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A NEW ANIONIC SOLVENT EXTRACTION
TECHNIQUE

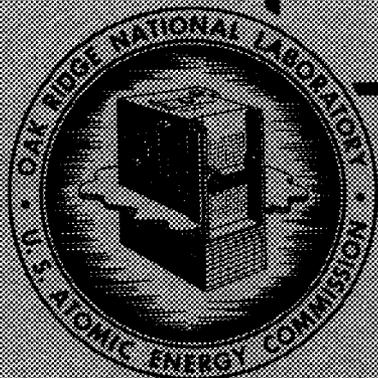
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ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director

C. D. Susano, Associate Director

A NEW ANIONIC SOLVENT EXTRACTION TECHNIQUE

F. L. Moore

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 CHEMISTRY-SEPARATION PROCESSES
 FOR PLUTONIUM AND URANIUM

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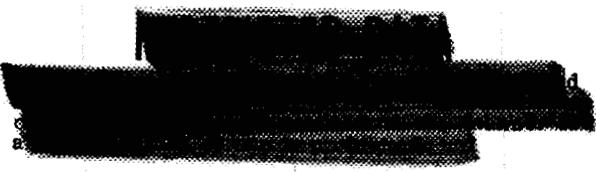
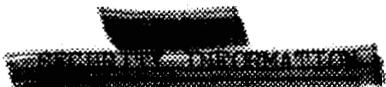
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ABSTRACT

The extraction of acids with long-chain amines is described. Preliminary results on the extraction of the amine salts of polonium, plutonium and uranium are given.

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Introduction

In the summer of 1950 an investigation of a new solvent extraction technique was initiated at this Laboratory. Smith and Page⁽¹⁾ previously had reported on the acid-binding properties of long chain aliphatic amines. The acid-binding properties of these bases depend on the fact that their salts with acids are almost insoluble in water, but readily soluble in organic solvents such as chloroform.

Several amines have been tried for the extraction efficiency of hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid. The two most promising amines studied were methyldioctylamine and tribenzylamine. The purpose was to explore the use of this anionic solvent extraction technique in simple acid extractions and then to extend it to the extraction of complex metal acids.

The Extraction of Various Acids with Tribenzylamine and Methyldioctylamine

The general method, arbitrarily chosen, was to shake a known quantity of acid with a slight excess of a 5% solution of the amine in chloroform for five minutes. The organic phase was then "stripped" with excess sodium hydroxide, and the original aqueous phase and the final aqueous phase ("strip") were analyzed for ions of the acid. The principle was that water insoluble amines form the corresponding amine-acid-salts which are also insoluble, in general, and preferentially extract into organic solutions. Table I shows typical extraction values for several mineral acids using one milliliter of 1 N acid.

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Table I

The Extraction of Mineral Acids with Chloroform Solutions of Tribenzylamine (TBA) and Methyldioctylamine (MDOA)

<u>Amine</u>	% Acid Extracted*			
	HCl	HNO ₃	H ₂ SO ₄	H ₃ PO ₄
Tribenzylamine	50	68.4	0	1.5
Methyldioctylamine	96.8	98.3	97.6	76.5

*Average of at least two determinations. Blank extractions with chloroform (no amine) indicated that negligible HCl, HNO₃, H₂SO₄ or H₃PO₄ extracted.

No attempt was made at this time to extract the acid remaining in the aqueous phase. In most cases, it probably represents the slight solubility of the amine salt in the aqueous phase and could be removed by an additional extraction with chloroform.

It is interesting to note that tribenzylamine may have applications in extracting certain anions from a sulfuric acid solution.

From the preliminary scouting experiments, methyldioctylamine was selected for further investigation. In attempting to improve the extraction of phosphoric acid, it was observed that the extraction of orthophosphoric acid with methyldioctylamine seemed to vary with the aqueous volume. This was checked experimentally by performing a series of extractions in which the aqueous volume was varied. The same amount of phosphoric acid was added to each aqueous and the same volume of chloroform containing a slight excess of methyldioctylamine was used in all cases. Table II indicates the dilution effect.

Conditions - Aqueous phase containing 1 ml of 1.5 N H₃PO₄
aqueous volume varied
7.65 ml of 5% methyldioctylamine in CHCl₃
5 min. extraction.

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Table II

The Effect of Aqueous Dilution on the Extraction of Phosphoric Acid
with Methyldioctylamine in Chloroform

<u>Aqueous Volume</u>	<u>% H₃PO₄ Extracted</u>	<u>Apparent Distribution Coeff. $\frac{\text{Organic}}{\text{Aqueous}}$</u>	<u>Notes</u>
2 ml	87.1	1.7	Aqueous cloudy. Cleared upon dilution.
2 ml	86.5		
5 ml	76.6	2.1	"
5 ml	76.4		
10 ml	54.0	1.5	Much foam, slow phase separation
10 ml	53.9		
20 ml	34.3	1.3	Stable foam persisted.
20 ml	32.1		

It was found that the foam and emulsion trouble could be eliminated readily by making the aqueous phase 1 M in nitric acid, hydrochloric acid or sulfuric acid or 2-3 M in hydrofluoric acid. Also it was found that small additions of sodium chloride or sodium fluoride prevented emulsions; however, the sodium ion reduced the recovery of phosphoric acid. Aerosol O.T. appeared to make the emulsion worse.

In order to learn more about the salt-forming properties of methyldioctylamine, the extraction of several more acids was checked. The technique used was the same as that described in Table I. The results given in Table III indicate that methyldioctylamine is an efficient extractant for inorganic and organic acids in general. The non-extractability of the amino acids verifies the report of British investigators⁽¹⁾.

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Table III

<u>Acid</u>	<u>% Extracted</u>	<u>Blank (no amine in the CHCl₃)</u>
Hydrofluoric	87.1	0.1
Acetic	75.8	7.2
Formic	89.9	0.5
Trichloroacetic	98.7	10.2
Aspartic	0	0
Glutamic	0.3	< 0.5
Glutaric	86.9	< 0.5
Picric	> 96.0	54.0
Fumaric	95.9	0
Maleic	97.5	< 1.0
Malic	90.8	0

The Extraction of Anionic Radioactivities

An obvious extension of this technique was to explore its use in the extraction and separation of various anionic radioactivities. It was thought that it might prove profitable to investigate the behavior of various elements present in a system as anions rather than cations.

Polonium (210) and plutonium (239) tracers, which are known to form anionic species in hydrochloric acid, were extracted with a 5% solution of tribenzylamine in chloroform. The results are shown in Tables III and IV.

Table IVThe Extraction of Po(210) Tracer with a 5% Solution of Tribenzylamine in Chloroform

<u>Aqueous Phase Acidity</u>	<u>Volume of Solvent</u>	<u>Time</u>	<u>% Po Extracted</u>
6 M HCl	1 2/3	5 min.	(1) 99.3 (2) 99.4
6 M HNO ₃	1 2/3	5 min.	(3) < 10 (4) < 10
5 M HCl-1 M HNO ₃	1 2/3	5 min.	(5) 93.3 (6) 92.0

Table VThe Extraction of PuO₂⁺⁺ (239) Tracer with a 5% Solution of Tribenzylamine in Chloroform

<u>Aqueous Phase Acidity</u>	<u>Volume of Solvent</u>	<u>Time</u>	<u>% PuO₂⁺⁺ Extracted</u>
6 M HCl - 0.5 M HNO ₃	(control - no amine in the CHCl ₃)	5 min.	(1) 0.03 (2) 0.03
6 M HCl - 0.5 M HNO ₃	Equal	5 min.	(3) 51.3 (4) 51.3
9 M HCl - 0.5 M HNO ₃	Equal	5 min.	(5) 74.3 (6) 73.6

The stock Pu(VI) tracer contained 0.05 M Na₂Cr₂O₇ as a holding oxidant, and the dichromate was observed to extract. At the same time some reduction of dichromate (and probably PuO₂⁺⁺) was observed and the chromic ion appeared not to extract. While no attempt was made at this time to make the PuO₂⁺⁺ extraction quantitative, it could be done probably by maintaining the oxidized state of plutonium and by using higher concentrations of hydrochloric acid.

While the behavior of plutonium(IV) was not investigated at this time, it is thought that it will readily extract from strong hydrochloric acid with tribenzylamine in chloroform.

Using the anionic solvent extraction technique described above studies are being made of the behavior of niobium, tantalum, zirconium, hafnium, thorium, protactinium, tin, antimony, nickel, cobalt, chromium and uranium in various anionic systems. Very little data is available at this time, but tentative results indicate that the new technique offers rapid separations of niobium from tantalum, protactinium from thorium, tin from antimony, cobalt from nickel and chromium, chromium from nickel, and uranium from many elements. Exploratory work recently has shown that uranium may be extracted readily from many dilute acids -- hydrochloric, sulfuric, nitric, phosphoric, acetic, oxalic, hydrofluoric, formic and maleic with a solution of methyldioctylamine in xylene. The results of these various metal separations will be reported as progress is made.

Summary

A solution of methyldioctylamine in chloroform is shown to be an efficient extractant for mineral acids and many organic acids with the exception of the amino acids. Preliminary results indicate that polonium and plutonium extract well from 6 M hydrochloric acid with a solution of tribenzylamine in chloroform. The possibility of the use of this general anionic extraction technique for the rapid separation of several other metals is outlined.

References

- (1) Smith, E. L. and Page, J. E., J. Soc. Chem. Ind. 67, 48, Feb. 1948.