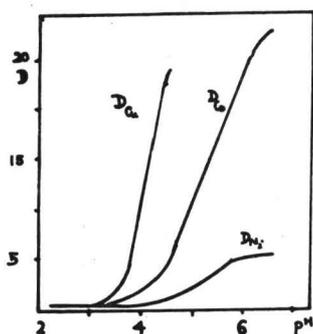


Fig.1. The effect of pH on distribution ratio of Cu, Co, Ni

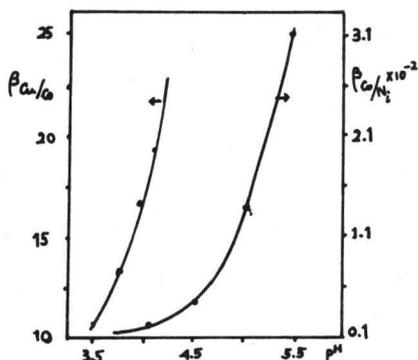


Fig.2. The effect of pH on separation factors

Fig.2 shows that both the separation factors $\beta_{Cu/Co}$ and $\beta_{Co/Ni}$ have the tendencies to increase when the pH of the equilibrium aqueous solution increases.

The extraction percentage (EX) at different ammoniated ratios of HEH(EHP) were measured when the initial metal ion concentration was constant. It is shown that there exists certain linear relation between

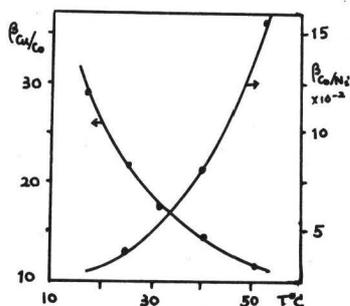
* The Project Supported by National Natural Science Foundation of China.

the extraction ratio and ammoniated ratio of HEH(EHP) ($\text{NH}_3\%$). Then we can easily reason out the linear relation between the metal concentration in organic phase and $\text{NH}_3\%$.

The effect of metal ion concentration on the separation factors is also studied. Experiments show that $\beta_{\text{Cu/Co}}$ has little variation with change of initial Co^{2+} concentration when the Cu^{2+} initial concentration is set constant. Whereas $\beta_{\text{Cu/Co}}$ varies greatly when the initial concentration of Cu^{2+} changes and $C_{\text{Co}^{2+}}$ keeps constant. Similar regularity exists in the system of Co and Ni.

The effect of temperature on $\beta_{\text{Cu/Co}}$ and $\beta_{\text{Co/Ni}}$ are shown in Fig.3. It can be seen that $\beta_{\text{Cu/Co}}$ falls while $\beta_{\text{Co/Ni}}$ raises with the increase of temperature.

Fig.3. The effect of temperature on separation factors



2. The technology of the simultaneous separation

The simultaneous separation experiments of Cu, Co, Ni was carried out at room temperature. The feed composition is $\text{Cu:Co:Ni}=1:1:1$

Technology 1

The scheme of technology 1 is as Fig.4. The conditions are $N=14$, $NF=3$, $NG=6$, $NW=10$

$\text{VOE:VOG:VAW:VAG:VAF}=15.0:4.0:11.4:7.4:7.5$

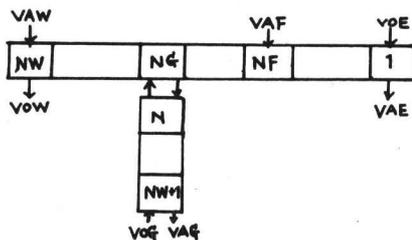


Fig.4. The scheme of three-exit technology 1

The initial concentration of extractant is 0.74M and ammoniated ratio is 68%. Sulphuric acid scrubbing concentration is 0.61N. The feed solution has the total concentration of 0.498M.

After equilibrium, the qualities of the three products are as follows

- The first aqueous exit: Ni > 90%
- The second aqueous exit: Co > 85%
- The organic exit: Cu > 99.5%

Technology 2

The scheme of technology 2 is as Fig.5. The conditions are N=16, NF=3, NG=10

VOE:VAW:VAF:VAG=19.0:11.6:7.5:4.3

The initial concentration of extractant is 0.72M. Ammoniated ratio is 72%. Sulphuric acid scrubbing concentration is 0.59N. Feed solution is 0.49M. The products of the three exits have the qualities as follows

- The first aqueous exit: Ni > 99.5%
- The second aqueous exit: Co > 97%
- The organic exit: Cu > 99%

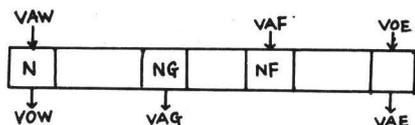


Fig.5. The scheme of three-exit technology 2

Nomenclature

- NF, N - feeding stage number and total stage number;
- VAF, VAW - volumes of feed and scrubbing solution;
- VAE, VAG, VOW - volumes of the first, second and third exit products;
- VOE, VOG - volumes of extractant;
- NW - exit stage number of organic product for technology 1;
- NG - back flowing stage number for technology 1; exit stage number of second aqueous product for technology 2.

Acknowledgement

We are thankful to Chunfu He and Hongxing Ren for providing X-ray fluorescence analysis.

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Research work carried out by us enabled us to accumulate certain experience in the use of trialkylbenzylammonium salts (TABAS) for extraction, separation, and refining of metals. The use of nonpurified tertiary amines and benzyl chloride in the synthesis of the extractant results in the final product containing some free amines. Their presence does not practically interfere with metal extraction from neutral and alkaline solutions whereas in acid solutions one has to take into account the possibility of an accompanying extraction of acids and metals by these amines. If required, the extractant can be easily freed from the amine impurities by extracting them with kerosene from where they can be isolated into a separate phase by an acid treatment of the extract.

TABAS has a high viscosity and for extraction purposes it is employed in the form of solutions in nonaqueous solvents. The viscosity of the solution depends on the properties of the solvent, the extractant concentration, and the temperature of the solution. Owing to the tendency of TABAS to aggregation the solution viscosity strongly increases with increasing extractant concentration.

The solution viscosity and the average degree of TABAS aggregation n_x in solutions can be estimated using equation 1 which relates the specific viscosity of a solution with the molecular mass of the polymer in this solution [1]

$$\eta_x = K C_x (\bar{M})^a, \quad (1)$$

where $\eta_x = (\eta_s - \eta_s^0) / \eta_s$, and η_s and η_s^0 are the viscosities of the solution and solvent, respectively, and "a" is the permeability coefficient of the polymer. For equilibrium systems the amount of TABAS aggregates will decrease with decreasing TABAS concentration and will tend to unity ($n_x \rightarrow 1$) in the region of diluted solutions. Equation (1) can be used to estimate the values of n_x .

$$\log \eta_x = \log K + a \log n_x + \log C_x. \quad (2)$$

In the region of diluted solutions (at $n_x \rightarrow 1$) the slope of the $\log \eta_x$ vs. $\log C_x$ plot will also tend to unity ($\Delta \log \eta_x / \Delta \log C_x \rightarrow 1$). The increase in the slope indicates the appearance of aggregates in the solution. Calculated values of n_x for TABAS solutions are given in Fig. 1. It is characteristic that with the same concentration of TABAS the viscosity of a solution is proportional

that of the pure solvent. It can be assumed that the TABAS aggregates consist of chains or plane species sandwiched with the solvent. With increasing temperature there is a noticeable increase in the solution viscosity (Fig. 2).

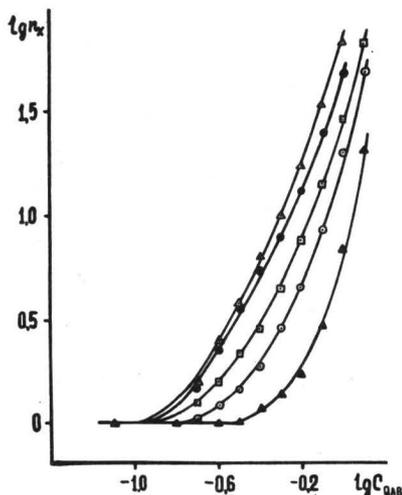


Fig. 1. The degree of TABAS aggregation as a function of concentration

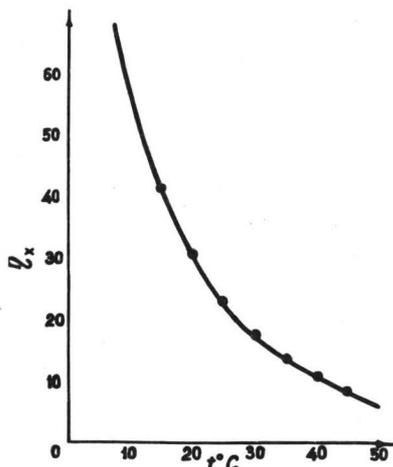


Fig. 2. The viscosity of TABAS solutions as a function of temperature

In order to maintain high metal distribution coefficients TABAS is used in the form of solutions in aromatic hydrocarbons such as polyalkylbenzenes of various origin. But for many systems mixtures of kerosene with aliphatic alcohols are used.

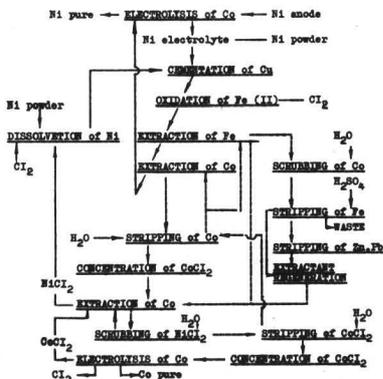
The metal extraction isotherms, in particular of metal chlorides, with TABAS solutions are well described by the following empirical equation which takes into account non-ideality of the extractant solution

$$C_{M(o)} = m^m K (C_{NR_4Cl} - n C_{M(o)})^p C_{M(a)}^{\frac{(m+1)}{2}} \gamma_{\pm}^{\frac{(m+1)}{2}}, \quad (3)$$

where m is the metal cation charge, n is the charge of the anion being extracted and $p = 1.6-1.8$ in the extraction of Co(II), Cu(II), Mn(II) and other metals and $p = 0.7-0.9$ in the extraction of Fe(III) and Cu(I).

Using TABAS a technology has been developed for extractive purification of nickel electrolytes producing pure nickel and copper together with cobalt concentrates [2]. In addition, a method has been developed for extractive treatment of the cobalt concentrate which, in combination with the first scheme, form a close-circuit technology (Fig. 3).

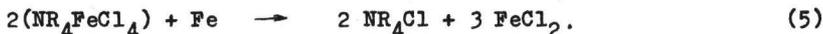
Fig. 3. Flowsheet for selective extraction of impurities from nickel electrolytes



Arsenic is effectively extracted from acid electrolyte solutions with a molybdate form of TABAS.



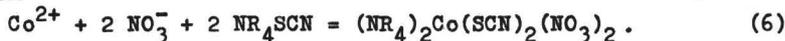
The cobalt is stripped from the extract with water to give a cobalt solution. The iron is also stripped with water but after its reduction with an iron powder [3]



A method has been developed for waste water processing which allows creation of a waste-free technology.

A NR_4SCN form of TABAS selectively extracts some metals from nitrate and sulfate solutions (Zn, Cd, Cu, Co) [4].

The NR_4SCN extractant has been used in a technological scheme in the processing of cobalt solutions resulting from dissolution of wastes with nitric acid [5]. Copper and iron were removed from the solution with carbonic acid and cobalt was extracted by the reaction



Stripping of cobalt was carried out with a solution of ammonium oxalate.

(NR_4SCN) solutions extract copper (II) from sulfuric acid solutions by the reaction



Due to the slow rate of the iron extraction copper is selectively recovered from acid solutions with $pH > 1$ (Fig. 4) [6]. The distribution coefficients of copper are considerably increased when extraction is carried out from a mixed sulfate-chloride solution.

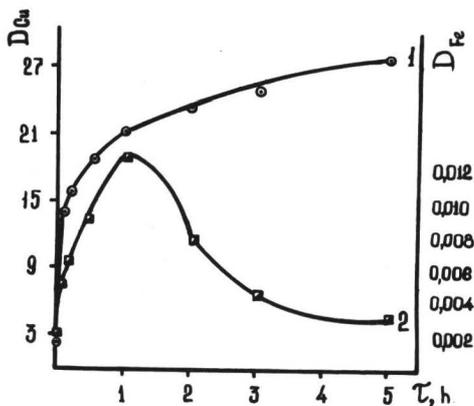


Fig. 4. The extraction of Cu(II) and Fe(III) with TABAS solutions as a function of time.

The NR_4NO_3 form of the extractant has been used to purify W and Mo from many impurities. In H_2O_2 solutions complex anions of the type $\text{Mo}_2\text{O}_{11}^{2-}$ are formed which prevent formation of heteropoly compounds. The method allows a high level of purification of metals from As, P, Si, Al, Na and other.

Various salt forms of TABAS are the most promising extractants for extraction of anionic metal complexes from neutral and alkaline media.

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The carboxylic acids as the extractants are widely used in scientific investigations, technological testings and some of them are already used on a limited scale for separation of metals in industry. Naphtenic acids represent one of the interesting extractant of this class. They are natural substances having a number of properties which meet the most part of the industrial requirements for extractants: low solubility in water and high solubility in organic solvents, nontoxicity, availability and low cost. They extract metals at pH value, close to precipitation of their hydroxides [1,2]. These are the approximate coefficients of separation: Fe(III)/Cu- 300-700; Cu/Zn- 100-350; Zn/Co- 3-6; Ni/Co- 1,5-2,0; Co/Mn- 1,0-1,5; Co/Ca- 2-5. The above indicates high efficiency of Fe(III), Cu and Zn separation. Multi-stage extraction needed for other metals (Zn/Co-12, Ni/Co- 35-40 stages) is a drawback of this extractant. The possible ways of increasing the application efficiency of naphtenic acids are discussed below.

Studying the kinetic regularities at temperature 15-90°C we determined [3] considerable variations in extraction rates for non-ferrous metals (Cu, Ni, Zn) and Ca (Fig.1). On this basis there had been worked out a process of refining these metals from Ca that permitted to increase the coefficient of separation Co/Ca to 15-45. The realization of this process in the one stage of mixer-settler centrifugal extractor (Pilot-industrial scale) with low residence time, permitted to reach a deep refinement of Co and Ni from Ca and Mg.

It is known that reducing Cu, Ni and Co by hydrogen in aqueous solutions is a highly efficient industrial method of purification and producing them as powder metals

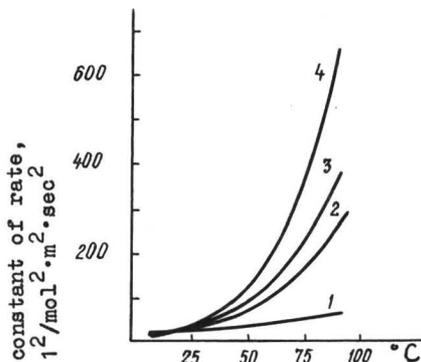


Fig.1. The conditional extraction constant of rate as a function of temperature. 1-Ca, 2-Ni, 3- Co, 4-Zn

The realization of these processes in organic extracts [4] permits to decrease pressure and temperature

and to increase selectivity of Co and Ni separation. Here is shown that these processes take place at $t = 130-220^\circ\text{C}$ and $P_{\text{H}_2} = 1-2 \text{ MPa}$, the

rate of processes being higher. Thus, in the 33% solution of D2EGPA at temperature 140°C and pressure 2MPa Ni is reduced in 30 minutes but Co remains in the extract. We studied Cu, Ni and Co reducing in naphtenic extracts in an autoclave (3 l volume). The parameters of the processes lie in the limits shown above. The naphtenic acids repeatedly used in these processes did not change their extraction properties.

Impossibility of application of standard equipment for the metal separation processes based on kinetic regularities and on processes complicated by the third solid phase formation brought about the necessity of the construction of the mixer-settler centrifugal extractor (Fig.2) /3/. The rotor-separator has mud chambers on the peripheric part (inside) with fixed nozzles taking out the solid phase together with the major part of water. Periodical washing out of rotor is realiz-

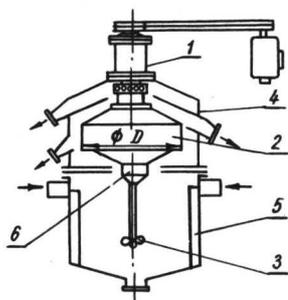


Fig.2. The scheme of construction of mixer-settler centrifugal extractor: 1 - driver; 2 - rotor-separator; 3 - mixer; 4 - frame with annular receiver; 5 - chamber of mixing; 6 - pumping over equipment

ed under the very low concentration of solid phase. The required residence time for realizing processes is achieved by mounting corresponding volumes of chamber mixers. The pilot models of extractors (productivity from 0,5 to 1,5 m³/h for all phases) have been used to test the technique and have shown satisfactory results in the wide ratio range of flows and densities of phases. During the testing of the geometrically similar models it has been determined that with equal centrifugal factors of separating the ratio of their capacities is equal to the ratio of the outside diameters of rotors to the third power: $Q_1/Q_2 = (D_1/D_2)^3$. The equation is necessary for calculating the basic sizes and number of revolutions in designing industrial extractors.

On the basis of distribution regularities and metal extraction kinetics the technological scheme for treatment of sulphuric solution (contents g/l: 2-3 Cu; 3-4 Zn; 2-5 Co; 1-1,5 Ni; 0,3-0,5 Ca, 8-10 Mg) has been worked out and tested on a pilot-industrial scale (Fig.3). The worked out technology permits to obtain goods products in the sort of salts and oxides with 99,4% extraction of metals (92% Mg). The technology could be improved by reduction of Cu, Ni and Co in organic extracts. It permits to cut down by more than 3 times the number of extraction stages (because of simplification of separation of Co, Ni, Zn) and by 2 times - the expenditure of reagents.

It is known that the use of the extraction processes is limited by concentration of metals in the solution treated. The expenditures on the fill up (supplying) of losses of extractant at low concentration

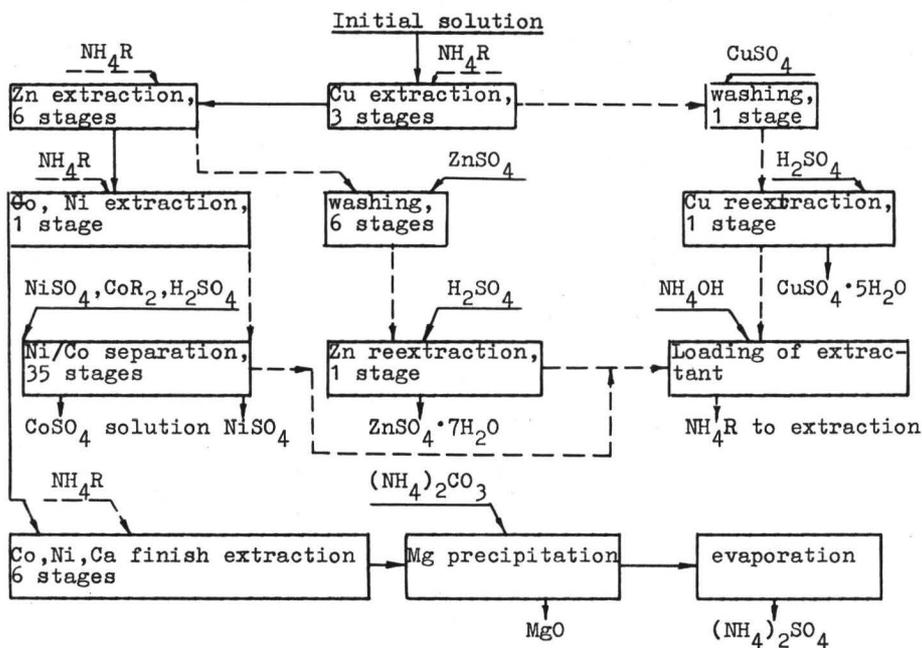


Fig.3. The technological scheme of treatment sulphuric solution;
 ——— water phase; ----- organic phase

increased relatively to the cost of the good products which leads to the reduction of economical efficiency of the processes. For naphthenic acids this deficiency could be avoided by application of combined flotation-extraction technology. The basis principles are the following: flotation is applied for preliminary concentration of extracted metals; pneumatic product is treated by extraction methods; combination of flotation and extraction is attained by use of the same reagents as the collector and extractant. The use of flotation in the heading operation provides a high productivity of the technique and permits to decrease a wastage of naphthenic acids from 50-100 mg/l to 5-8 mg/l. This permits to treat 20 times more diluted solutions. The combined technique is developed for extraction of Cu from solution containing g/l 0,2 Cu; 0,5 Co; 2,0 Mn; 35,0 Mg /5/. Below is the succession of operation (Fig.4): ionic flotation of Cu by naphthenic ammonium at $\text{pH} = 6-7,5$; dissolving of pneumatic product in the kerosine solution of naphthenic acids; treatment of the organic solution by the known extraction processes (washing of CuSO_4 solution and reextraction of Cu) and regeneration of collector. The regeneration of collector is realized by its transferring into aqueous solution with the help of treatment of organic phase by NH_4OH -solution at $\text{pH} = 8,3-8,5$ and $t = 50-60^\circ\text{C}$.

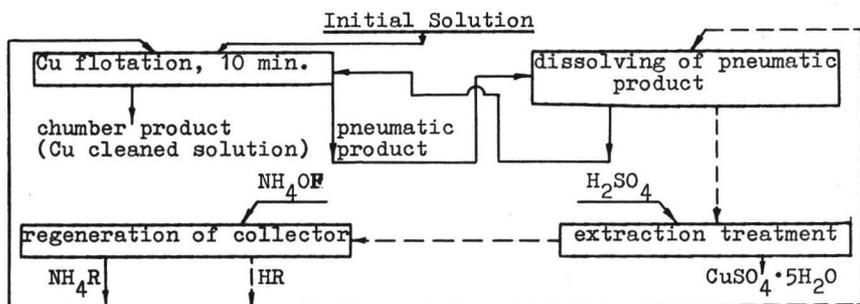


Fig.4. The scheme of flotation-extraction isolation of Cu from solution; ——— water phase; - - - - - organic phase

The expenditure on reagents, including the cost of wastage of the naphtenic acids, reaches 2,5% from cost of the goods CuSO_4 .

The combined method permits efficiently use of naphtenic acids for utilization of non-ferrous metals in flotation technology for purification of the sawage [6]. The technique of purification of the waste mine waters for one of the mining plants (with utilization Cu and Zn to the good products in sort of sulphates) has been worked out too.

Thus, the combination of the considered processes and centrifugal extractor in the technological scheme permits: to increase the efficiency of application of the naphtenic acids; to realize the complex treatment of the different content solutions and concentrations of metals; to receive the wide range of the goods products in sort of salts, oxides, powder metals; to solve ecological problems.

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In the USSR studies on the application of extraction in hydrometal-
lurgy of nickel and cobalt began with the use of carboxylic acids for
removal of impurities from cobalt solutions [1] and with the use of
tertiary aliphatic amines for separation of cobalt from nickel [2] .

Studies of extraction processes from the point of view of electro-
chemistry were carried out under the leadership of V.L.Kheifetz [3,4].
The potential jump at the extract-aqueous phase interface and its role
in the extraction processes, as well as the influence of the electro-
lytic dissociation of extractants and extractive compounds in the or-
ganic phase on the processes of ion-exchange extraction were consi-
dered.

It is stated that the selectivity of the cation-exchange extrac-
tion increases with the decrease of the strength of the organic acid
used as an extractant; electrophilic reagents reduce the values of the
anion-exchange extraction of metals; the strength of the organic ba-
ses (nitriles, amides, amines) correlates with their extractive power
towards cobalt and nickel chlorides being extracted from 4M solutions
of NaCl. Despite their relatively low conductivities, the organic so-
lutions of extractants and extracts behave like typical electrolytes.
Oxidation-reduction potentials of Fe^{3+}/Fe^{2+} system in organic solu-
tions of their salts with caprylic acid and D2EHPA [5] and of Cu^{2+}/Cu^{+}
system in organic solutions of QAB and tertiary amine salts [6] are
measured.

The electrochemical measurements are useful for the explanation of
the mechanism of metal extraction and for the determination of the
composition of extractive complexes. The above measurements are also
effective for practical control of extraction processes because they
make it possible to determine quickly the type of emulsion in an ex-
tractor mixing chamber, phase interface in a settler and the oxida-
tive state of metals in extracts.

As selective extractants for nickel, long-chain dialkyl- α -dioximes
of the general formula $R-C(NO_2H)-C(NO_2H)-R^1$ were synthesized and studied
with the following R and R^1 : 1) CH_3 , C_3H_7 , 2) CH_3 , C_6H_{13} , 3) CH_3 ,
 C_7H_{15} , 4) CH_3 , C_8H_{17} , 5) C_2H_5 , C_3H_7 , 6) C_3H_7 , C_4H_9 , 7) C_6H_{13} , C_7H_{15} ,
8) C_7H_{15} , C_8H_{17} , 9) C_8H_{17} , C_8H_{19} , 10) $C_{10}H_{21}$, $C_{11}H_{23}$ [7].

Dioximes extract nickel at $pH=4.2$ and copper at $pH=5.4$ from sul-
phate solutions. With the help of dioximes, nickel is effectively se-
parated from cobalt, copper, ferrum, zinc, arsenic, calcium, magne-

sium and sodium in ammonia solutions. Among the synthesized dioximes, ethylpropyl- and methylcephyl- α -dioximes are the most effective extractants of nickel. Stripping of nickel from organic phases is performed by aqueous solutions of mineral acids.

Extraction of heavy non-ferrous metals by trialkylbenzylammonium rhodanide was tested and the following order of extractiveness of their salts was found: $Zn(NO_3)_2 > ZnCl_2 > Cu(NO_3)_2 > Co(NO_3)_2 > CdCl_2 > Cd(NO_3)_2 > CuCl_2 > CoCl_2 > ZnSO_4 > CuSO_4 > CoSO_4 > CdSO_4$ [8]. In the hydrometallurgy of nickel QAB rhodanides can be used for the selective extraction of impurities, in particular zinc from sulphate solutions.

Organic salts formed by a cation of quaternary ammonium or phosphonium and by an anion of carboxylic acid, $n(ZX)_o^+ (MY_n)_o \xrightleftharpoons{H_2O} n(ZY)_o^+ + (MX_n)_{aq.}$, where $Z = R_4N, R_4P$; $Y = RCOO$; M - metal; $X = Cl^-, NO_3^-, SO_4^{2-}, HSO_4^-$, were tested as extractants of non-organic salts [9]. The extraction proceeds according to a reverse reaction and depends on the total concentration of salts in the aqueous solution. Non-organic cations and anions are extracted according to the cation- and anion-exchange extraction for organic acids and bases forming the extractant. Non-organic ions in the extract are mobile and can be exchanged which makes it possible to carry out an extensive non-organic synthesis.

The crystallization of salts from extracts during the stripping process studied by us on the examples of nickel, cobalt and copper stripping from their salts with carboxylic, naphthenic and di-2-ethylhexylphosphoric acids by concentrated solutions of mineral acids is of practical significance [10]. The following crystalline hydrates of salts were produced from extracts: $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$.

The selectivity of liquid-liquid extraction of metals is studied on the examples of extraction of cations, anion complexes and salts [11]. Equations are derived describing the dependence of the distribution coefficients S_{m_2/m_1} on three factors, which are the ratios of equilibrium constants of extraction reactions (K_e), the activity coefficients of metal aquo complexes in the aqueous phase ($\gamma_{M_{aq}}$) and the extractive complexes in the organic phase ($\gamma_{e.c.}$), correspondingly:

$$S_{m_2/m_1} = \frac{{}_2 K_e}{{}_1 K_e} \frac{{}_2 \gamma_{M_{aq}}^{2+}}{{}_1 \gamma_{M_{aq}}^{2+}} \frac{{}_1 \gamma_{e.c.}}{{}_2 \gamma_{e.c.}}$$

The flowsheets tested on a pilot plant scale are shown in the table. Besides, a method of production of nickel electrolyte from the hydrate of nickel oxide dissolving it with the help of carboxylic acids [12] and a method of copper-nickel matte treatment which combines the process of electrolysis with extraction [13] are developed on a laboratory scale. In the last few years a number of new technologies using ex-

Extraction flowsheets [14]

Sl. nos.	Feed	Extractant	Products	Number of stages
1	Cobalt anodes, composition, %: 77 Co, 8.3 Ni, 10 Fe, 0.14 Cu, 1.3 S	1. Trialkyl-amine - 6%, fatty alcohols - 10%, kerosene - 84% 2. Amine - 30%, alcohols - 10%, kerosene - 60%	1. Electrolytic cobalt 2. Hydrate of nickel oxide	9
2	Cobalt concentrate composition, %: 23 Co, 1.15 Ni, 0.03 Cu, 1.25 Fe	1. 6% solution of amine in aromatic hydrocarbons 2. 30% solution of amine in aromatic hydrocarbons	1. Cobalt oxide 2. Hydrate of nickel oxide	20
3	Concentrate, composition, %: 19.8 Ni, 13.7 Co, 12.3 Cu, 3.8 As, 2.0 Zn, 0.5 Fe, 75 H ₂ O	1. Synthetic fatty acids C ₇ -C ₉ 2. 50% solution of tri-alkylbenzylammonium chloride in aromatic hydrocarbons	1. Cobalt oxide 2. Copper sulphate 3. Nickel carbonate	31
4	Chloride solution, composition, g/l: 102 Co, 4.6 Ni, 6.2 Cu, 2.7 Fe, 2.1 Ca, 0.4 Mn, 202 Cl ⁻	1. 6% solution of amine in aromatic solvent 2. 50% solution of QAB chloride in aromatic solvent	1. Cobalt oxide 2. Hydrate of nickel oxide	23
5	Nitrate solution, composition, g/l: 67 Co, 6 Fe, 17Cu, 5.9 Ni, 18.8 Ca, 37 Na	50% solution of fatty acids C ₇ -C ₉ in kerosene	1. Cobalt oxalate 2. Fe-Cu cake 3. Mn-Ca cake 4. Ammonium nitrate	24
6	Sulphate solution, composition, g/l: 30-32 Cu, 15 Ni, 15 Co	50% solution of fatty acids C ₇ -C ₉ in kerosene	1. Copper sulphate 2. Solution, 30 g/l Ni, 30g/l Co 3. Sodium sulphate	12
7	Solution, 22-39g/l Co	Fatty acids C ₇ -C ₉	Cobalt Sulphate	5

traction processes combined with autoclave leaching processes, electrolysis or autoclave hydrogen reduction have been developed.

The advantages of the extraction technologies over the settling ones lie in the elimination of labour-consuming operations of filtration, reducing of reagent consumption and technological equipment volumes, in the increase of metal recovery into finished products and in the improvement of their quality at the expense of deeper separation of metals by extraction. In some cases the extraction technologies have no wastes, they provide the regeneration of the most part of reagents and eliminate the formation of salt effluents.

The economic calculations confirm the high effectiveness of extractive technologies of nickel and cobalt production.

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BY SOLVENT EXTRACTION FOR GETTING HIGH-PURE (0[#]) ELECTROLYTIC NICKEL

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For overcoming the disadvantages of purification process of nickel electrolyte mainly by precipitation method, a new process based on the solvent extraction purification method was developed.

The composition of nickel electrolyte is as follows: Ni 70-75g/l, Co 0.15-0.20g/l, Cu 0.45-0.5g/l, Fe 0.15-0.20g/l, Zn 0.004-0.005g/l, Pb 0.002g/l, Na 40-45g/l, H₃BO₃ 3-8g/l, Cl⁻ 110-120g/l, SO₄²⁻ 80-90g/l, PH 1.3-1.5

The new purification process are divided into the following four steps:

1. Oxidation of Cu⁺, Fe²⁺ to Cu²⁺, Fe³⁺ by chlorine;
2. Extraction of Fe³⁺ by extractant N503 (N503 is a extractant of neutral amidate sort);
3. Extraction of Co, Cu, Zn by EHPNA (its chinese trademark is P507);
4. Removal of Pb by ion exchange with 701[#] resin.

After the above-mentioned purification steps, the qualified nickel electrolyte is obtained for producing 0[#] electrolytic nickel.

In this paper only the extraction of Co, Cu, Zn from Ni by EHPNA is mentioned.

As known, EHPNA is a efficient extractant for the separation of Co from Ni [1-5], but it is less investigated for the extraction process taken place in the mixed acid (HCl+H₂SO₄) medium.

At first, the extraction equilibrium studies were carried out, based on this studies extraction cascade and bench-scale extraction experiments were finished.

I. Extraction equilibrium studies. In this experiments the parameters affecting the extraction equilibrium, the PH value, concentration of EHPNA, operation temperature and acidity of stripping solution are studied.

The feed is prepared according to the composition of given nickel electrolyte, and all the reagents are analytical pure. EHPNA is the product of Shanghai Organic Reagent Factory No.4, the diluent kerosene 260[#] is produced by Shanghai Oil Refinery. For controlling the equilibrium PH value, 12.5N NaOH is added into the prepared organic phase for saponification.

Equilibrium studies were carried out in the special test tube with the volume of 25ml.

Based on the obtained experimental results, the extraction equilibrium mathematic models of Ni, Co and Cu were developed as follows:

$$\log D_{Ni} = -2.5995 + 2.7278 \log[\overline{RH}] + 0.9513PH$$

with the average deviation 9.8%;

$$\log D_{Co} = -1.9566 + 2.1127 \log[\overline{RH}] + 1.2373 PH$$

with the average deviation 9.7%;

$$\log D_{Cu} = -1.8307 + 2.2109 \log[\overline{RH}] + 0.6928PH$$

with the average deviation 13.3%,

and the following main points can be concluded:

1. The equilibrium PH value is the main parameter affecting the extraction

equilibrium of various metals, and their extracted order, in the mixed HCl + H₂SO₄ medium is similar to that in the sulphate medium [1]. It is easy to separate Zn.Cu.Co and Ni by controlling the equilibrium PH value, but for the separation of Cu and Co there are some difficulties owing to their similar extraction characteristics.

2. The concentration of EHPNA affects the extraction equilibrium of metals remarkably. At the same equilibrium PH value the extraction ratios of metals increase with the increasing of EHPNA concentration, but the extracted order of various metals has not change.
3. The operation temperature mainly affects the extraction equilibrium of Co, and the distribution coefficient of Co increases with the increasing of temperature, so it is benefit to the separation of Co from Ni to raise the temperature.
4. For complete stripping of Zn.Cu.Co.Ni in organic phase, the equilibrium PH value must be controlled below 1, then the H₂SO₄ concentration in stripping solution can be determined according to the concentration of metals in loaded organic phase and the volume ratio between organic and aqueous phases.

II, Extraction cascade experiments. The cascade experiments were carried out in the same test tube as used in the equilibrium studies.

Because the separation factor of Co from Ni is high enough in the EHPNA extraction system, the simple counter-current method was adopted, and the optimized computation was carried out based on the extraction rate of metals > 99% according to the following objective function $N \times [RH] \times V \Rightarrow \text{minimum}$. The computation results are as follows:

[RH].%(v/v)	Equilibrium PH	V(L=1)	N
10	4.4	0.2	5
10	4.4	0.15	7
15	4.4	0.2	4
15	4.6	0.2	3

According to the computation results the appropriate operation parameters for extraction cascade are determined as follows:

$$\begin{array}{ll}
 [RH] & 15\%(v/v) \\
 v/L & 0.2 \\
 t & 35 \pm 1^{\circ}\text{C} \qquad N \quad 6
 \end{array}$$

A part of extraction cascade experimental results is tabulated in Table 1.

The number of stripping stage is calculated by the following equation;

$$N = \frac{\log\left(\frac{\xi - \beta}{1 - \beta}\right)}{\log \xi} - 1$$

Table 1. Experimental results of extraction cascade

[RH], %(v/v)	Feed, g/l	Extraction stage	Aqueous phase, g/l			organic phase, g/l			Equilibrium PH
			Ni	Co	Cu	Ni	Co	Cu	
15.0 sapo- nific- ation =76.6%	Ni77.6	1	77.47	0.0665	0.0472	1.2750	0.8116	2.852	4.62
	Co0.152	2							
	Cu0.492	3	77.46	0.0091	0.0012	1.3700	0.1551	0.0335	4.80
	PH 3.64	4							
		5	77.43	0.0012	0.00018	1.7250	0.0416	0.0023	4.82
		6		0.00066	0.00018				4.97

and the calculation results show that near four ideal stripping stages is needed for the complete stripping of Zn, Cu, Co, Ni. Under the experimental conditions of stripping phase ratio (o/A) = 10:1 and ambient temperature, after four stripping stages the concentration of Ni, Co, Cu in the organic phase is 0.00088g/l, 0.00013g/l and 0.00007g/l, respectively.

Based on the cascade experiments, the following operation parameters are determined; for extraction step:

concentration of EHPNA	15%(v/v)
saponification of EHPNA	75%
PH value in feed	3.5-3.7
operation temperature	~35°C
PH value in raffinate	5.0
flow ratio (o/A)	1:5
number of ideal stage	6

for stripping step:

concentration of H ₂ SO ₄	2N.
operation temperature	ambient
flow ratio (o/A)	10:1
number of ideal stage	4

III. Extraction bench-scale experiments. According to the determined operation conditions the bench-scale extraction and stripping experiments were carried out in a laboratorial mixer-settler with mixer volume 0.5l and settling volume 1.5l. In this experiments the feed solution is the practical nickel electrolyte. The experimental results are tabulated in Table 2.

It can be seen from this results that the purification of nickel (Co 0.0005g/l, Cu 0.00031g/l in purified nickel electrolyte) and recovery of Ni, Co, Cu (Ni > 99%, Co.Cu > 99.9%) are satisfied, and the qualified nicked cathode plate was produced in the succeeding electrolytic process.

Table 2. Bench-scale experimental results (Extraction stages: 6, stripping stages: 4)

stage No.	in aqueous phase, g/l			in organic phase, g/l			PH in aq.	t, °C	o/A
	Ni	Co	Cu	Ni	Co	Cu			
1	77.42	0.1108	0.0402	0.9000	0.6920	1.9860	4.24	38-40	1/5
2	77.32	0.0325	0.0282	1.4000	0.5050	0.9240	4.76		
3	77.35	0.0160	0.0094	1.2300	0.1575	0.1686	4.82		
4	77.30	0.0059	0.00097	1.5100	0.0390	0.0113	4.89		
5	77.35	0.0017	0.00079	1.2300	0.0107	0.0025	4.90		
6	77.23	0.0005	0.00031	1.8300	0.0095	0.0013	5.03		
1'		2.9360	10.164	0.0475	0.0120	0.0680		Amb.	10/1
2'		0.1025	1.3400	0.0200	0.0008	0.0010			
3'		0.0346	0.0415	0.0001	0.0001	0.0001			
4'		0.0042	0.0016	0.00005	0.0001	0.0001			

At the end of this paper it can be concluded that:

1. EHPNA is still an excellent extractant for purification of nickel electrolyte in the mixed $\text{HCl}+\text{H}_2\text{SO}_4$ system.
2. The purified nickel electrolyte may be used to produce $\text{O}^\#$ electrolytic nickel, and the loss of nickel in the extraction process is only 0.23%.
3. Owing to the high flow ratios adopted in the extraction and stripping steps, the stripped solution of Co, Cu is concentrated by about 50 times, it is of benefit to be treated further.

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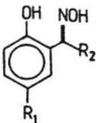
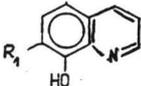
An ammoniacal leaching process was developed to extract metal values from oxidized zinc and lead-zinc ores not amenable to flotation (1). Leach solution arising out contain dissolved zinc as cationic amine complex and attempts were made to recover it by solvent extraction. The use of carboxylic acids, naphthenic acids and organophosphorous extractants results in reagent losses owing to their appreciable solubility in aqueous phase.

The recent application of hydroxyoximes and 8-hydroxy-quinoline derivatives has broadened the variety of commercial chelating reagents available for the extraction of metal ions from both acid and alkaline solutions (2).

A detailed investigation was carried out and the extraction of zinc from an ammoniacal solution was studied as a function of contact time, aqueous solution composition and pH.

The chelating extractants employed for the experimental work are indicated in Table 1.

Table 1, Commercial chelating reagents for zinc extraction

	Reagent	Substituents	
		R ₁	R ₂
	LIX-65N	C ₉ H ₁₉	C ₆ H ₅
	SME-529	C ₉ H ₁₉	CH ₃
	P50	C ₉ H ₁₉	H
	Kelex 100	C ₁₀	—

The organic phase for all the extraction tests was a 10% (by volume) solution of unpurified extractant dissolved in a diluent: kerosene for LIX-65N, Acorga P50 and SME-529 and toluene for Kelex with 10% p-nonyl-phenol as modifier. All the extractions were performed at room temperature (about 20°C) in a mixing vessel described previously (3). The ratio of the volumes of the organic phase to the aqueous phase was 1:1.

The concentration of the constituents in the feed liquor was chosen based upon available pilot plant data (21.3 g/l Zn) and the physical constraints of the system. The extraction equilibrium is attained after about 3 min for all the chelating reagent tested; however, equilibration was allowed to proceed for 30 min. After phase disengagement, duplicate aliquot of organic

Table 2. Zinc extraction from ammoniacal solutions with hydroxyoximes

Extractant	$(\text{NH}_4)_2\text{CO}_3$ g/l	Distrib. Coeff.	Extraction
		D	E _z %
LIX-64N	50	0.21	17.0
	100	1.34	57.2
	200	0.36	26.2
SME-529	50	0.21	17.0
	100	0.51	33.7
	200	1.30	56.4
P-50	50	0.44	30.6
	100	1.41	58.5
	200	0.23	18.7

and aqueous phases were taken for metal content determination by plasma atomic emission spectrophotometry. Distribution ratios of the metal were reproducible within less 5%.

The first series of extraction tests was run on the Zn-NH₃⁻-(NH₄)₂CO₃ system varying pH and ammonium concentration. The most evident conclusion that can be drawn from examination of the experimental results (Table 2) is that zinc extraction by means of hydroxyoximes (LIX-65N, P-50, SME-529) is poor at low ammonium carbonate concentration (50 g/l) at pH 9.0 .

Extraction is low with all the hydroxyoximes when low ammonium carbonate concentration is involved. An increase in (NH₄)₂CO₃ concentration to 100 g/l however, raises zinc extraction with all the hydroxyoximes, but more markedly with LIX-65N and P-50. When SME-529 is utilised as extractant, zinc extraction is further increased at 200 g/l (NH₄)₂CO₃ in solution. Conversely in this case zinc extraction is depressed with the other hydroxyoximes.

Good zinc extraction can be achieved, however, with Kelex 100. Fig. 1 demonstrates the influence of ammonium carbonate concentration and pH on zinc extraction. This decreases with increase in ammonium concentration and pH in solution, while still remaining high. The best results (over 90% zinc recovery) have been obtained at pH 8.0 and 50 g/l ammonium carbonate.

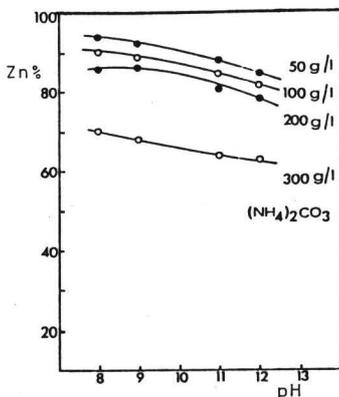


Fig.1. Zinc extraction with Kelex 100

The detailed examination of the results of the extraction test of zinc from ammoniacal solution, allows to assert that hydroxyquinoline (Kelex-100) extracts zinc in a bigger extent than hydroxyoximes.

These results can be explained by reference to the coordination chemistry. In fact, according to the principle of soft and hard acids and bases (PSHAB), zinc ion belongs to the borderline class

and its behaviour is more like that of the hard cations (4). The ligand NH_3 also belongs to the hard class. Pearson's rule thus postulates that the hard Lewis acids (or cations) react preferentially with hard bases. This explains why zinc amine complexes form readily in ammoniacal solution.

In the system examined -hydroxy-oximes and hydroxy-quinoline- the properties of the extractant depend on the properties of the nitrogen electron-donor atom, i.e. on the oxime group =N-OH and the nitro group =N-(5). The structure and composition of LIX-65N and Kelex-100 have received ample study (2,6). Kelex-100 consists of β -alkenyl-8-hydroxy-quinoline; the alkyl chain contains about 10 carbon atoms and a least one double bond. LIX-65N, instead, is a β -hydroxybenzophenoxime.

The formation of the metal chelate depends on the ease of proton release by the extractant molecule and the facility with which the nitrogen atom of the quinoline derivative (in the case of Kelex 100) and the alkyloxime (where LIX-65N is concerned) can donate their electron pair to the empty orbitals of the zinc ion.

Regarding the first point, it must be considered that in Kelex 100 molecule electrons associated with the hydroxyl group occur in a aromatic ring and hence proton is given up more readily than in the case of the LIX-65N (alkyl-oxime) molecule. In fact the acidity of the extractants increases as follows (6):



Turning now to the second point, it must be stressed that electron-donor properties of the nitrogen atom are associated with the electron density on that atom. The latter ensues from the molecule (inductive effects) and steric factors, when bulky substituents are close to the atom which is the active centre of the reaction.

Taking due account of these phenomena, it is fairly evident why only Kelex-100 extracts zinc with sufficiently high distribution coefficients with respect to the hydroxy-oximes. More precisely, at a given pH, extraction with Kelex-100 is greater owing to the higher intrinsic acidity and the bigger electronic density in the hydroxy-quinoline molecule. So chelates are readily formed with zinc ion. LIX-65N, instead, whose molecule is less acid and whose electronic flexibility is lower, does not form chelates with the zinc that is already in solution as stable amine complex $\text{Zn}(\text{NH}_3)_4^{2+}$.

The effects of structural modifications of the hydroxyoximes extractants on the zinc extraction are evident considering that

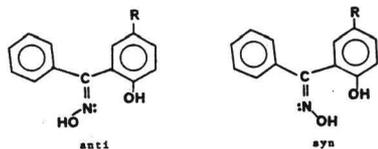


Fig.2. The isomers of LIX65N

In conclusion zinc can be extracted from ammoniacal solutions using Kelex 100 and the hydroxyoxime extractants are less effective. The extraction is sensitive to pH as well as NH_4^+ concentration.

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LIX-65N molecule contains two isomers: syn and anti (Fig.2). The syn structure is inactive towards the coordination of the zinc atom because the nitrogen ion pair is not capable for coordination and a structural rearrangement in favour of the anti form occurs slowly (7).

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Previous works showed that zinc can be extracted from industrial waste liquors by using DEHPA and naphthenic acid as solvents (1,2). When the liquors are strongly acidic, e.g. spent electrolytes of the zinc industry, sulphuric acid can be previously extracted with iso-butyl alcohol to reduce the acidity of the original liquor and to recover the acid itself (3).

Zinc can also be recovered from acidic sulphate liquors by direct extraction with TBP (4), which is very selective and gives high recovery yields. A drawback of the TBP use is that a salting agent, such as NaCl, must be added, so that the extracted species are zinc chloride complexes not suitable for the sulphate electrowinning process actually used.

However, electrowinning can be carried out from chloride electrolytes by using a diaphragm cell and DSA anodes for chlorine evolution (5).

The purpose of this work was to prepare a suitable chloride electrolyte for zinc electrowinning by zinc extraction with TBP from an industrial bleed off stream and to experimentally study the whole process including both sections of solvent extraction and electrolysis.

EXPERIMENTAL

The investigations were carried out on a lab-scale pilot plant with flow rate of 1-2 l/h.

The pilot plant essentially consisted of the following sections (Fig.1):

- a battery of mixer-settlers ERIES AT-1 (with 6-8 steps in the extraction stage, and 4-8 steps in the stripping stage);
- an electrowinning cell with Al cathode and DSA anode (De Nora, Italy) separated by Nafion 120 diaphragm (Du Pont, Usa); the anode compartment was closed and designed for chlorine collection. The anolyte (1 M NaCl) was continuously recycled to the compartment after NaCl make-up.
- an active carbon treatment of the electrolyte from the stripping section to reduce the TBP content to less than 2 ppm.

Industrial spent electrolytes were used containing (g/l): 14-15 Zn, 230-250 H₂SO₄, 15-20 Mg, 1-3 Mn, and 4-10 mg/l Fe, together with Cl and minor amounts of Cu, Cd, Ni, Sb, Co etc.; NaCl was added in various amounts to the bleed off stream as a salting agent. The extractant was technical grade TBP containing Kerosene (30-50% TBP by vol.); the stripping solutions were pure H₂SO₄ solutions (25 g/l) or solutions containing various amounts of the exhausted catholyte.

All experiments were carried out for several months, frequently changing the operating conditions of the extraction section to prepare the most suitable zinc solution for the electrowinning cell, and the most favourable stripping system. Zinc deposits on Al cathode were stripped every day.

* Work supported by Ministero Pubblica Istruzione, Italy.

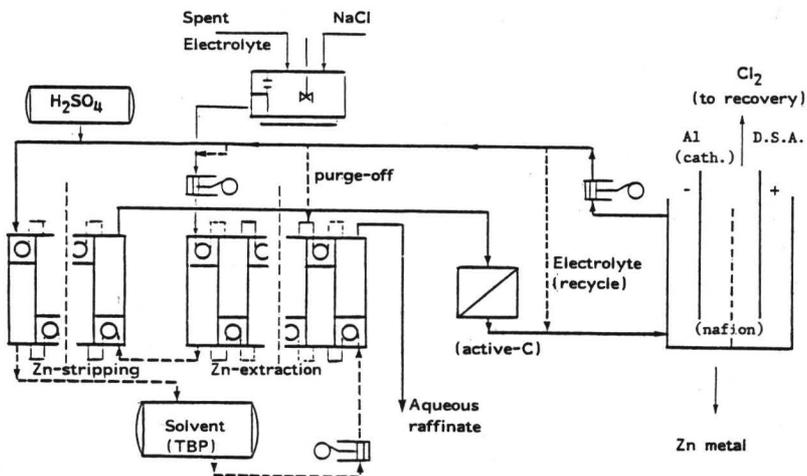


Fig. 1. Flowsheet of the pilot-plant

RESULTS AND DISCUSSION

During a first set of experiments, carried out with 6 extraction steps and 4 stripping steps, as shown in Fig. 2, acceptable zinc extraction yields were obtained (87%). The extraction selectivity of TBP towards zinc was high: major impurities normally contained in industrial electrolytes were, in reality, not extracted; only few ppm of iron, which did not effect zinc chloride electrolysis, were extracted.

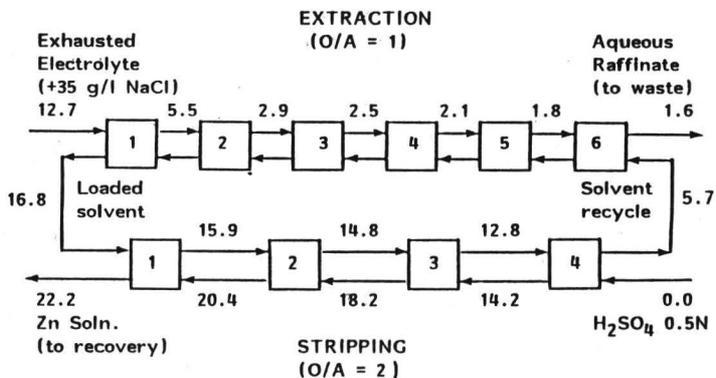


Fig. 2. Zn-concentration profile of a typical run with 6-4 steps

The extracted liquor, stripped by a sulphuric acid fresh solution, was treated with activated carbon and sent to the cell. TBP losses in aqueous phase were relatively low (0,06-0,08 g/l), but a carbon treatment was all the same necessary before the electrolysis. From the cell, the effluent electrolyte (containing 8-10 g/l Zn) was sent to the first extraction step mixed with the spent industrial electrolyte.

The described procedure had the drawbacks of low zinc extraction yields, high zinc recycle (with the effluent electrolyte from the cell), and of relatively high TBP losses due to the greater amount of aqueous raffinate.

In an other set of experiments, the electrolyte from the cell was used as stripping solution; for this purpose, part of the electrolyte (40-60%) was sent to the stripping section while an other portion was sent back to the cell together with the recovered zinc solution. Combining these two streams, the resulting Zn and acid concentration in the electrolyte to the cell was the most convenient.

Electrolyte purge was provided to avoid build up of impurities, such as Fe and Mg.

More steps (8+8 or 8+7) were necessary to reach good zinc extraction (Fig.3); zinc recovery yields of over 94% were obtained, leaving a residual zinc content of less than 1 g/l in the aqueous raffinate, and reaching a Zn concentration of 14 g/l in the solvent to be stripped.

Advantages of such approach were the following:

- more convenient utilization of the zinc solutions;
- higher zinc recovery;
- high purity of the electrolyte into the cell;
- no sulphuric acid consumption;
- lower TBP losses;
- lower cost of the carbon treatment.

The amount of the salting agent NaCl was varied during the tests in the range 35-50 g/l. The higher concentration (50 g/l) was the most favourable, giving zinc extraction yields between 90 and 94%.

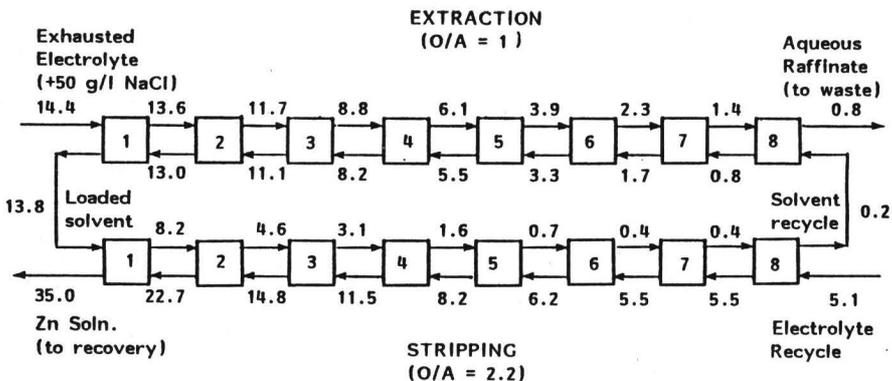


Fig. 3. Zn-concentration profile of a typical run with 8-8 steps

The TBP concentration into the kerosene varied between 30 and 50 % by vol.: lower contents gave low zinc extraction yields, while higher concentrations were not interesting due to high viscosity, small Zn extraction increase, and high cost.

Organic to aqueous ratios between 1 and 2.2 were used during stripping; O/A=2 was the best ratio, giving a liquor which after mixing with the recycled cell effluent had the right Zn and acid contents for the electrolysis.

Considering the electrowinning section of the pilot plant, high current efficiency (92-93%) and low specific energy consumption (2.7-2.8 kWh/kg) were obtained during the best runs (5).

It should be pointed out that the current efficiency is comparable with that obtained in the traditional sulphate electrolysis, and that energy consumption is appreciably lower.

A high quality zinc deposit on the cathode was obtained by using TBACL as additive at a concentration of 15-30 ppm, as suggested in Mac Kinnon and Brannen work (6).

The overall zinc recovery from the bleed off stream was averagely between 85-90%.

In conclusion, it can be said that the whole process (i.e. solvent extraction, stripping by using the electrolyte from the cell, and electrolysis in chloride medium) looks promising. The evolved chlorine could be used to prepare ipochlorite solutions or for other purposes.

Preliminary cost estimates showed the advantages of zinc recovery by this way, due to the negligible cost of the raw materials (spent electrolytes). Moreover, the process partially solves the problem of waste disposal in zinc industry.

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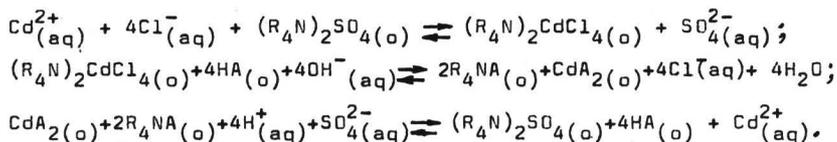
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The technique of cadmium extraction from zinc sulfate solutions with simultaneous removal of chloride-ions from the solutions should prove a good example of the advantages of binary extraction.

This method makes use of the separate stripping of chloride-ions and cadmium with binary extractant [1].

The stages of extraction and stripping of cadmium and chloride-ions are described by the equations (the solution and polymerization effects have been neglected):



The process is described similarly in the case of utilization of tri-alkylammonium carboxylate R_3NHA . Chloride-ions are stripped with NaOH solution fully when equilibrium pH-value of aqueous phase is equal to 6-7. The rise of HA concentration in the organic phase extends the range of pH-values retaining cadmium in the chloride strip product solvent, but this process rises the consumption of sodium hydroxide (Table 1).

Cadmium is completely stripped with solution of H_2SO_4 when equilibrium pH-value in the aqueous phase 2 is reached. At the stage of stripping cadmium can be concentrated in the strip product solvent up to 150-180 g/dm³, i.e., 15-30 times compared to the initial solution. The chloride-ion concentration in the same strip product solvent reaches 75-90 g/dm³. Sodium hypochlorite can be obtained from chloride strip product solvent by electrolysis while cadmium is extracted from its strip product solvent either by electrolysis or by electrolytic precipitation of zinc.

The isotherms of the extraction of cadmium and chloride-ions with binary extractant from zinc sulfate solutions are shown in Figure 1. The sequence of procedure of extraction of cadmium from zinc sulfate solutions obtained in the processing of lead powders is provided in the diagram in Fig. 2.

The composition of the initial solutions (given in g/dm³) is as follows: 60-80 Zn, 5-15 Cd, 5-10 Fe, 1-2 As, 0,1-0,3 Sb, 3-5 Cl^{-} , 15-25 H_2SO_4 .

For the industrial process the parameters and composition of the products obtained by this technique are given in Table 2.

The engineering method has been tested in pilot scale [2]. The extraction of cadmium from the initial solutions into strip product solvent makes up 98.9-99.9%, the purification of zinc sulfate solution from chloride-ions reaches 96-98%. The engineering process can be applied in the processing of sulfate-chloride solutions resulting from salt leaching of lead-zinc sulphide concentrates as well as in the reduction of cadmium electrolytes in galvanic production and the extraction of cadmium from the slimes of blast furnace production.

Table 1. The effect of VIK-2 (HA) concentration in organic phase on the stripping of chloride-ions with NaOH solution (O : W= 1:1) The extract composition: 0,6 M R_3N with the 10% addition iso-octanol; 5.0 g/dm³ Cd²⁺; 13.5 g/dm³ Cl⁻

R ₃ N:HA in organic phase	C _{NaOH} , M	pH	Concentration aqueous phase, g/dm ³	
			Cd	Cl ⁻
1:0.5	0.3	4,2	1.90	6,7
	0.5	6,2	0,60	13,1
	0,7	8,8	0,02	13,5
1:1	0.5	5,0	1,80	11,4
	0,7	6,4	0,60	13,1
	0,9	8,0	0,03	13,5
1:2	0,8	6,9	0,50	13,3
	1,1	7,6	0,05	13,4
	1,2	8,1	0,03	13,5

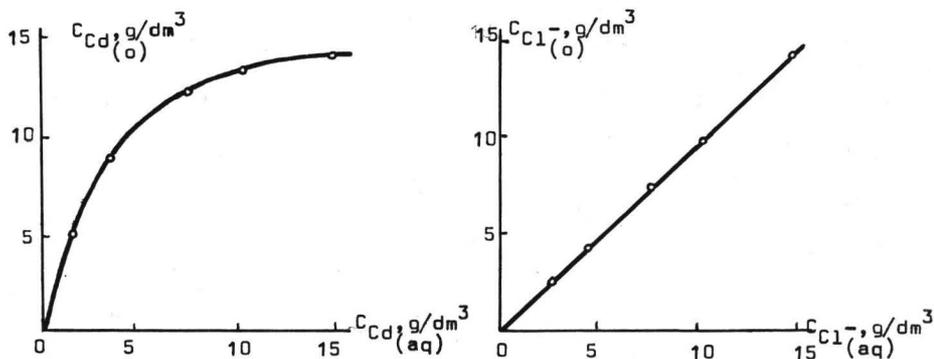


Fig. 1. The isotherms for the extraction of Cd (a) and those for chloride-ions (b) from zinc sulfate solutions ($2M ZnSO_4; 0.2M H_2SO_4$) with binary extractant: a) 0.6 M R_3NHCl and 0.6 M HA (VIK-2)

b) 0.3 M $(R_3NH)_2SO_4$ and 0.6 M HA (VIK-2)

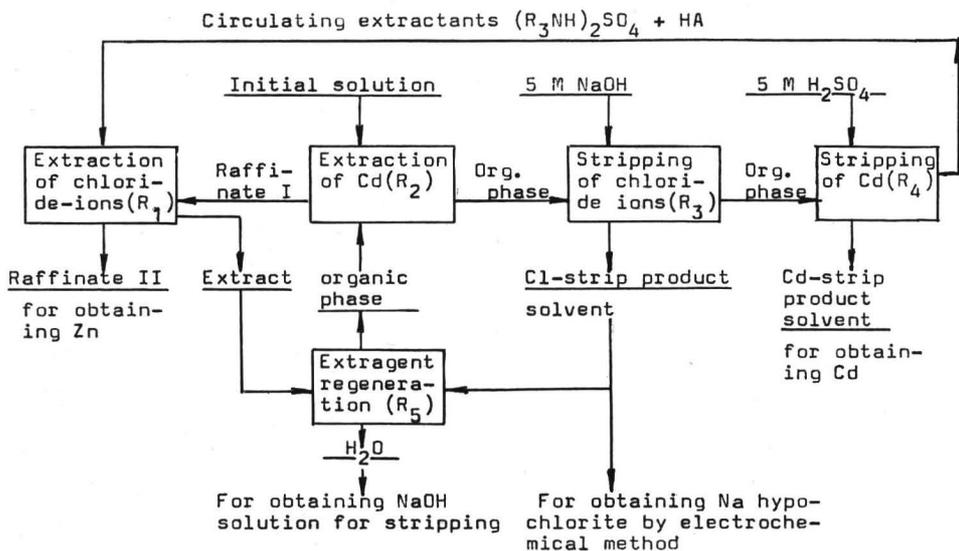


Fig.2. The technological diagram of the extraction of cadmium with binary extractant from zinc sulfate solutions with simultaneous removal of chloride-ions

Table 2. Technological parameters and composition of the obtained products

Stage	Parameters		Products	Concentration, g/dm ³	
	Phase ratio O:W	The number of steps		Cd	Cl ⁻
R ₁	1:3	5	Raffinate II	0,1	0,2
R ₂	1:3	4	Raffinate I	.0.1	1-2
R ₃	5:1	2	Cl-strip product solvent	0.02	75-90
R ₄	10:1	2	Cd-strip product solvent	150-180	0.5-1.0
R ₅	3:1	3	Liquor	0.05	1-2

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Rapid development of extraction technology of copper is considerably connected with a large range of selective extractants for it between which the reagents of oxyoximes class are most widely used in industry [1,2]. The extractant alkylbenzophenoneoxime - ABP, making possible the selective extraction of copper from complex solutions is created in the USSR.

The influence of nitrogen-containing additions such as: aliphatic amines and salts of quaternary ammonium bases and neutral phosphororganic compounds - TBP, di-2-ethylhexylmethylphosphonate (D2EGMP) and trialkylphosphineoxide (TAPO) is described in present work.

It has been shown, that the acidity of initial water solutions containing copper can be rised. In this way pH of aqueous phase increases from trialkylamine (TOA) to the salts of quaternary ammonium bases (TAMAS) and in the range: TBP < D2EGMP < TAPO in accordance with basicity of reagents in it. The addition of above said reagents doesn't lead to the decrease of selectivity, while kinetic parameters of the process are improved.

The fact of effective stripping of copper from organic phases containing mixtures of ABP with nitrogen - and phosphorus containing reagents by solutions of 100 g/l H₂SO₄ is of great interest.

Table. Stripping of copper by solutions of sulphuric acid (O:A=1:1; τ = 5 min; t = 22°C; copper concentration in organic phase 2,1-2,2 g/l)

Concentration of H ₂ SO ₄ in stripping solutions	Efficiency of copper extraction, %					
	0.21m ABP	0.21m ABP + 0.18m TOA	0.21m ABP + 0.19m TAMAS	0.21m ABP + 0.21m TBP	0.21m ABP + 0.19m D2EGMP	0.21m ABP + 0.18m TAPO
203	81.9	83.0	81.8	82.5	80.9	82.8
180	75.3	79.7	79.0	78.4	77.6	78.5
151	71.3	77.6	77.3	75.5	74.5	77.2
130	68.2	76.3	76.2	74.5	73.6	75.8
112	51.6	73.7	74.9	73.0	72.5	75.0
91	45.5	68.0	69.8	67.1	67.7	69.8
73	30.8	54.6	59.7	51.8	55.2	59.5
51	22.8	45.4	51.0	42.0	43.8	48.7
32	16.1	30.2	35.6	28.7	32.9	36.2

It is known that hydroxyoximes are slowly-kinetic extractants of copper and this is a considerable defect of that class of reagents.

The addition of reagent being an extractant with higher kinetic parameters is one of the most effective methods in order to improve copper extraction. For example extractant LIX 64 N is a mixture of slowly-kinetic alkylbenzophenoneoxime and aliphatic oxyoxime LIX 63 possessing high kinetic properties. The application of ortho-nitrosophenoles as kinetic additions is described in present work. It has been determined that the extraction rate increases in 5-10 times in the presence of 0,1-1% of ortho-nitrosophenole. Probably the mechanism of catalyzing influence of ortho-nitrosophenoles is like the mechanism realized when LIX 63 is used as a modifier of LIX 65N. So, rapid reaction of copper extraction is taking place at first with following exchange of ortho-nitrosophenole's extreme radical for the hydrooxime one.

It should be noted that the saturation of organic phase and acidity interval required for effective extraction and also the efficiency of copper stripping by solutions of sulphuric acid 150-170 g/l are not changed by using mixture of ABP with ortho-nitrosophenole as an extraction agent. The selectivity of extraction of ferrous, zinc, nickel and cobalt doesn't change when this mixture is used.

The laboratory investigations of copper extraction from solutions with low acid content were carried out using mixture of 10% alkylbenzophenoneoxime ABP and 0,1% 2-(α,α dimethylbenzyl)-4-methyl-6-nitrosophenole. The extraction process and stripping of copper were carried out at $\phi/a=1:1$ and 10:1 in 2 and 3 stages using one minute agitation time. The extraction of copper into raffinate after stripping has reached 96,7% at initial content of 1,32 g/l and pH 1,98. Using 10% ABP without ortho-nitrosophenole the extraction level of 73,5% was received.

Pilot-plant tests of copper extraction by ABP from the solutions after leaching of balanced out copper ores were carried out in accordance with technological line: leaching - extraction - electrowinning. The productivity of this plant using 15% solution of ABP in kerosene was 100-150 m³/day. Pulse columns with "KRIMZ" plates and mixer-settlers were used for extraction.

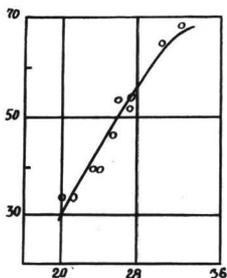
The analyses of the results shows that copper extraction largely depends on intensity of pulsation, flows ratio and temperature of solutions.

For example the increase of pulsation from 900 up to 1200 mm/min and detention of dispersed phase from 20 up to 32% leads to growth of copper extraction from 30 up to 68% other things being equal (Fig.).

The change of stream ratio from 0,5 up to 1,3 leads to increase of extraction from 40 to 88%. The growth of temperature from 22 to 28°C also results in its increase from 40 up to 70% that can be explained, probably, by the improvement of systems kinetic parameters.

The comparison of main technological parameters of copper extrac-

tion in pulse column with "KRIMZ" plates and in mixer-settler shows that the application of pulse columns allows to decrease the load of organic phase by 20% and the losses of extractant.



Dependence of the detenting capacity of pulse column on the extraction efficiency
 Diameter 0,9; effective height 5 m;
 $aq = 5 \text{ m}^3/\text{h}$; $o:a = 0.9$; $t = 27^\circ\text{C}$

Whereas the equipment of "mixer-settler" type is more safe and simple in work. Thus the choice of necessary equipment can be made only after some comparative calculations. On the base of this tests an optimal parameters of copper extraction in pulse columns were determined.

Extraction: frequency of pulsation - $1200 \pm 100 \text{ mm/min}$; summary specific load - $16-20 \text{ m}^3/\text{m}^2 \cdot \text{hour}$; ratio $o:a=1$.

Stripping: frequency of pulsation - $1800 \pm 200 \text{ mm/min}$; summary specific load - $15 \text{ m}^3/\text{m}^2 \cdot \text{hour}$; ratio $o:a=20:40$.

To reach extraction efficiency of 90-95% an overall height must be above 12-15 m. An extractant losses with stripping solution 0,06-0,08 g/l.

An optimal parameters of copper extraction in "mixer-settler" were determined as following.

Extraction: agitation time - 3 min; line speed of agitation - 300-350 m/min; summary settler load - $2,5 \text{ m}^3/\text{m}^2 \cdot \text{h}$; ratio $o:a=1$.

Stripping: agitation time - 5 min; line speed of agitation - 300 m/min; summary settler load - $2,0 \text{ m}^3/\text{m}^2 \cdot \text{h}$.

An extractant losses with raffinate 0,1-0,18 g/l; with solvent - 0,07 g/l.

Strip raffinate contains (g/l): Cu 39-41; H_2SO_4 180-200; Fe 0,31; Sn 0,3; Bi 0,003; Ni, Pb, Sb, As no more than 0,1.

Copper from the cathodes after electrowinning contained the following contaminants (%): Bi 0,00005; Sb 0,0004; As 0,0002; Fe 0,0008; Ni 0,0004; Pb 0,0048; Sn 0,00006; Zn 0,0003. Lean electrolyte containing 20 g/l and 200 g/l H_2SO_4 was returned to stripping. ABP expense by the extraction technology of copper from solutions after leaching was 10-12 kg/lt of cathode copper.

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Processing of low-grade polymetallic ore resulted in considerable accumulation of harmful impurities - Fe, As, Sb - in recycled solutions at some copper-electrolytic plants, in fall of technical-economic indices of electrolytic refining and in lowering of a product quality. As a rule purification works are not able to cope with the needed volumes of solutions because of low capacity of traditional schemes of neutralization by copper pellets and deep electrolytic decopperization. The processes proceed under hard sanitary conditions with high material and energy expenses, copper and nickel salts being of poor quality.

New high efficient technology of stepwise extraction of valuable components from strong acid copper electrolyte solutions has been developed and tested. The first step is the step of sulphuric acid separation with tertiary alkyl amine (alkyl C_7-C_9) solution in benzene as acid salts such as $(AmH)_2SO_4/2 \cdot H_2SO_4$. To increase extraction product solubility it was proposed to add to the extraction agent alkylated phenols as more effective and cheaper among known up to date solubilization additives-high molecular alcohols [1].

Sulphuric acid reextraction proceeds with hot water as it is known that heating essentially improves the process as a result of exothermic reaction. By calculations and experiments in continuous regime on a pilot-scale plant made up of extractors such as mixer-settler with 4.5 l/h production over phase sum it was found that 5-6 steps of extraction with the mixture of 1 mole/l of trialkylamine with the addition of 5% alkylphenol (organic:water volume ratio (3.5-4):1) were quite enough to decrease electrolyte acidity. After washing of the extract with water at the same phase volumes at 60°C regenerated sulphuric acid 125 g/l and middle amine salt returned for extraction were obtained.

After hydrolytic refining electrolyte comes in contact with the solution in kerosene of cheap commercial extractant-naphthenic acids (molecular mass 230-250) to which alkylphenols with synergistic additive were added to improve its extraction properties [2]. As a result copper distribution coefficients are found to increase owing to alkylphenol molecule substitution for solvated naphthenic acid ones and more lyophilic mixed complex formation. As a result the time of segregation of phases reduces and useful capacity of extractant increases. Different methods of physico-chemical analysis allowed to determine the composition of the formed mixed complexes. Optimum con-

ditions of copper and nickel selective separation by mixed extractant are determined on the basis of the calculations of entropy of mixing value which takes into account component redistribution between phases.

The developed technology was carried out in continuous regime on a pilot-scale plant which consists of tanks and extractors such as mixer-settler with 120 l/h output over phase sum. Mother solutions (pH 4) containing 50 g/l of copper and 40 g/l of nickel were used as model ones. The schemes of crossing current and countercurrent flow were tested taking into consideration the high metal concentration in solutions. Practically quantitative extraction of copper was provided in four steps of extraction (pH 4.5-5.0), while nickel remained in raffinate. Copper saturated organic phase was reextracted by equivalent amount of sulphuric acid (125 g/l) in two steps, the extractant being recycled. Nickel (pH 6.5-7.0) was extracted by analogy, pH correction was carried out by addition of the soda solution (6%). All the processes were characterized by stability without accumulation of detrimental impurities and intermediate phases. Reagents rate turned out to be close to stoichiometrical one, losses of extractant being insignificant.

Metals distribution in the products of technology (%)
(entered with initial solution 100%)

Copper extraction	Cu	Ni	Nickel extraction	Cu	Ni	Technological extraction	
						Cu	Ni
Crossing current flow scheme							
Copper vitriol	56.25	-				} 96.63	
Mother solution	40.38	30.52					
Raffinate	3.37	69.48	Nickel vitriol	-	39.59	} 68.09	
			Mother solution	3.37	28.50		
			Raffinate	-	1.39		
Countercurrent flow scheme							
Copper vitriol	73.52	-				} 98.89	
Mother solution	25.37	2.93					
Raffinate	1.11	97.07	Nickel vitriol	-	57.45	} 95.98	
			Mother solution	1.11	38.53		
			Raffinate	-	1.09		

High-class commercial copper and nickel sulphates out of vaporized reextracts have been obtained. Balance calculations give evidence of higher counterflow scheme efficiency by which technological copper extraction into end product amounts to 99%, nickel - 96%.

Combination of the extraction and electrolysis with insoluble anodes is more advantageous and economic method of metal extraction from the solution. In these schemes evolving at the electrolysis acid is consumed for saturated organic phase reextraction resulting in concentration of recycled electrolyte with precipitated metal. On this scheme using naphthenic acids nickel has been obtained.

The tests were carried out in the cell with cloth countercurrent diaphragm, separating cathodic and anodic spaces to store up sulphuric acid in the latter. The composition of nickel reextracts met the requirements to obtain high-grade metal. Great role of organic impurities, pH and electrolyte hydrodynamics in dense cathodic residue formation was determined.

pH fall of accessing catholyte up to 2-3 results in decrease of possibility of hydrateformation and cathodic nickel cracking and in facilitating of natural solution convection on account of cathodic space expansion up to 4 cm. Electrolyte refining from organic impurities was carried out by filtration through the column with activated coal BAU with the rate up to 20 volumes per hour amounting to 76 volumes. The coal has been easily regenerated with 1-2 volumes of sodium solution and water. Multiple long-term (3-5 days) experiments on the scheme "extraction-reextraction-electrolysis" allowed to obtain cathodic nickel specimens of the mark H-I from spent copper-electrolyte solutions with 85-96% current efficiency and showed that detrimental impurities storage in the nickel electrolyte and on the coal did not take place.

The developed technology is based on the application of cheap and non-deficient reagents, the processes are stable and easily automated. Utilization of ammonia for electrolyte neutralization and recycle of obtained solutions for sulphate storage gives the opportunity to vaporize waste waters up to the products used in agriculture. Expected economical effect at Balkhash mining and metallurgical plant amounts to more than 300 thousand roubles.

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Introduction. The waste flows of numerous technological processes contain a significant amount of copper compounds. In printed circuit board production, for example, about 65% of copper cover is dissolved which makes its recovery worthy. Copper isolation from the spent etchants is complicated because of the multicomponent composition of the solution. Some methods apply treating with chemicals. Generally, low quality product is obtained along with many chemical wastes [1].

When electrolyse directly spent etchants many attendant processes take place, harmful gases are released, the process is unstable and the yield get down [2-4]. The above methods seek to recover the metal and not to regenerate wasteless the etchant in order to use it in a recycle. If apply liquid extraction methods [5], it is possible to solve both problems. Copper can be partially extracted from the etching solution which is returned in the production cycle. By stripping the solvent, an acid solution of copper salt is obtained, from which copper can be easily recovered by electrolysis.

The aim of this work is to study several extractants in order to test their ability for selective extraction of copper from spent etchants and to develop an appropriate continuously operating installation.

Extractant studies. The main extractant properties needed for a successive resolution of the particular problem are:

- Selective extraction of copper from the multicomponent mixture, i.e. only the reaction $[\text{Cu}(\text{NH}_3)_n]\text{Cl}_2 + 2\text{RH} \rightleftharpoons \text{R}_2\text{Cu} + 2\text{NH}_4\text{Cl} + (n-2)\text{NH}_3$ takes place.
- High copper loading
- It is favourable if the stripping could be carried out with $2-3\text{N H}_2\text{SO}_4$ according to the reaction $\text{R}_2\text{Cu} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CuSO}_4 + \text{RH}$ in order to obtain a standartised solution for electrolysis.
- Fast kinetic of both processes.
- Low viscosity and good phase separation. The last two requirements are connected with the maximum flowrate and the volume of the contact and phase separation units.

The laboratory studies for choosing appropriate solvents were carried out with real spent etchants. The qualitative results for the general properties of 4 extractants are given in Table. Full quantitative results are listed in [6]. Evidently the most fitting are the properties of LIX 54, which was used as a solvent in the process carried out in the installation described below.

Installation. Its scheme is shown on fig.1. According to the laboratory results, the extraction and stripping processes could be realized in one step apparatus under intensive mixing for a good phase contact.

Extractant	Copper loading	Selectivity	Extraction kinetic	Stripping kinetic	Phase separat.
Fatty acids C ₁₃ -C ₁₈ up to 10%	+	~ ^x	+	+	-
Acorga P5100 up to 10%	~ ^{xx}	+	-	-	+
HS-LIX-65N up to 15%	~ ^{xx}	+	+	-	+
50%	+	+	+	no stripping at room temp.	+
LIX 54 100%	+	+	+	+	+

xExtraction of ammonia takes place. Soaps as well as stable dispersions are formed.

xxHigh O/W phase ratio is needed to reach the required extractuon.

In the installation two similar contact units I and II, 100 mm in diam. are used for extraction and stripping operations. Each of them include a mixing zone(6) with a turbine stirrer(7) and settling zones(5,9) incorporated in the apparatus body. The exit flows pass through adhesive phase separators(10,11) for fine phase separation. The feeding(4) is directly in the mixing zone. In the apparatus I a reduction of copper contents in the spent etchant(3) takes place. In fact this is a regeneration of the etching solution which is returned in the etching baths(1). The organic solvent containing the extracted copper(12) is stripped in apparatus II by sulphuric acid solution(15) coming from the electrolysis baths after copper winning. The regenerated extract-

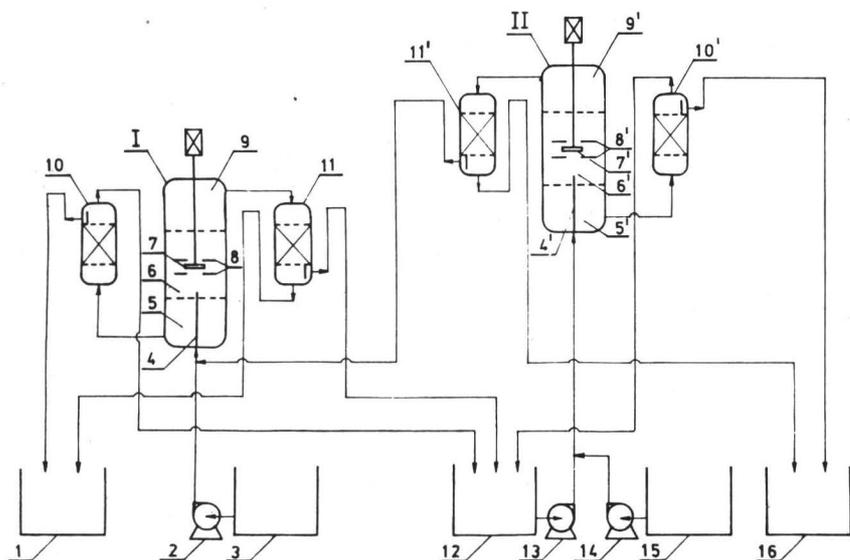


Fig. 1

ant is fed into I for a new extraction cycle. The spent stripping flow ($\text{CuSO}_4 + \text{H}_2\text{SO}_4$), tank(16), is used for electrowinning of copper.

This brief description gives an idea for the basic advantage of the applied principles—all flows are used in a closed cycle and no waste flows exist. Furthermore, the installation is simplified in construction and easily controlled. As the stripping column is mounted in a higher level over the extractor, the solvent is fed by gravity, avoiding a feeding tank and a pump. Thus the solvent flowrates in two apparatuses are self-synchronized and no special mutual regulation is needed. The flowrate in two columns is specified by controlling a single pump(13).

Determination of optimal processing conditions. For the considered particular case the efficiency of the units is provisionally defined as "g/l copper extracted from the etchant(extraction case) or from the organic solvent (stripping case). The extraction efficiency E_E under

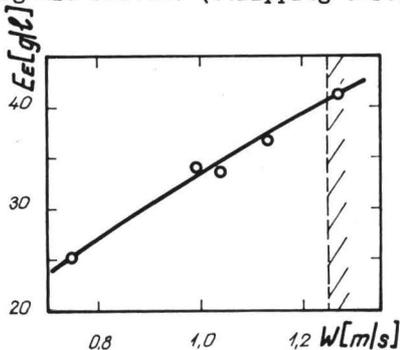


Fig. 2

various mixing intensities W is given in fig. 2. Optimal hydrodynamic regimes (good mixing and no phase separation problems) are created when the stirrer peripheral velocity W is 1-1,2 m/s. Significant phase retention and unstable regimes are seen when get over 1,25 m/s (//)

The extraction efficiency vs etchant flowrate F , resp. total throughput Q is seen from fig.3. under optimal mixing regimes and O/W ratio 2, chosen

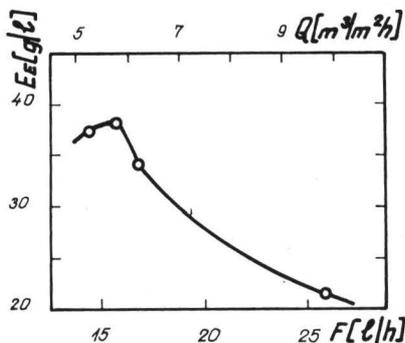


Fig. 3

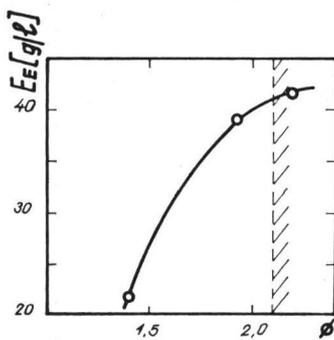


Fig. 4

by laboratory tests. It follows that throughput over $5-6 \text{ m}^3/\text{m}^2\text{h}$ means low efficiency regimes due to the shorter residence time.

Fig. 4 shows the extraction efficiency when vary O/W ratio ϕ . The throughput and mixing regimes are fixed at optimal values according to previous tests. When ϕ is less than 2, the extracted amount of copper

is not enough. When ϕ is greater than 2,2 (1/3) the apparatus is overloaded and flooding effects are seen. Thus, the value of ~ 2 seems reasonable for apparatus operation and ensures the extraction of required quantity of copper.

The efficiency of stripping unit E_R at various mixing regimes is plotted on fig. 5. The system solvent-sulphuric acid allows more intensive agitation since phase separation problems arise at peripheral stirrer velocity over 1,43 m/s (1/3).

In table 2 results for stripping efficiency at various phase ratio is given. It is worthy to operate at higher O/W flow ratio since lesser stripping solution is spent. But its output concentration cannot over-

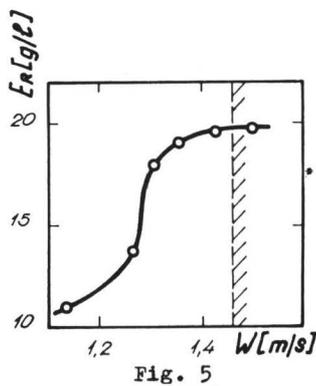


Table 2

come 55 g/l H₂SO₄ because crystallisation takes place which might block the pipelines. Thus, suitable values of phase ratio are 1,1-1,3. The flowrate of organic phase is the same for both units. The stripping solution flowrate is adjusted by choosing phase ratio as stated above.

Phase ratio, O/W	Stripped quantity, g/l	Output conc. of strip. solution, g/l
2,25-2,35	18,5-20,5	54-61
1,45	18	55
1,21	17,5	44
1,11	17	35
1,07	16	30
0,83	14	25

Conclusion

A solvent extraction process for recovery of copper from alkali solutions with high contents of ammonia and ammonia salts is developed and continuously operating installation is constructed. Studies for Choosing of copper selective extractants are carried out as well as study on the optimal apparatus performance. An extraction stripping technology with wasteless recycling of technological flows is described. It is successfully tested for continuous regeneration of industrial spent etching solutions.

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A COMBINED PRECIPITATION-EXTRACTION METHOD FOR TREATING
MANGANESE-NITRATE SOLUTIONS WITH IMPURITIES OF NON-FERROUS METALS

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Kremikovtzi ore deposits can be characterized as low-grade polymetallic iron ores with high content of manganese. Because of the presence of copper, lead, zinc, mercury, alkaline-earth and noble metals, whose contents vary depending on the locality, the hydrometallurgical methods of treatment prove to be the most efficient ones from economical point of view. Leaching by sulphuric acid I1I, nitric acid I2I or combined roasting and water leaching I3I were proposed as an initial stage in technologies of this type. Further utilization of manganese from the leaching solution has been subject of a number of investigations I3.4, 5.6I involving either extraction processes I4.6I or purification by cementation and precipitation.

A suitable method for production of high-grade iron concentrate consists of leaching with diluted nitric acid I2I. The solution in addition to containing Mn contains also copper, zinc, lead, barium and other metals of certain practical significance. In the majority of cases their concentrations are quite low compared to those of manganese, and the direct application of extraction processes for their separation requests scrubbing stages and large sized extraction equipment.

Another approach that could prove to be successful consists in consecutive alternation of precipitation and extraction. This allows to diminish considerably the volumes of the treated solutions and respectively the equipment used and extractant losses during the technological process. The aim of this work is to determine whether or not a combined precipitation-extraction method can be realized, thereby providing a manganese solution amenable to thermal treatment and allowing the reuse of the valuable metals.

The experiments were carried out by nitrate solutions, containing: 70-75 g/l manganese, 0.75-0.83 g/l copper, 1.5-3.6 g/l lead, 0.15-0.16 g/l zinc, 9-30 g/l calcium, 4-5 g/l magnesium with initial pH = 2.1-2.3. The test programme included experiments with model and models of real solutions. The organic phase consisted of 5 V% Lix 65N, 20 V% di-2ethylhexylphosphoric acid (D2EHPA), with addition of 5 V% tributylphosphate as an emulsion inhibitor. All experiments in extraction were performed in AKUFUE 110 apparatus combined with a system for automatic control and pH regulation. The results obtained characterize the behaviour of lead, copper, zinc, barium, calcium, magnesium and manganese during precipita-

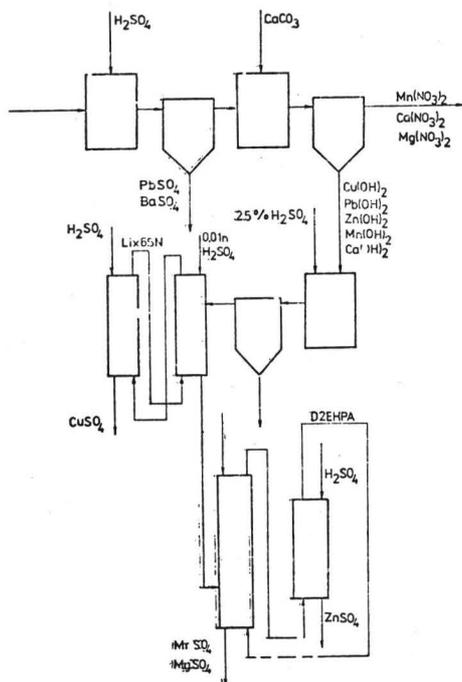


Fig. 1. General Technological Flowsheet

tion and extraction. Fig. 1 shows a general technological flowsheet proposed on the basis of the experimental results.

The first stage of this flowsheet consists in precipitation of barium as BaSO_4 with addition of concentrated sulphuric acid in amount 1/1000 of the initial volume. The precipitate obtained contains about 40-50% PbSO_4 and the data for the concentrations of different metal cations in the solution after filtration are shown in Table.

Concentrations of metal cations in the filtrate solution (g/l)

Operation	Mn	Cu	Pb	Zn	Ca	Mg
Precipitation by H_2SO_4 up to pH = 0,62	70	0.75	1.5	0.15	30	4
Precipitation by lime milk up to pH = 6,18	49	-	0.02	0.02	13.6	3
Solving the hydroxide precipitate by 25% H_2SO_4	39	3.8	0.014	0.6	0.008	0.43

By addition of lime milk to the filtrate solution up to pH = 6,2-6.3 precipitation of all accompanying non-ferrous metals (copper, lead, zinc as well as a large part of the present calcium) is obtained.

The manganese solution, after removing the precipitate (see Table 1) is amenable to thermal decomposition.

The precipitate, containing hydroxides of copper, lead, zinc, calcium and particularly of manganese, was treated by 25 V% sulphuric acid. In this manner $PbSO_4$ and $CaSO_4$ remain in the precipitate and $MnSO_4$, $CuSO_4$ and $ZnSO_4$ go into the solution in concentrations as shown in Table.

The volume of the obtained solution is ten times smaller than this of the initial one. It was processed by extraction to separate and reuse the contained metals. A route that can prove to be successful is the separation of copper and zinc from manganese, the purified sulphate manganese solution being amenable to thermal decomposition.

On the basis of the results obtained by Ritcey and Ashbrook [3] as well as results from performed experiments, the extraction of copper prior to zinc-manganese separation is very suitable. For this purpose 5 V% solution of Lix 65N in normal paraffins $C_{11}-C_{15}$ was used, and the equilibrium value of pH was maintained within the range of 1.85-1.95 where the separation factors are $\beta_{Cu/Zn} = 5$ and $\beta_{Cu/Mn} = 16$ respectively. Because of the low distribution coefficient of manganese $m_{Mn} = 0.5$ the two scrubbing stages of the extract allow its complete separation from copper, which can be utilized after stripping with 20 V% sulphuric acid.

Figs. 2 and 3 show the relationships $l_{gm} = f(pH)$ for the cases of zinc and manganese recovery by 20 V% D2EHPA and 5 V% D2EHPA + 50 V% fatty acids.

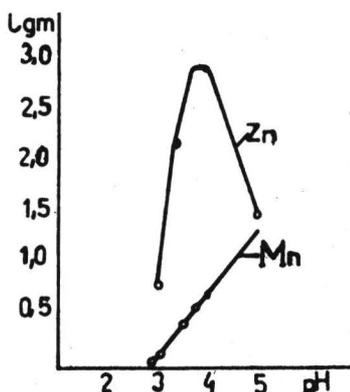


Fig. 2. $l_{gm} = f(pH)$

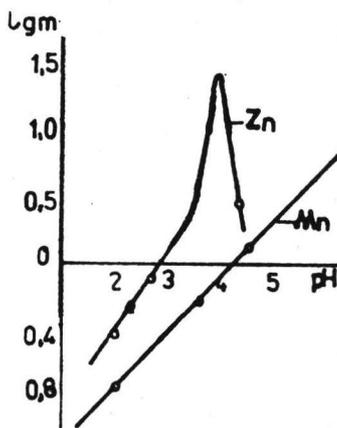


Fig. 3. $l_{gm} = f(pH)$

It is clear that maximum separation between zinc and manganese in the first case is realized at pH = 3.3-3.5 where the zinc concentration is lower than 10 mg/l and the separation coefficient $\beta_{Zn/Mn} = 135-198$. However, regardless of this value, due to the high distribution factor of manganese, $m_{Mn} = 1.6$ a significant amount of it goes into the extract and can not be efficiently scrubbed.

An approach for separation improvement consists in application of the so called mixed extractants, in the present case D2EHPA and a mixture of fatty acids $C_{14}-C_{18}$. The latter recover zinc and manganese at quite higher pH, the pH values of semiextraction being 5,15 for zinc and 5,65 for manganese. Their introduction to the system should move apart the ranges of extraction of these metals. In fact the replacement of D2EHPA by a mixed extractant on the basis of an industrial mixture of fatty acids $C_{14}-C_{18}$ -oleic fraction + D2EHPA shows that the best separation of the two metals is obtained at considerably higher values of pH, i.e. pH = 4.20-4.40, the separation factor $\beta_{Zn/Mn}$ being much lower - 44. However the use of this extractant is justified because of the lower distribution coefficient of the manganese, $m_{Mn} = 0.95$, which allows its complete separation from zinc by four scrubbing stages of the extract.

The obtained $MnSO_4$ solution is suitable for producing high purity manganese salts.

It can be concluded that the general flowsheet, given in Fig.1 makes possible to obtain purified manganese solutions and at the same time assures the reuse of the valuable metals, accompanying the manganese in the initial solution.

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RECOVERY OF HYDROCHLORIC ACID
FROM ACIDIC IRON-CONTAINING EFFLUENT
BY SOLVENT EXTRACTION OF LONG-CHAIN ALKYLAMINES

11-24

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Hydrochloric acid is widely used in rust-washing process in steel factories and machine building plants. A large amount of acidic effluent from these plants containing various amount of iron in 2-3 M hydrochloric acid causes a serious pollution of environment. In order to recover the residual hydrochloric acid in the effluent and avoid the environmental contamination, high-temperature baking treatment of the acidic iron-containing effluent is currently used in large-scale plants. However, high-temperature process loses its feasibility in medium and small plants for its high investment and huge energy consumption. Therefore, we have developed a solvent extraction process by tertiary long-chain alkylamine for the treatment of the acidic iron-containing effluent from rust-washing process, which is an easily feasible and economic method with high efficiency.

The acidic iron-containing effluent is a dark yellow-green liquid and its typical composition is 102.8 g/l in Fe(II), which makes up about 99% of the total amount of iron, and 2.60 M in hydrochloric acid. Usually, divalent iron cation in aqueous solution can only be extracted by chelating extractants with low capacity as well as poor applicability. The Fe(II) in the effluent is then subject to oxidation to Fe(III) by chlorine gas or concentrated hydrogen peroxide. Experimental result indicates that 99% of the Fe(II) in the effluent can be oxidated in 2 hrs by bubbling chlorine gas at room temperature.

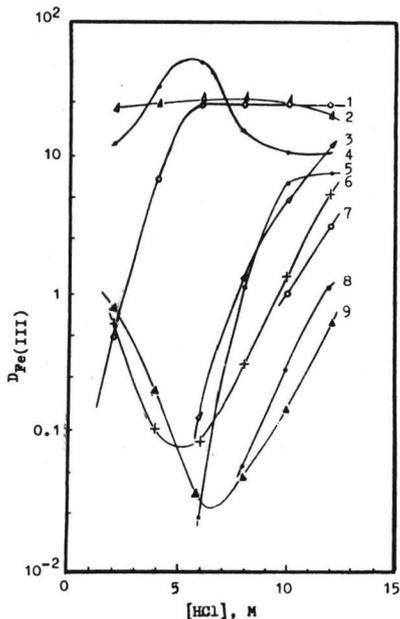
Fe(III) can be extracted by many organic extractants such as quaternary and tertiary alkylamines, neutral and acidic organophosphorous compounds, ethers, ketones and alcohols from HCl solution as indicated in Fig.1. However, only tertiary and quaternary long-chain alkylamines show high distribution coefficients for Fe(III), $D_{Fe(III)}$, in sufficiently wide range of concentration of HCl and are used in the subsequent

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Fig. 1. Effect of concentration of HCl in aqueous phase on distribution coefficient of trace amount of Fe(III) by various extractants (30 v/o in kerosene).

1. Tributylphosphate;
2. n-Trioctylamine;
3. sec-Octanol;
4. N-263;
5. Methyl isobutyl ketone;
6. P-507, commercial product equivalent to 2-ethylhexyl(2-ethylhexyl)phosphonic acid;
7. isopropylether;
8. P-215, equivalent to di(1-methylheptyl)-phosphoric acid;
9. P-204, equivalent to HDEHP



experiments. Experimental results show that extraction equilibrium of Fe(III) can be established within 3-5 min. for both N-235 and N-263, which are the commercial products equivalent to Alamine-336 and Aliquat-336 respectively, and Fe(III) is probably extracted in the form of a anion FeCl_5^{2-} or FeCl_6^{3-} showing a very strong absorption peak at 381 cm^{-1} (Fig.2). $D_{\text{Fe(III)}}$ decreases dramatically as the concentration of iron(III) in aqueous phase increases (Fig.3). As the concentration of N-235 or N-263 in organic phase increases from 30 v/o to 45 v/o, $D_{\text{Fe(III)}}$ increases from 0.827 or 1.10 to 2.02 or 6.00 respectively.

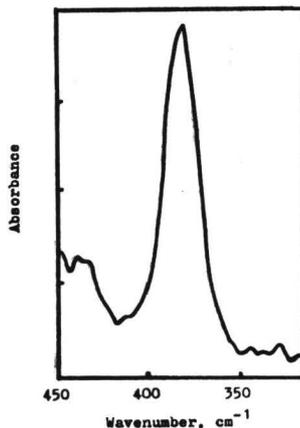


Fig. 2. Far infrared absorption spectrum of iron(III) in the phase of N-235/s-octanol/kerosene.

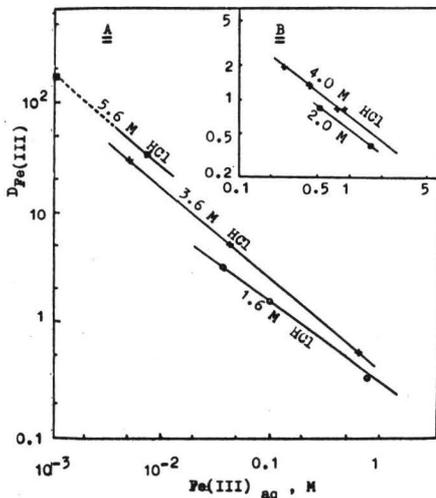
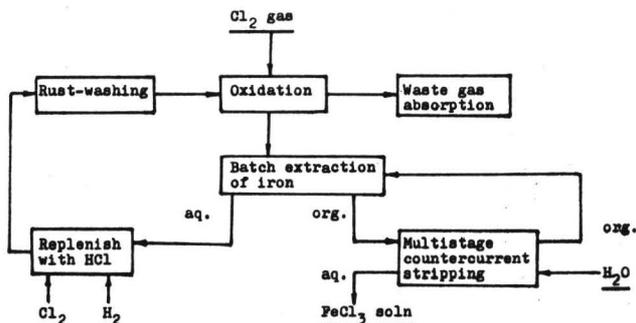


Fig. 3. Effect of concentration of Fe(III) at equilibrium in aqueous phase on its own distribution coefficient for
 A. 20 v/o N-235/30 v/o s-octanol/kerosene;
 B. 30 v/o N-263/30 v/o s-octanol/kerosene.

Although result indicates that both N-235 and N-263 show sufficient extractability for Fe(III) in HCl solution even in high concentration of Fe(III) in aqueous phase, N-235 is superior over N-263 for its higher yield in multistage countercurrent stripping experiments (Table 1). Therefore, the tertiary long-chain alkyl(C_8-C_{10})amine N-235 is finally chosen as the extractant for Fe(III) and the HCl left in the raffinate is recovered for recycling in rust-washing process. The final aqueous solution after stripping ($pH \leq 1$) contains 210 g/l $FeCl_3$ with only trace amount of Cu, Mg and Si (mg/l) and can be easily reprocessed to obtain solid $FeCl_3$ products for sale. The overall flowsheet proposed for recovering HCl in acidic iron-containing effluent from rust-washing process of machine building plants is schematically indicated as follows.



Stripping of iron(III) from organic phase in multistage countercurrent process

Run no.	1	2	3	4
Org. phase	30 v/o N-263/ 30 v/o s-octanol	40 v/o N-263/ 35 v/o s-octanol	30 v/o N-235/ 30 v/o s-octanol	45 v/o N-235/ 35 v/o s-octanol
Temperature (°C)	38	38	38	38
No. of stages	6	8	6	8
Stripping reagent	water	water	water	water
Flow ratio (org./aq.)	2:1	2:1	2:1	2:1
Conc. of Fe(III) in final org. phase, M	0.184	0.320	0.100	0.021
Conc. of Fe(III) in final aq. phase, M	0.978	0.800	1.25	1.32
Yield of stripping (%)	55.6	55.6	82.4	97.1

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In common with many metal extractions, the solvent extraction of borates normally depends on careful prior solid-liquid separation. Solvent-in-pulp systems are rarely feasible because of solvent loss and emulsification. However, incentive remains to avoid the costs of thickening, filtration and clarification, particularly in the Turkish borate industry, where borax deposits are interlayered with clay minerals and carbonates.

Previous reports (1,2) considered the solvent extraction of borax from kerosene solutions of 2-chloro-4-(1,1,3,3-tetramethylbutyl)-6-methylphenol (CTMP). The rate and equilibrium position of extraction were found to be largely unaffected by the presence of 5 weight percent of -75 micrometre quartz, calcite or kaolinite in suspension. The present paper deals with phase interaction and disengagement characteristics, which were affected by these solids.

Preliminary experimental work indicated that, when various mixtures of CTMP, kerosene, water, and aqueous borate were stirred together at 800 rpm in a baffled beaker, emulsification occurred above pH 6 and increased in intensity with increase in pH. On settling, the phases slowly separated. After settling for 30 minutes at pH 8, the upper bulk phase still contained about 30% water and the lower phase a small concentration of oil microdroplets (giving it a hazy appearance). When solids were added at pH 8, and the mixing and settling procedures carried out as before: quartz remained predominantly in the aqueous phase with little alteration of the emulsified state without solids; calcite (or colemanite) was totally transferred to the oil phase giving an emulsion of enhanced stability above a clear aqueous phase having some 70% of its original volume; kaolinite (or bentonite) similarly 'oil-floated' with most of the aqueous phase incorporated in the emulsion; and talc formed a stable emulsified phase between relatively clear organic and aqueous phases. As expected, increased ionic strength (by additions of borax or halite) or decreased stirring rate reduced the intensity of emulsification. When the phases were mixed gently in fully filled cylindrical flasks, by means of a wheel rotating at 10 rpm for 30 minutes, and allowed to settle for a further 30 minutes, there was no significant entrainment of one phase in the other and no emulsification in the presence of solids. UV spectrophotometric analysis of the aqueous phase for CTMP (carried out by back extraction into kerosene and measurement in this phase at 285 nm) gave values similar to the solubility of the reagent, e.g., 60 ppm at pH 8. The same boron extraction was observed regardless of the mode of mixing.

From the preliminary results it appeared that solvent-in-pulp boron extraction might be feasible if the behaviour of the suspended solids was better understood (and controlled) and if extractions were carried out with sufficiently controlled mixing of the phases. More detailed studies were undertaken on the effects of CTMP adsorption onto solids, CTMP acid dissociation, interfacial tension, ionic strength, and mixing conditions on emulsification and phase disengagement.

CTMP adsorption. Measurements of CTMP adsorption onto calcite, quartz and kaolinite represented (i) the relative tendencies of the minerals to become oleophilic and therefore to collect at the oil-water interface or disperse in the organic phase and (ii) potential solvent losses by adsorption in a solvent extraction process.

A known mass (in the range 0.1-1.0 g) of mineral (nominal specific surface area 1.0 m²/g) was mixed for 30 minutes with 50 ml aliquots of purified petroleum ether or water solutions of the reagent (5-100 ppm CTMP) by initial ultrasonic dispersion for one minute followed by gentle shaking. After centrifuging, the liquid phase was analysed spectrophotometrically and the CTMP adsorbed found by difference. The results obtained are shown in Fig. 1. For increasing CTMP concentration greater than 10⁻⁴ M, adsorption increased rapidly for calcite dispersed in petroleum ether until saturation was

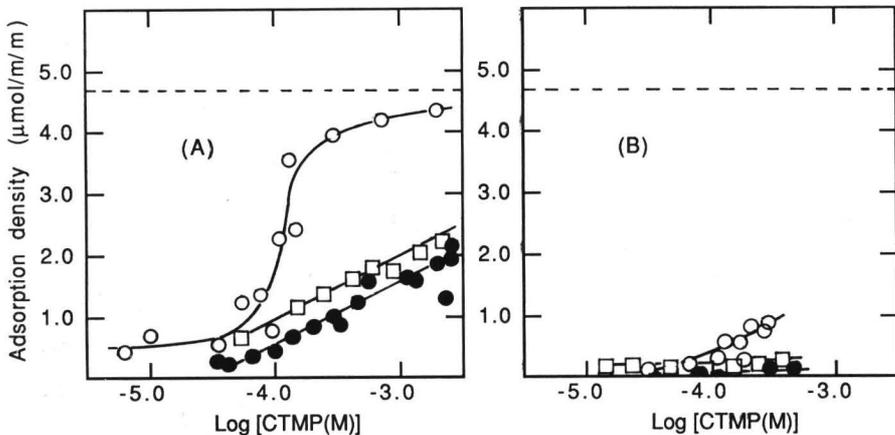


Fig.1. Adsorption of CTMP onto calcite \circ , kaolinite \square and quartz \bullet from (A) petroleum ether and (B) water at pH 9.

reached. This saturation was taken to correspond to a monolayer coverage of CTMP molecules of $4.61 \mu\text{mol m}^{-2}$, assuming a functional head group area of 0.36 nm^2 (estimated from a 3D model of the CTMP molecule). For kaolinite and quartz the increase was more gradual. The extent of adsorption decreased in the order calcite > kaolinite > quartz. In the presence of an aqueous phase, CTMP adsorption was less than 15% of monolayer coverage under all conditions, presumably because of competition by water molecules for surface active sites: at pH 9 the aqueous solubility of CTMP is about 100 ppm ($3.4 \times 10^{-4} \text{ M}$) while the concentration of water molecules is 55 M. The same order of adsorption persisted.

At pH 8-9 the surfaces of calcite are approximately electroneutral, whereas those of kaolinite and quartz carry a net negative charge (3). Thus electrostatic repulsion should reduce adsorption of (negatively charged) CTMP species on kaolinite and quartz. Conversely, specific chemisorption at Ca^{2+} sites on calcite might be facilitated.

From these results, the mass of CTMP adsorbed was less than 10% of that dissolved in aqueous solution. Solvent losses due to adsorption would be relatively unimportant. However, a small percent of monolayer coverage was clearly sufficient to cause significant changes in surface chemical properties, and thus a more stable interaction with an oil phase, as has been reported for other systems (4,5).

CTMP acid dissociation. Measurements of acid dissociation -- which occurs via the CTMP phenolic group -- related to the effects (on phase interactions) of increased solubility and ionization of interfacially adsorbed molecules at higher pH values.

The acid dissociation constant K_a of $\text{R}(\text{OH})_2$, i.e., CTMP represented as a diol (1), was determined by (i) equilibrating equal volumes of 0.50 M CTMP in petroleum ether with water at different pH values in the range 3-10 and determining the aqueous concentration (solubility) spectrophotometrically, as outlined above; (ii) calculating the distribution ratio as $D = 0.50 / \{[\text{R}(\text{OH})_2] + [\text{R}(\text{O}_2\text{H})]\}$ at each pH; and (iii) interpreting a plot of $\log D$ vs pH, as shown in Fig. 2(A). The theory behind this determination has been given by Poslu (6). Fig. 2(B) shows the calculated relative concentrations of species based on $K_a = 10^{-8}$. It can be seen that the organic phase concentration $[\text{R}(\text{OH})_2]_0$ remains essentially constant while $[\text{R}(\text{OH})_2]$ falls above pH 8 and $[\text{R}(\text{O}_2\text{H})]$ (together with the overall aqueous solubility) increases rapidly above pH 7.

As will be seen below, the liquid-liquid interface is likely to be saturated with CTMP species. The proportion of these in ionized form should also increase above pH 7. The ions should orientate with the

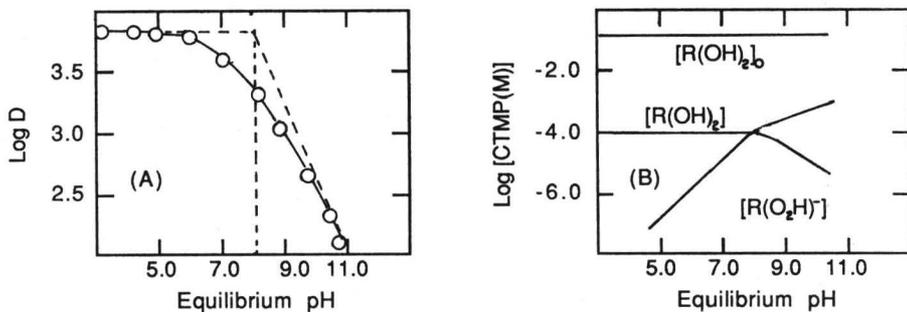


Fig. 2. Logarithmic plots of distribution ratio (A) and CTMP concentration (B) vs pH indicating CTMP apparent pK = 8.0 and calculated concentrations of species

polar (ionized) part in the water phase (the minus charge being counter balanced by Na^+ and H^+ ions in this phase) and the non-polar part in the petroleum ether, thus giving rise to an electrical double layer. In consequence, any globules in an emulsion would carry the same electrical charge and be mutually repellent, thus retarding aggregation and coalescence.

Increases in solubility and implied development of surface negative charges on oil globules accompanying acid dissociation are consistent with the observed onset of relatively stable emulsification, and make practical solvent extraction difficult above pH 7-8.

Interfacial tension and ionic strength. Measurements of interfacial tension (Kruss digital tensiometer) between water and CTMP in petroleum ether indicated (i) an upper limiting value of 45 mN m^{-1} at zero CTMP concentration; (ii) a rapid decrease from 35 to 20 mN m^{-1} in the range $10^{-3} - 10^{-2} \text{ M}$ CTMP; and (iii) the approach to a lower limiting value of $10 - 12 \text{ mN m}^{-1}$ at $0.1 - 1.0 \text{ M}$ CTMP as the interface became saturated with CTMP species. Increases in ionic strength (by addition of sodium chloride at $0.2 - 1.0 \text{ M}$) or decreases in pH (from 11 to 3) increased the interfacial tension marginally, by about 1%. Ionic strength above 0.1 caused rapid separation of metastable emulsions.

The small interfacial tension at industrially relevant CTMP concentrations ($> 0.5 \text{ M}$) indicates a relatively large interaction at the interface and partly explains the observed tendency for emulsions to form easily with this system. Interfacial tension cannot readily be manipulated to advantage but, of course, ionic strength can be increased to aid phase separation.

Mixing conditions. Photographic measurements of droplet size distributions after mixing at different stirring rates gave (i) relationships between energy input and intensity of emulsification / demulsification and (ii) information on emulsion structure without and with the presence of solids.

Equal volumes of 0.5 M CTMP in kerosene and 0.048 M boron as borax (at pH 7.5, 8.5 and 9.7) were stirred in a baffled beaker at 600, 800 and 1000 rpm for 10 min. Samples of each resulting emulsion was immediately transferred to a glass cuvette and photographed (SLR camera with macro lens and bellows) at suitable time intervals at the mid point of one of the optical flats of the cuvette. Postcard sized prints provided an overall magnification of 50 times. The droplet size distributions were determined by direct counting of 100 droplet images on each print.

Fig. 3(A) shows the observed decrease in size (average droplet diameter) from about 125 to $65 \mu\text{m}$ on increasing the stirring rate from 600 to 1000 rpm. Increase in pH caused a marginal decrease in size. Also plotted (Fig. 3(B)) is the logarithm of the time taken for the static emulsions to break down completely against original stirring speed. The straight line relationship observed facilitates extrapolation to lower stirring speeds (for which the photographic technique is too slow). For instance, a stirring speed of 200 rpm gives an estimated demulsification time of 10 min. Clearly, in a successful industrial

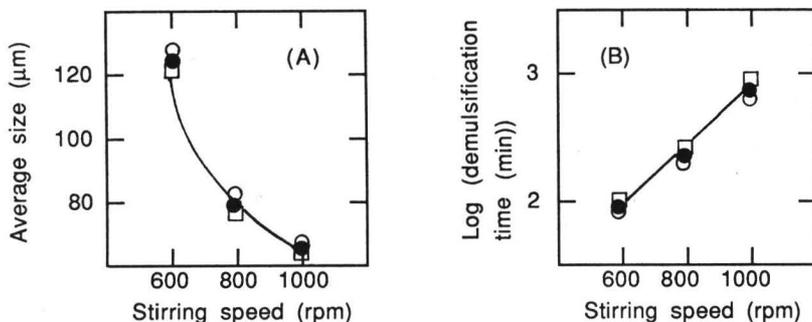


Fig. 3. Plots of average droplet size (A) and log (demulsification time) (B) against stirring speed: ○, ●, □; pH 7.5, 8.5 and 9.7 respectively.

process the energy input from stirring would have to be relatively low, even in the absence of solids. In the presence of calcite or kaolinite (800 rpm, pH 8) the photographs showed little change in droplet size. The particles seemed to have been trapped between two or more organic droplets, but with the mineral staying mostly in the aqueous phase, and tended to form a 'monolayer' of particles around each droplet. Such a collection of particles would cause a mechanical barrier to coalescence. The emulsions containing the mineral particles were stable for several days at rest, although they were readily disrupted by centrifuging for 2 min at 1000 rpm. With quartz, the mineral rapidly settled under all conditions and the demulsification times were similar to those without solids present. Evidently, chemisorption stabilised the droplet - mineral - water associations in the cases of calcite and kaolinite but not quartz.

To provide appropriate mixing conditions, a 15.2 cm diameter contactor (2,6), which was supplied by RTL Contactor Holding SA, was used in the semi-continuous, counter current, solvent-in-pulp extraction of boron. Under the conditions employed (rotor speed 5 rpm, flow rate 90 ml per minute, inlet boron concentration 1000 ppm adjusted to pH 10.8 with lime, solids content 1% as a 50% mixture of calcite and bentonite, and CTMP concentration 0.3 M) a 93.6% boron extraction was achieved with an outlet pH of 8.4. Initial organic entrainment was about 1000 ppm. After settling for 30 minutes this was reduced to 450 ppm and centrifuging readily reduced the losses to the CTMP solubility level (60 ppm). A preliminary flowsheet was designed to reduce the content of plant effluents to less than 10 ppm boron. This will be described elsewhere.

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INTRODUCTION

Oxidative leaching processes have recently gained an increasing interest in the hydrometallurgy of sulphur ores. Nevertheless, at present, they are not applicable with profit to all minerals, nor are they free from drawbacks of technological nature. In particular, the formation of muds with unleached or partially leached sulphides, inerts and precipitates makes quite expensive the separation of reaction products and the recovery of sulphur.

The Authors developed an original process for the continuous oxidative leaching of metallic sulphides in the presence of an organic solvent of sulphur [1-3]. This process allows the total recovery, from the organic phase, of the elemental sulphur produced in the course of the reaction. The kinetic analysis of the process, with reference to synthetic and natural minerals, allowed to determine the dependence of the rate of sulphide dissolution from the operative parameters. The reaction rates observed were much higher than those obtainable in the absence of the solvent.

A pilot reactor-extractor plant, operating continuously in countercurrent, was then designed and built, on the basis of the preliminary results of batch runs carried out at constant temperature in shaken flasks.

MATERIALS

Two different minerals were used in the experimental runs: an Italian high sulphur content sphalerite (Raibl) and a mixed sphalerite-pyrite-chalcopyrite concentrate. This mineral was selected in order to investigate the possibility of selectively recovering copper and zinc in the course of the leaching process. Elemental chemical analyses are reported in table.

Chemical analysis of the minerals (wt %)
 A - mixed concentrate B - sphalerite

	A	B		A	B
Cu	5.82	0.04	Al	0.049	-
Zn	8.90	53.50	Ag	29.45 ppm	0.0005
Pb	0.078	2.50	Au	0.99 ppm	-
S	47.81	30.00	Co	-	0.001
Fe	36.76	1.70	Hg	-	0.003
Bi	0.011	-	Ni	-	0.0015
Cd	0.033	0.10	As	-	0.15
Ba	0.198	-	Sb	-	0.025
Hg	0.005	1.25	Ge	-	0.04
Si	0.077	1.00	Ga	-	0.005
Mn	0.05	-	Sn	-	0.005
Mo	0.073	-	Cl	-	0.15
Ca	0.012	2.00	F	-	0.005

The leaching solution consisted of ferric sulfate dissolved in distilled water. Carbon tetrachloride was used as solvent.

EXTRACTION APPARATUS

A reactor-extractor, consisting of a glass column with an internal diameter of 44 mm and an overall length of 1700 mm was built up. Along the column axis a stainless steel shaft provided with agitators and driven by a variable speed motor was placed. A schematic representation of the apparatus is shown in fig. 1. The leaching solution, which is the continuous phase, is fed from the bottom, while the suspension of sulphide minerals in the organic solvent, which represents the dispersed phase, flows in from the top.

The reactor-extractor can be divided into three zones. The upper part is water-cooled, in order to accomplish the separation of the phases: in fact density change with temperature for the solvent is much greater than for the aqueous phase. In the central zone, which has a volume of about 2.5 l, the reactions take place, while in the lower part of the column the organic phase accumulates.

A comprehensive investigation of the performance of the reactor involves both a fluidynamic and a kinetic characterization. In a preliminary approach to the analysis of the process we determined the dispersed phase hold-up and performed some kinetic runs.

HOLD-UP MEASUREMENT

The hold-up measurement was performed by closing the inlet valves of the aqueous and organic phases after they had reached steady-state conditions. Then the motor was stopped, the two phases were drawn out of the column and their volume was measured. These runs were carried out at unitary conversion and at infinite recirculation ratio.

If V_t is the total volume of the reaction zone, the dispersed phase hold-up can be calculated as:

$$\varphi_d = V_d/V_t, \quad (1)$$

where V_d is the dispersed phase volume.

For the residence time of the phases inside the reactor we have:

$$\tau_d = V_d/F_d, \quad \tau_c = (V_t - V_d)/F_c, \quad (2)$$

where F_d and F_c are the flowrates of the dispersed and continuous phase respectively.

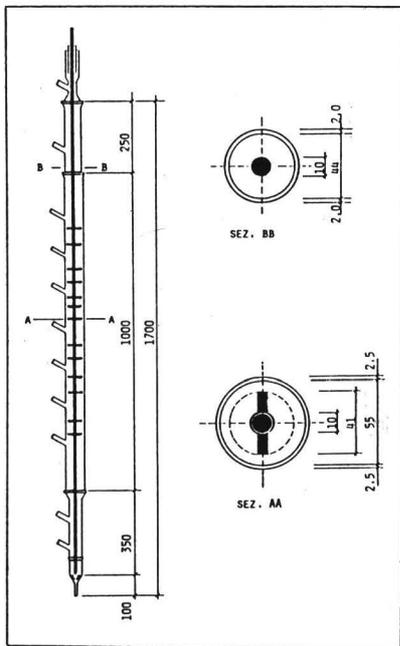


Fig. 1. Reactor-extractor

At this point, it is possible to evaluate the characteristic velocity, v_k , from the relation:

$$v_k = v_d / \{ \varphi_d (1 - \varphi_d) \} + v_c / \{ (1 - \varphi_d)^2 \}, \quad (3)$$

where v_d and v_c are the superficial velocities of the two phases, defined as the ratio of the flowrate to the column cross-sectional area.

Finally, the slip velocity can be determined by the following equation:

$$v_r = v_d / \varphi_d + v_c / (1 - \varphi_d) \quad (4)$$

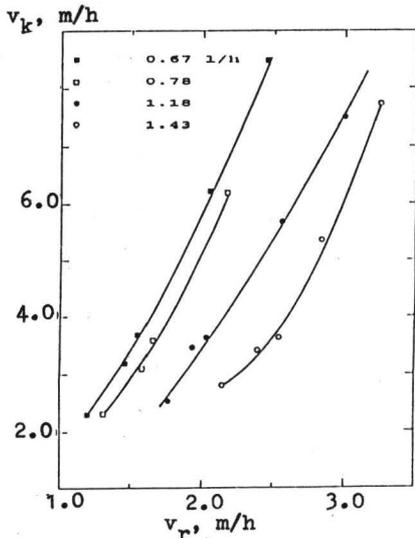


Fig. 2. Characteristic velocity patterns

In fig. 2 the characteristic velocity is plotted as a function of the slip velocity, at different flowrates.

KINETIC RUNS

Kinetic runs were carried out at the temperature of 70 °C and with a mineral to organic suspension ratio of 15 g/l. The conversion was determined by weighing the elemental sulphur after solvent evaporation. The experimental results were analyzed by the shrinking non-reacting core model. Its validity was verified in previous investigations [1-5] and justified by the non-porosity of both minerals and by the continuous dissolution of sulphur in the organic solvent.

The following equation was used to interpret the kinetic data:

$$1 - (1 - X)^{1/3} = \tau_d / \tau, \quad (5)$$

where X is the conversion, while τ is the time required for the complete conversion, which is defined as:

$$\tau = 3 / (r a_0 M). \quad (6)$$

In the above equation r represents the reaction rate, a_0 the surface area and M the molecular weight of the mineral. In fig. 3 some values of τ are reported as a function of the ferric sulfate concentration.

CONCLUSIONS

The use of a continuous process allows to carry out a correct kinetic analysis, under temperature and pressure conditions comparable with those used in batch industrial processes. The possibility of operating under pressure and in a continuous way is another innovative feature of the proposed process. Other non negligible advantages are the absence of air pollutants, the possibility of reacting low concentration ores and the economic recovery of elemental sulphur from the solvent by simple cooling and crystallization.

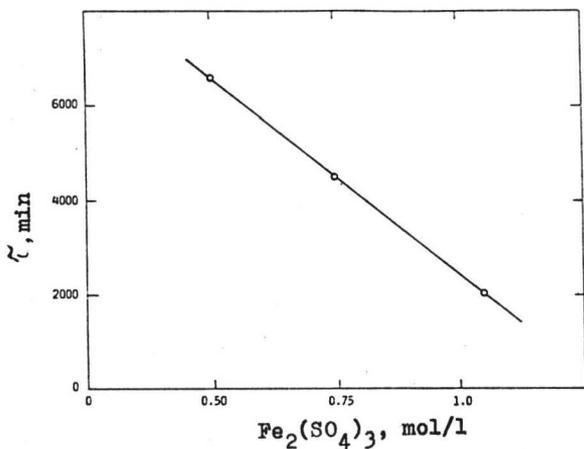


Fig. 3. Experimental values of τ

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The third (the second organic) phase formation at the phosphoric acid extraction by trialkylphosphate is associated with limited solubility of the solvates formed in an inert diluent and depends on the alkylphosphate type, diluent origin, phosphoric acid concentration and extragent concentration.

It has been established that in the alkylphosphate-alkylphosphin oxide series the phosphonates of DAMP or DOMP acid type do not form the third phase in all studied concentration ranges of phosphoric acid and extragent, which appears to be associated with raised solubility of isomer-forming phosphonates, solvated by phosphoric acid, in an inert diluent.

The study has shown that in the phosphoric acid concentration up to 15 mol/l the pure (100%) TBP does not form the third phase. The third phase is formed in diluted TBP solutions, at that the starting point of the third phase is displaced into the region of smaller equilibrium concentrations of phosphoric acid in the aqueous phase and for more diluted TBP solutions. The conditions for the starting point of the two organic phases formation are given in Table.

Table 1. Conditions for starting point of two organic phases formation

TBP, mol/l	H ₃ PO ₄ , mol/l	
	in kerosene	in octane
0.9	9.55	9.61
1.8	9.85	10.20
2.7	10.20	13.20

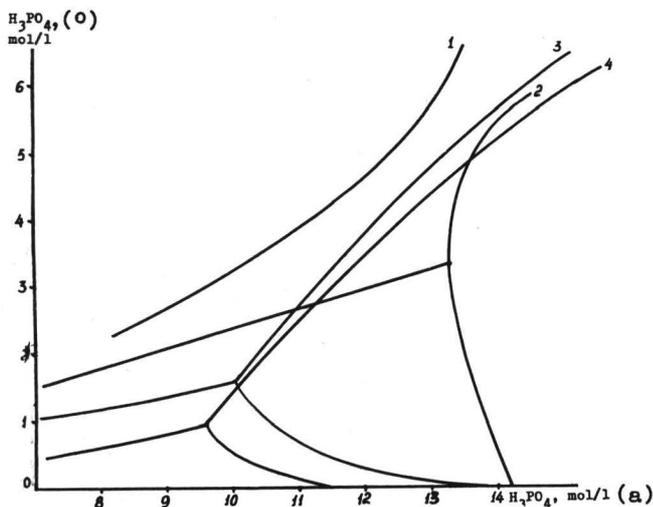
The third (lower) phase presents pure TBP, which is confirmed by the distribution coefficient value, being constant within the range 0.4-0.42 for all concentrations TBP studied.

The origin of diluent is of certain significance. TBP solution does not form the third phase in benzene.

Distribution of phosphoric acid in aqueous and organic phases during the two organic phases formation is shown in Fig.

The data on phosphoric acid distribution presence of solvates with different TBP and H₃PO₄ ratio. The character of solvation can be assessed from the composition of the third (second organic) phase. Analysis of the third phase, obtained by treating 25% TBP solution in octane with concentrated phosphoric acid, showed that molar ratio TBP : H₃PO₄ = 1 : 3 and TBP : H₂O = 1. Thus, one can suppose existence of hydrosolvate TBP · 3H₃PO₄ · H₂O.

Analysis of the third phase obtained by treating 25% TAPO solution in octane has shown that the molar ratio TAPO : H₃PO₄ = 1 : 4, and one



Distribution of phosphoric acid between aqueous and organic phases in the region of the third phase formation

1 - 100% TBP; 2 - 75% TBP; 3 - 50% TBP; 4 - 25% TBP in octane

can suppose presence of $\text{TAPO} \cdot 4\text{H}_3\text{PO}_4$ solvate. Thus, that can explain intensified extractability of phosphinoxides in regard of phosphoric acid.

Effect of extragent concentration on the distribution coefficient of phosphoric acid leads to possibility of obtaining the second aqueous phase, e.g. variation of TBP concentration in octane from 100 to 25%V decreases the distribution coefficient from 0.16 to 0.005, i.e. 30 fold. The second aqueous phase contained 4.2 mol/l H_3PO_4 .

An alternative to the process of the third phase formation is the process of mixing aqueous and organic phases with formation of homogeneous aqueous-organic solution. The character of phase volumes variation at the extraction of phosphoric acid with butanol has shown that there exists a threshold concentration for phosphoric acid above which phosphoric acid of any concentration can mix with a diluent. It means that the process passes from a heterogeneous into a homogeneous stage. It has been pointed out that the point of displacement is affected by water contents in butyl alcohol. For the butyl alcohol containing 0.088 mol/l H_2O mixing starts at an initial phosphoric acid concentration of 7.1 mol/l, for the butyl alcohol containing 8.3 mol/l H_2O - 8.45 mol/l. The above relationships are characteristic for other mineral acids as well, at that the complete mixing depends on the nature of acid. The series of extractability of mineral acids regarding butanol is retained under conditions of complete mixing, and the better mineral acid is extracted the lower concentration it takes to mix completely, e.g. for nitric acid concentration is 4.86 mol/l.

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Extraction of phosphoric acid is gaining attention in regard of manufacturing pure phosphoric acid and phosphates on its base from phosphorites of various type.

The extraction of phosphoric acid calls for utilization of solvents of various classes: aliphatic alcohols, organic phosphates, amines, ethers and their mixtures.

Phosphoric acid in aqueous solution is highly hydrated and, as a rule, the hydrosolvates of $mS \cdot nH_3PO_4 \cdot pH_2O$ type are extracted. The mechanism of phosphoric acid extraction by organic amines is different in some way.

Comparative characteristics of extractants of various classes show that the extractability decreases in the series $C_4 > C_5 > C_6 > \dots > C_{10}$. This is relevant to the series of organic phosphates, too. Besides, extractability increases in the series $R_3P(O) > (RO)_3P(O)$. In other words, extractability depends on the hydrocarbon chain in the organic solvent.

The class of aliphatic alcohols has a clearly expressed linear correlation between the distribution coefficient of phosphoric acid (D) and the number of carbon atoms in the hydrocarbon chain (n_C) with a correlation coefficient $r = 1$. E.g. the extraction from 6 mol/l H_3PO_4 is described by equation $D = 1/6.02 n_C - 18.58$. It is worth noticing that the coefficients in the equation are interrelated and have to be determined on the basis of mathematical statistics laws. At extraction of phosphoric acid by alcohols, e.g. by butanol, a certain linear correlation in many parameters is evident, such as one between phosphoric acid concentration in organic or aqueous phases (% weight) and density of the corresponding phase (kg/m^3), presented as $\gamma_o = 6.94/H_3PO_4/o + 838$. The study on equilibrium phases composition in system $BuOH - H_3PO_4 - H_2O$ has shown that there exists a correlation between parameters $/H_2O/w$ and $/BuOH/o$, the ratio approaches 1, the mean value - 1.006 with standard deviation $\sigma = 0.03$. There is a correlation between $lg H_2O_w/H_3PO_4 - lg BuOH/H_3PO_4$. The obtained correlations lead to empirical equation for phosphoric acid extraction with butanol.

$$lg /H_3PO_4/o = 1.45 lg/H_3PO_4/w - 0.45 lg/H_2O/w - 0.216 or$$

$$lg/H_3PO_4/o = lg/H_3PO_4/w + 0.015 /H_3PO_4/w - 0.833.$$

The joint solution of these equations brings about the possibility to determine the water contents in the aqueous phase and thus to calculate

the threefold diagram of the phase transformation in the system $\text{BuOH-H}_3\text{PO}_4 - \text{H}_2\text{O}$.

Phosphoric acid is satisfactorily extracted with TBP. The difference in the extractability of TBP according to its concentration is evident, which can be seen from Table 1.

Table 1. Extraction of H_3PO_4 with TBP

Distribution coefficient for concentration of H_3PO_4	TBP concentration, vol.%			
	25	50	75	100
1 mol/l	0.005	0.02	0.06	0.15
6 mol/l	0.04	0.11	0.19	0.28

For the phosphoric acid extraction with TBP the distribution coefficient rises with the increasing equilibrium concentration of phosphoric acid in the aqueous phase, such relation is characteristic for the phosphoric acid extraction with butanol, too, i.e. for the extragents having a concave isotherm. A sharp increase of the distribution coefficients affected by TBP concentration is also evident.

It is known that the nature of diluent can considerably affect the distribution coefficients of phosphoric acid. The TBP solutions in hydrocarbon diluents have higher D. The distribution coefficient in aromatic hydrocarbons is lower. Still, it is noticed that with increasing concentration of phosphoric acid in the initial solution the phosphoric acid concentration in the organic phase is practically independent of the diluent nature, which is supposed to relate to the character of solvation. The mechanism of the phosphoric acid extraction is complicated enough. The data on the phosphoric acid distribution point out to existence of solvates with various ratio between TBP and H_3PO_4 . In the saturated state the ratio $\text{TBP} : \text{H}_3\text{PO}_4 = 1 : 3$. Presence of the phosphoryl group both in the TBP molecule and H_3PO_4 molecule is the main reason of association in the system. The direct measuring testifies to it too. Viscidity of the saturated organic phase is about three times greater than viscosity of phosphoric acid $4 \cdot 10^{-4} \text{ m}^2/\text{s}$ against $1.4 \cdot 10^{-4} \text{ m}^2/\text{s}$. The study on the third phase composition also points out to this ratio.

The character of phosphoric acid hydration in the organic phase can be determined on the basis of the direct water determination. It has been established that the constant ratio $\text{TBP} : \text{H}_2\text{O}$ is retained throughout a wide range of phosphoric acid concentration in the organic phase, which makes one believe that phosphoric acid is hydrated with one molecule of water and the composition of hydrosolvate is $\text{TBP} \cdot 3\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$.

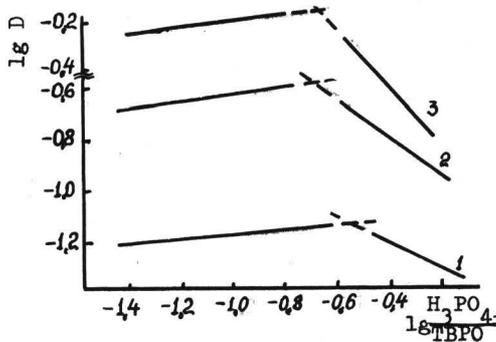


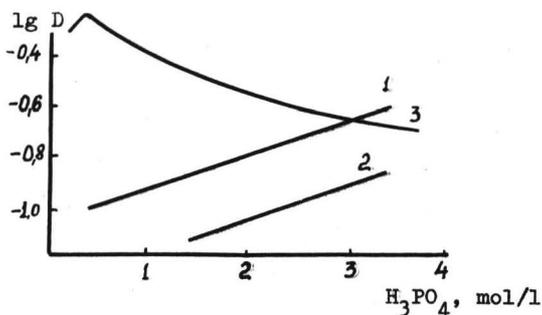
Fig. 1. H_3PO_4 extraction with TBPO
1-0.4; 2-0.8; 3-1.6 mol/l TBPO

The distribution character of phosphoric acid between its aqueous solutions by trialkylphosphin oxide shows that the curve of the $D-H_3PO_4$ relation passes through the maximum and then decreases monotonously with increasing equilibrium concentration of phosphoric acid in the aqueous solution. The maximum position is individual for each phosphin oxide of corresponding concentration. The isotherm for extraction of phosphoric acid by trialkylphosphin oxides is convex and the section ranging parallel to the X-axis is absent, thus, the saturation of extractant with phosphoric acid is not reached. It is characteristic both for alcohols and organic phosphates with the exception of amines. The increase of equilibrium concentration of phosphoric acid in the aqueous solution is accompanied by its increasing contents in the extractant. This increasing concentration of phosphoric acid in the organic phase brings about complete mixing of the two phases or formation of the third (second organic) phase. If the data on the phosphoric acid extraction are expressed in the coordinates of $D - H_3PO_4/TAPO$ then two straight sections will be evident, each one described by equation of the type $C_o = mC_w^s$ (Fig. 1). Some empirical equations are given in Table 2.

Table 2. H_3PO_4 extraction with TBPO

TBPO concentr., mol/l	Diagram equations
1.625	$C_o = 0.738C_w^{1.105}$ $C_o = 0.468C_w^{0.525}$
0.812	$C_o = 0.317C_w^{1.120}$ $C_o = 0.218C_w^{0.591}$
0.406	$C_o = 0.072C_w^{1.090}$ $C_o = 0.085C_w^{0.696}$

Fig.2. H_3PO_4 extraction
1-BuOH; 2-TBP; 3-TBPO



The joint solution of the equations makes it possible to find such phosphoric acid concentration at which the mechanism of phosphoric acid extraction with phosphinoxides is altered.

A comparative estimation for extractational ability with butyl alcohol, TBP and TBPO is given in Fig.2.

Table 3. Capacity of extragents for phosphoric acid, kg/t

Concentration of H_3PO_4 , mol/l	TBP	BuOH	DBAA	TBPO
1.0	16	18	66	120
2.0	51	52	150	187
3.0	78	101	233	220
4.0	92	140	275	248
5.0	109	193	316	297

A comparative assessment of extragent may be done proceeding from their capacity for phosphoric acid. Table 3 gives the comparison data.

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Organic-in-water dispersions are produced in many industrial processes. Separation of such systems is often needed in order to recover valuable organic liquids or to meet the restrictions for waste flow contaminations. In the case of organics partially soluble in water the dispersed fraction could be separated to some extent by using coalescence-promoting devices [1]. But for a total separation, including also the dissolved organic fraction, liquid extraction principles should be applied [2]. Most of high efficiency conventional extraction equipment use intensive hydrodynamic regimes for creating of great interphase surface. This is not convenient for the considered case because of fine droplets yet existing in the feed flow and the possibility for further unwanted drop breaking, which could cause additional phase separation difficulties. The laboratory scale study [3] lead to the development of equipment designed to fit the requirements for contact and separation of polyphasic liquid systems with fine granulometry. The evolution of apparatus construction from laboratory to industrial scale is presented in this paper and results of large scale tests are given.

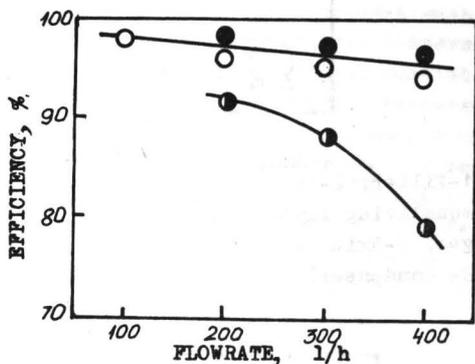
If compare the separation efficiency of bed columns of various size the classical scale-up problem is clearly manifested - the greater the apparatus size, the lower the separation efficiency. Trying to overcome this problem, multiple construction of repeated modules was studied. The single module was cylindrical cartridge-type construction. The separated layers are superimposed on a perforated tube-skeleton. The detailed description is given in [4]. An apparatus 100 mm in diam. with one module incorporated was tested. Its main features were stable extraction efficiency, not strongly influenced by the throughput and a good ability for separation of phases in a heterogeneous system. But the overall separation efficiency was not high enough mainly due to the incompleted mass transfer. It might be intensified when make interphase surface regularly renewed. Currently it is done by repeated mechanical mixing for dispergation of phases followed by settling and phase coalescence [5]. In our case the layer surface properties were used to create a similar effect. When the flow meets porous media with alternately changed surface properties (wetted-nonwetted), coalescence and redispergation is caused. This was the concept for construction of cylindrical cartridge with multilayer wall. Considerable improvement of mass transfer efficiency was obtained (over 90 % at throughput $40-45 \text{ m}^3/\text{m}^2\text{h}$). The wall thickness was significantly thin-

ner (~ 25 mm) in comparison with the thickness of the horizontal layer of comparable efficiency (25-30 cm).

The overall apparatus flowrate is increased by multiplying the number of single modules. What is necessary is to ensure relatively uniform crosssection flow distribution in the apparatus body in order to provide similar near-to-optimal operating conditions for individual modules. This requirement might be simply fulfilled by using a combination of a horizontal fixed bed section followed by a section of vertical cartridge modules. The higher pressure drop of I section equalizes approximately the crossflow distribution. Moreover, this bed contributes additionally to the mass transfer efficiency. The II section keeps its two main functions of efficient mass transfer and phase separation device.

Fig. 1. Separation efficiency vs throughput. Single module. Pine oil-water dispersion. Solvent (petroleum ether) to water ratio

- 1:50
- 1:100
- ◐ 1:200



The results for testing single multilayer modules are illustrated on Fig. 1. The approximate range of operating conditions for a good performance, which could be maintained in a multimodule construction is: flowrate 300-400 l/h (throughput $\sim 50 \text{ m}^3/\text{m}^2\text{h}$) under phase ratio 1:50-1:100.

The total flow capacity of the industrial scale installation was chosen according to the particular requirements of a common essential oil production plant (~ 2500 l/h). More than 85 % recovery of the essential oil is required.

The installation scheme is shown on Fig. 2. The flow to be treated passes through the filter (1) for removal of solid particles. A part of the flow (2) is used to disperse the solvent in the injector (3). The solvent droplet size is controlled by regulation of this flow (2). The extractive-separational unit includes the horizontal "equalizing" layer (4) and 7 identical modules (5) as described above. The deoiled water leaves the apparatus through the exit (6). The light organic phase (7) containing extracted oil, enters the distillation unit (8),

where the solvent is distilled, the vapours are condensed (9) and recycled in the column. The unevaporated rest is the extracted essential oil product (10).

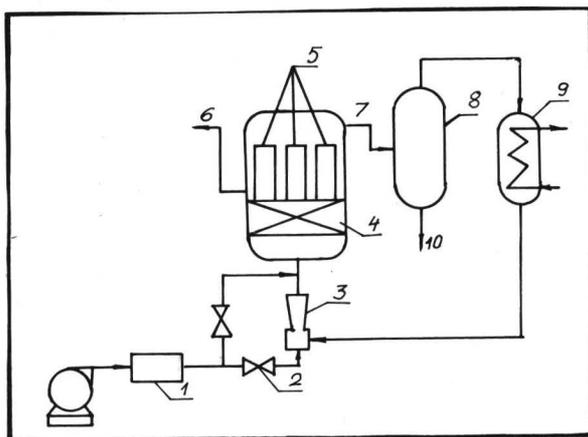


Fig. 2. Principal scheme of the industrial installation
 1-Filter; 2-Injector controlling valve; 3-Injector; 4-Horizontal equalizing layer, 400 mm in diam.; 5-Extractive-separatio nal cartridges; 6-Exit purified water; 7- Extract exit; 8-Distillation unit; 9- Condenser; 10-Extracted product

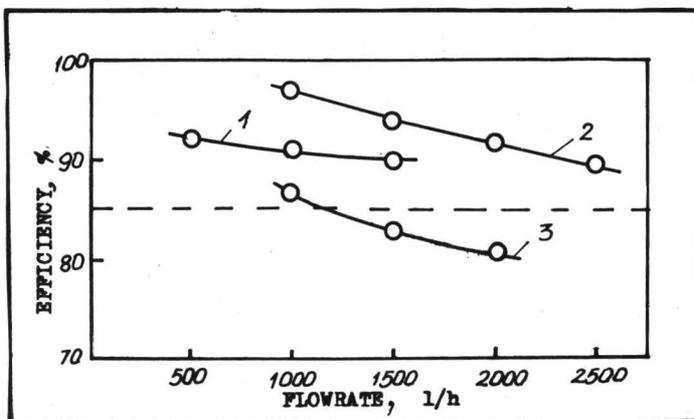


Fig. 3. Separation efficiency versus flowrate
 Large scale installation: 1- camomile oil-water dispersion, solvent to water ratio 1:75; 2- Lavanda oil-water dispersion, solvent to water ratio 1:50; 3- Lavanda oil-water dispersion, solvent to water ratio 1:100

During the industrial tests stable operation under continuous non stop regime was observed. General illustration of the efficiency of essential oil recovery is made on fig.3.

The industrial performance data confirm the expedient design and effective operation of the industrial scale extraction installation for treating of heterogeneous systems containing finely dispersed and dissolved organic liquids.

In the considered particular case currently decanters are used for the separation of the essential oil-water dispersion. When use extraction as a next step of separation, nearly 70 % additional product (camomile oil with a higher content of water soluble components) was obtained[6]. The reported quantities might be considered as recovered from waste flows using the proposed new technique.

CONCLUSION. The elaborated extraction process and equipment enables for a more complete separation of organic liquids finely dispersed and partially dissolved in water. The dissolution of organic droplets by the solvent is much more effective and faster than their coalescence and gravity settling. Moreover, the dissolved in water organics are also extracted. The process is low energy consuming[7]. Energy is used only for regeneration of a relatively small amount of low-boiling solvent. Treating of heterogeneous systems with dispersed phase density above or below water density does not require changes in apparatus construction because density difference solvent-water is essential for a normal operation. The application of this method to low density difference systems (their gravitational settling is slow and difficult) is very convenient and effective. The scaling-up problems are overcome by use of multiple module construction.

This process and industrial installation are applied in the essential oil production technology. The main area of other use are: pharmacy, food industry, petrochemistry, organic syntheses etc. for production or recovery of valuable substances as well as for removal of harmful and toxic components from water flows.

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Liquid-liquid extraction processes for metal separation and winning are always connected with the problem of the entrainment of organic phase (extractants and diluents) into the aqueous process solutions and waste water, respectively. Entrainments in raffinates or separate scrub raffinates take a lot of efforts in waste water treatment and organic impurities in stripping liquors lead to difficulties in further process steps. Both, physically dissolved parts and microemulsions of extractants and diluents in the aqueous phase, must be removed to a required degree.

The object of the present investigations is the adsorption of di(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant and aliphatic hydrocarbons as diluents from acidic zinc-bearing solutions, produced by zinc recovery from process solutions of rayon industry. On principle activated carbons and macroporous resins - obtained by copolymerization of styrene and divinylbenzene - as adsorbents are suitable for the removal of organic compounds from aqueous solutions. The main advantages of macroporous resins in comparison with the carbons are the simple regeneration process and the low energy consumption. Furthermore they are effective for many process cycles [1-3].

Investigations have been carried out with the nonionic macroporous resins Wofatit EP 61 (specific surface on BET 380-480 m²/g) and Y 77 (> 1000 m²/g) - both from Chemiekombinat Bitterfeld (GDR) - in comparison with activated carbon (> 1000 m²/g). The adsorption resin Y 77 contains not only macropores, which are typical of well-known resins, but also many mesopores and micropores. It has an excellent adsorption efficiency.

The adsorption of D2EHPA and n-dodecane - as example for technical hydrocarbons - by the various adsorbents have been investigated under variation of the H₂SO₄- and ZnSO₄-concentrations as a function of time. Adsorption isotherms of D2EHPA and n-dodecane have been determined for typical process solu-

tions. The possibilities for the elution of these compounds from the adsorbents, which are entirely saturated with the extractant and the diluent, has been studied. Best results were found using methanol or alkaline methanol solution, and in the case of steam stripping, respectively. The obtained eluate has a very high concentration of extractant or diluent, i. e. an economic recovery can be carried out. The best adsorption efficiency shows Wofatit Y 77. Acidic zinc sulfate solutions with an initial content of 10-500 ppm of organic compounds could be purified to a level of lower than 1 ppm. The capacity of this resin is higher than that of the activated carbon used and is sufficient for application in an industrial process. Regeneration is possible without losses of capacity. A very high stability against osmotic and chemical stress was observed too.

The results, obtained on laboratory scale, have been confirmed on a pilot equipment with two parallel columns.

This adsorption process can be successful applied for the separation of surfactants from feed solutions.

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