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THE EXTRACTION OF IONIUM BY ORGANIC SOLVENTS

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THE EXTRACTION OF IONIUM BY ORGANIC SOLVENTS

Earl K. Hyde and Jean Tolmach

During the course of radiochemical experiments with thorium isotopes and investigations directed toward the isolation of ionium* from natural sources, it became desirable to study the solvent extraction characteristics of ionium.

The extraction of macro quantities of thorium nitrate by organic solvents has been investigated previously. A group at Iowa State College^(1,2,3,4) has investigated a considerable number of solvents in a preliminary way and has found several which show quite high extraction under their test conditions. This group selected hexone (methyl isobutyl ketone) for quite extensive study and put it into service for large-scale purification of thorium nitrate by countercurrent column extraction. Hyde and Wolf⁽⁵⁾ in a study of uranyl nitrate and protactinium nitrate extraction by organic solvents made a number of determinations of thorium extraction, finding it to be quite low under their salting conditions.

There are a number of reasons why the previously reported work is not directly applicable to the experiments

*Ionium, a member of the uranium decay series, is a thorium isotope of mass 230. Its half-life for alpha particle emission is 8.0×10^4 years.

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in which we are interested. First of all, extraction of macro quantities of thorium may be significantly different from the extraction of trace concentrations because of differences in salting effects and for other reasons. Furthermore, in most cases in order to get high thorium extraction, the above investigators used quite powerful salting conditions. (The composition 3 N nitric acid and 6 N calcium nitrate was frequently employed.) This practice has the two serious disadvantages that it tends to decompose the organic solvent and that it increases the extraction of impurities. It has been the general experience that the extraction of impurities by the solvents ordinarily used for heavy metal nitrates goes up markedly, if the aqueous phase is strongly acidified and strongly salted.

For these reasons a study of the extraction of small concentrations of thorium was undertaken using ionium as a tracer. High extractability under moderate salting conditions was sought for. This study, while far from complete, has yielded some useful information which is presented in this report.

Preliminary Survey

A variety of solvents including most of those which previous work had shown to be promising were tested in a preliminary way with two standard aqueous phase compositions. The first consisted of a 6 N calcium nitrate solution acidified to 2 N with nitric acid. Any solvent which shows no

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appreciable extraction under these moderately strong salting conditions can be safely eliminated from consideration. The second was an 8 N ammonium nitrate solution acidified to 2 N with nitric acid. Any intrinsically good ionium solvent should show appreciable extraction under these comparatively mild salting conditions.

The experiments were carried out in the following manner. The calculated quantities of concentrated nitric acid, water and ammonium nitrate or calcium nitrate were added to a 50-ml mixing cylinder to make 40 ml of solution of the desired concentration. Five ml of this solution was pipetted into a calibrated 15-ml centrifuge cone and to this solution was added about 10^5 alpha counts per minute of a concentrated ionium tracer solution. Seven ml of the solvent under investigation was placed in the 50-ml mixing cylinder containing the remainder of the aqueous solution and shaken for a few minutes. Five ml of the solvent was then pipetted into the cone containing "spiked" solution and intimately mixed with this aqueous phase for five minutes by means of a glass motor-driven stirrer. The purpose of the preliminary contact of the solvent with the inactive aqueous solution was to adjust the acidity of the solvent approximately to equilibrium with that of the "spiked" aqueous solution. By means of a volumetric micropipet, an aliquot of the organic phase was removed and evaporated directly on a platinum counting disc. When the solvent was difficultly volatilized it was necessary to strip

the ionium from the solvent by contact with a small volume of distilled water and to evaporate this water on a platinum disc. These samples were counted in an ordinary air-filled, pulse-ionization alpha counting chamber. The results of individual experiments were considered accurate to within 5%. In a number of cases material balances were obtained by assaying the aqueous layer. This was done by saturating an aliquot of this phase with calcium nitrate, acidifying strongly with nitric acid and extracting with dibutoxy tetraethylene glycol. The ionium so extracted was stripped from the glycol with pure water and evaporated on a platinum counting disc.

Tables 1 and 2 list the results of the preliminary survey.

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Table 1

Percent Ionium Tracer Extracted from an Aqueous Solution
of Composition 2 N HNO_3 , 6 N $\text{Ca}(\text{NO}_3)_2$ by an Equal
Volume of Pre-equilibrated Solvent.

<u>Solvent Class</u>	<u>Solvent</u>	<u>Percent Extraction</u>
Alcohols	Heptadecanol	0.3%
	n-heptyl alcohol	11
	2-ethyl hexanol	2
	di-isopropyl carbinol	5
Ethers	hexyl ether	0.7
Ketones	methyl n-amyl ketone	19
	diisopropyl ketone	9
	methyl isobutyl ketone (hexone)	45
	cyclohexanone	85
Cellosolve and Carbitol Derivatives	butyl cellosolve	52
	dibutyl cellosolve	3
	2-ethyl butyl cellosolve	33
	diethyl cellosolve	92
	dibutoxytetraethylene glycol (penta-ether)	89
	dibutyl carbitol	59
Miscellaneous	triglycol dichloride	42
	2-ethyl butyric acid	0

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Table 2

Percent Ionium Tracer Extracted from an Aqueous Solution of Composition 2 N HNO_3 , 8 N NH_4NO_3 by an Equal Volume of Pre-equilibrated Solvent.

<u>Solvent</u>	<u>Extraction</u>
Butyl cellosolve	31%
Dibutyl carbitol	62
Triglycol dichloride	28
Cyclohexanone	62
2-ethyl butyl cellosolve	21
Methyl isobutyl ketone (hexone)	14
Diethyl cellosolve	71
Dibutoxytetraethylene glycol (penta-ether)	96

Of the several solvents in Table 1 which show high ionium extraction, three were studied in some detail over a variety of aqueous solution compositions using nitric acid, ammonium nitrate and calcium nitrate as the salting agents.

Hexone (methyl isobutyl ketone) was studied in detail, in spite of the fact that many other solvents in Tables 1 and 2 show higher ionium extracting power, because hexone is frequently employed in the extraction of other heavy metal nitrates and it is important to understand the behavior of thorium under the various conditions which might be employed.

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From the data presented in Figures 5, 6 and 7, the last being a plot of the data of Spedding, Kant et al.⁽³⁾, one may conclude that hexone is only a moderately good solvent for thorium, although it can be made to serve. On the other hand, one may not expect to decontaminate thorium from other heavy metal nitrates by hexone extraction unless the acidity is kept low.

Extraction by diethyl cellosolve is quite high as shown by the Figure 1, 2, 3 and 4. Unfortunately, the physical properties of diethyl cellosolve are such as to make its use in column operations questionable, while re-extraction of thorium from the solvent into water is complicated by the moderate to high solubility of diethyl cellosolve in water or dilute nitric acid solutions. A characteristic of thorium extraction in diethyl cellosolve, hexone and several of the other solvents is that the acid concentration must be maintained quite high. This is strikingly demonstrated for diethyl cellosolve by Figure 2. This is a distinction from uranium extraction in the same solvents which requires a very low concentration of acid.

Dibutoxytetraethylene glycol (penta-ether) was found to be quite an excellent solvent as shown by Figures 8 through 12. Good extraction is obtained even in solutions salted with dilute nitric acid and ammonium nitrate. The settling time of this solvent is too high to permit its use, undiluted, in a column, but it would be quite suitable for batch operations.

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Mixtures of penta-ether and hexone show high extraction and probably could be used successfully in a column⁽⁶⁾. The water solubility of this solvent (about 1%) is so low that no difficulty is experienced in re-extracting thorium from it into pure water.

Increasing the nitric acid concentration in the aqueous phase increases the extraction by penta-ether, as a comparison of Figures 10 and 11 indicates, but the effect is not the pronounced one observed in diethyl cellosolve (Figure 2). High ionium extraction is obtained from solutions only 0.5 N in nitric acid as shown in Figures 8 and 10.

From an examination of the curves one must conclude that penta-ether is an excellent solvent for ionium. Just how specific it is under the conditions which result in high ionium extraction has not been studied extensively as yet. The nitrates of the elements from 91 to 94 will extract. From what information we have found in the Project literature⁽⁷⁾ and from laboratory experiments with ore samples, etc. it is apparent that decontamination from most of the lighter element nitrates is quite good, but a few will extract and have to be separated by different procedures, if present. Further work is being done on this.

A number of duplicate determinations were made using in one case preequilibrated penta-ether and in the second penta-ether which had not been preequilibrated, and significantly

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different results were obtained for the same aqueous phase compositions as shown in Figures 9 and 10. This can be attributed to the extraction of nitric acid from the aqueous phase by the solvent, a very important factor to consider in the solvent extraction of any heavy metal nitrate. We have not determined detailed nitric acid extraction data as yet, but from previous work of others (2,3,6), it is known that hexone and diethyl cellosolve will extract 50-80% of the nitric acid from the aqueous layer depending on the aqueous phase composition. Extraction of acid from the aqueous phase by penta-ether is nearly 100% for any dilute acid concentration (1 N or less) and drops to about 50% for the higher acidities.

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Figure 1. Percent I^{230} Tracer Extracted by Pre-equilibrated Diethyl Cellosolve from an Equal Volume of an Aqueous Solution 1 N in HNO_3 and Varying in NH_4NO_3 Normality.

Figure 2. Percent I^{230} Tracer Extracted by Pre-equilibrated Diethyl Cellosolve from an Aqueous Solution 8 N in NH_4NO_3 and Varying in HNO_3 Normality.

Figure 3. Percent I^{230} Tracer Extracted by Pre-equilibrated Diethyl Cellosolve from an Aqueous Solution 1 N in HNO_3 and Varying in $\text{Ca}(\text{NO}_3)_2$ Normality.

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Figure 4. Percent I^{230}O Tracer Extracted by Pre-equilibrated Diethyl Cellosolve from an Equal Volume of an Aqueous Solution 2 N in HNO_3 and Varying in $\text{Ca}(\text{NO}_3)_2$ Normality.

Figure 5. Percent I^{230}O Tracer Extracted by Pre-equilibrated Hexone from an Equal Volume of an Aqueous Solution 1 N in HNO_3 and Varying in $\text{Ca}(\text{NO}_3)_2$ Normality.

Figure 6. Percent I^{230}O Tracer Extracted by Pre-equilibrated Hexone from an Equal Volume of an Aqueous Solution 2 N in HNO_3 and Varying in $\text{Ca}(\text{NO}_3)_2$ Normality.

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Figure 7. Extraction of $\text{Th}(\text{NO}_3)_4$ by Methyl Isobutyl Ketone from an Equal Volume of an Aqueous Solution 1 N in HNO_3 , 2 N in $\text{Th}(\text{NO}_3)_4$ and Varying in NH_4NO_3 Normality. (Taken from CC-2393; see Reference (3)).

Figure 8. Percent I^{230} Tracer Extracted by Pre-equilibrated Penta-ether from an Equal Volume of an Aqueous Solution 0.5 N HNO_3 and Varying in NH_4NO_3 Normality.

Figure 9. Percent I^{230} Tracer Extracted by (o) Pre-equilibrated, (x) not Preequilibrated Penta-ether from an Equal Volume of an Aqueous Solution 1 N in HNO_3 and Varying in NH_4NO_3 Normality.

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