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The Extraction of Uranium into Hexone as Uranyl Thiocyanate from Thorium Nitrate Solutions

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Abstract

In CC-2730 a process has been proposed for separating uranium from thorium by a counter current extraction column using hexone as the solvent. In this process the uranium is extracted into the hexone as uranyl thiocyanate. Since the publication of the above report certain problems have been encountered which will be described in this report.

The first section of this report deals with the nitric acid reaction with potassium thiocyanate. It was found that hexone prevented the formation of insoluble reaction products, probably by lowering the concentrations of nitric acid and thiocyanic acid in the aqueous phase due to their partial extraction into the hexone. Conditions were also found where there was no solid formation in the absence of hexone.

The distribution of nitric acid between hexone and water was determined up to 1.0 M HNO_3 . The extraction of nitric acid into hexone is small for at 1.0 M HNO_3 about 11% of the nitric acid is extracted.

The distribution of potassium thiocyanate between hexone and aqueous solutions containing various nitric acid concentrations was measured. It was found that on the average the value of the constant for the reaction $\text{H}^+(\text{aq.}) + \text{SCN}^-(\text{aq.}) = \text{HSCN}(\text{hexone})$ was 6.

The solubility of thorium sulfate in the extraction solution is discussed. The maximum concentration of Na_2SO_4 which can be used at 0.50 M and 0.25 M thorium nitrate is 0.35 M and 0.22 M respectively.

Experiments were performed to determine the distribution of protoactinium and fission elements between hexone and water. The minimum decontamination factor for protoactinium was about 23 under the conditions used while the soft γ decontamination factor for fission products was about 6. Zirconium has been identified as the main fission element which is extracted into the hexone from a nitric acid-potassium thiocyanate solution.

The last section describes extraction experiments which were performed at 0.25 M $\text{Th}(\text{NO}_3)_4$. Although a better uranium-thorium separation is obtained at 0.25 M $\text{Th}(\text{NO}_3)_4$, the separation of uranium from 0.5 M $\text{Th}(\text{NO}_3)_4$ might be used to good advantage if the extraction column were provided with a stripper column.

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1. The Reaction of HNO₃ with HSCN

In a recent report (1) experiments were described in which uranium was separated from thorium in solutions containing nitric acid and thiocyanate ion. The possibility of the formation of insoluble compounds by the reaction of thiocyanate with nitric acid was called to our attention by a report from English's group at Clinton (2) in which it was stated that perthiocyanogen formed in nitric acid solutions containing thiocyanate. In the time necessary to perform the uranyl extraction experiments cited above no insoluble matter was observed to form. It became apparent that if a solid were slowly formed in the extraction solution, the rate of formation of the solid as well as some of the properties of the solid would have to be determined in order to decide whether or not such a process could be used.

In most of the extraction experiments the thiocyanate and nitric acid concentrations were about 1 M. A solution having this composition was prepared and allowed to stand for about 12 hours at room temperature. At the end of that time a large precipitate had formed which looked as though it were a mixture of two different precipitates, one golden yellow in color and the other colored orange. From the literature it was found that thiocyanate ion reacted with most acids to form a variety of compounds. For example, thiocyanate solutions react with concentrated HCl or H₂SO₄ to form iso-perthiocyanic acid, H₂C₂N₂S₃ (3). Potassium acid sulphate is reported to react with thiocyanate ion with the formation of trithiocyanuric acid, H₃C₃N₃S₃. (4) Concentrated potassium thiocyanate solutions are reported to react with strong oxidizing agents such as HNO₃ or Cl₂ with the formation of perthiocyanogen, HC₃N₃S₃. (5) It has also been reported that when solutions of thiocyanate are treated with sulphuric acid of different concentrations, the solids which are produced are not the same but vary in composition as the sulphuric acid concentration is varied. (6)

The solid which formed in the solution containing 1 M HNO₃ and 1 M KSCN may be a single compound even though the precipitate was of two colors since perthiocyanogen has been reported to exist in several colors, i.e., yellow, red, and sometimes blue. (5) However, since this precipitate was formed under conditions which are different from any of those cited in the literature, there is an uncertainty as to what the precipitate actually is.

The effect of hydrogen ion concentration upon the rate of precipitation of this insoluble precipitate was studied. The experiments performed will be found in Table 1.

(1) W.H. Reas, CC-2730, February 16, 1945.
 (2) English's group at Clinton, CL-P-387, p. 35, Feb. 15, 1945.
 (3) J. Newton Friend, A Textbook of Inorganic Chemistry, Charles Griffen and Co., 1917, Vol. 5, page 173.
 (4) Hofman, Ber., 36, 57, (1887); *ibid*, 18, 2201, (1885)
 (5) McAlpine and Soule, Qualitative Chemical Analysis, D. Van Nostrand Co., 1933, page 466.
 (6) B.S. Sharma, JACS, 52, 581 (1930).

Table 1

Effect of Acidity on Precipitation of the Water Insoluble
Reaction Product of NO_3^- and SCN^-

Fixed Conditions:

$\text{Th}(\text{NO}_3)_4 = 0.506 \text{ M}$
 $\text{UO}_2(\text{NO}_3)_2 = 0.0974 \text{ M}$
 $\text{KSCN} = 1.00 \text{ M}$
 $\text{Na}_2\text{SO}_4 = 0.388 \text{ M}$

Expt.	Conc HNO_3 moles/liter	Conc NH_4NO_3 moles/liter	Total NO_3^- Conc moles/liter	Time in hours necessary to ob- serve precipitation
1	1.00	0.00	3.21	2
2	0.25	0.00	2.46	5
3	0.10	0.90	3.21	* No precipitation
4	0.01	1.0	3.21	† 1

* No precipitation was observed at the end of several days.

† The precipitate which formed was white in color instead of the yellow-orange precipitate which was formed in experiments 1 and 2.

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Table 1 shows that if the extraction were carried out at 0.10 M HNO_3 , there would be no precipitation of any insoluble compound. It was found that the precipitate which formed in experiments 1 and 2 was not soluble in hexone. Therefore, it is imperative that the extraction be carried out under conditions where there is no solid formation.

The solid which formed in experiment 4 was analyzed by Charles Koch, and the precipitate was found to have the empirical formula $\text{Th}_{1.8}\text{H}_{3.99}\text{S}_{0.56}\text{N}_{0.15}\text{O}_{3.7}$ which is probably a mixture of several basic salts. The formation of a basic salt or salts from solutions of low acidity is not unreasonable. The precipitates which were formed in experiments 1 and 2 were not analyzed.

The rate of oxidation of SCN^- by nitric acid in the presence of hexone was studied. Two experiments were performed. In the first experiment 20 ml. of hexone was shaken with 20 ml. of a solution containing 1.0 M HNO_3 and 1.0 M KSCN . The amount of thiocyanate in the aqueous phase was determined by titrating aliquots of the aqueous phase with silver ion using ferric ion as an indicator. The concentration of thiocyanate in the aqueous phase was determined approximately every hour for a period of eight hours. It was found that the concentration of thiocyanate remained constant over the eight hour period, and that no precipitation took place. In the second experiment 20 ml. of hexone was shaken with 20 ml. of a solution containing 1.0 M $\text{Th}(\text{NO}_3)_4$, 0.097 M $\text{UO}_2(\text{NO}_3)_2$, 0.456 M Na_2SO_4 , 1.0 M HNO_3 and 1.0 M KSCN . Again it was found that over an eight hour period the concentration of thiocyanate in the aqueous phase remained constant, and no precipitation occurred during this time. Other experiments have been performed which have shown that precipitation of the yellow-orange solid does not take place in the presence of hexone. Since this yellow-orange precipitate is not soluble in hexone, the hexone must prevent the reaction between thiocyanate and nitric acid. The hexone probably prevents the formation of this solid by extracting a large part of the thiocyanate ion as thiocyanic acid. The nitric acid concentration in the aqueous phase is also probably decreased somewhat since it too is extracted by hexone. The combination of these two extractions is most likely the reason as to why the solid formation is slowed down or stopped.

From the last two experiments it can be seen that the nitrate reaction with thiocyanate is stopped or slowed down by hexone, and thus the extraction of uranium from potassium thiocyanate solutions containing nitric acid can be performed.*

*

Some solutions were saved as long as a week, and at the end of that time no precipitation of the yellow-orange solid was observed.

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II. The Distribution of Nitric Acid between Hexone and Water

The distribution of nitric acid between hexone and water has been studied. In these experiments solutions of various nitric acid concentrations were shaken with an equal volume of hexone.* An aliquot of the hexone layer was removed for the nitric acid determination. The nitric acid present in the hexone was reextracted into water, and then the water extract was titrated with 0.10 N sodium hydroxide. The results of the experiments will be found in Table 2.

* Eastman Kodak Company, grade 416.

Table 2

The Distribution of Nitric Acid between Hexone and Water

Expt.	Equivalents of HNO ₃ Total	Equivalents of HNO ₃ in the Hexone	(1) K _c	(2) μ	(3) γ±	(4) K _γ
1	1.992	0.056	0.1495	0.194	.76	0.259
2	3.984	0.220	0.155	0.376	.73	0.291
3	5.976	0.440	0.144	0.554	.715	0.282
4	7.968	0.736	0.141	0.723	.71	0.280
5	9.960	1.100	0.140	0.886	.71	0.278

(1) K_c is the concentration constant for the reaction $H^+(aq) + NO_3^-(aq) = HNO_3(\text{hexone})$
Thus

$$K_c = \frac{(HNO_3)_{\text{hexone}}}{(H^+)_{\text{aq}}(NO_3^-)_{\text{aq}}}$$

(2) μ is the ionic strength of the aqueous phase after the extraction.

(3) γ± is the mean activity coefficient of nitric acid in water at ionic strength μ.

(4) K_γ is defined as follows: $K_{\gamma} = \frac{K_c}{\gamma_{\pm}^2}$

It can be seen from Table 2 that the extraction of nitric acid into hexone is relatively small at nitric acid concentrations from 0.2 M to 1.0 M. At 1.0 M HNO_3 about 11% of the nitric acid in the aqueous phase is extracted when the solution is shaken with an equal volume of hexone. The values of the concentration constant, K_c , are essentially constant. Since the mean activity coefficients of nitric acid in the concentration range of the experiments are nearly constant, the values of K_Y , which is defined by the relation

$$K_Y = \frac{(\text{HNO}_3)_{\text{hexone}}}{(\text{H}^+)_{\text{aq.}} (\text{NO}_3^-)_{\text{aq.}} \gamma_{\pm}^2}$$

are also constant. It is not possible to make a correction for the activity coefficients of nitric acid in hexone. It is seen that the data agree with the assumption that the nitric acid is ionized in the aqueous layer and unionized in the hexone layer.

III. The Distribution of HSCN between Hexone and Water

The extraction of HSCN into hexone as a function of the hydrogen ion concentration has been investigated. It is important to know the distribution of HSCN between hexone and water since the amount of uranium which is extracted into the hexone is a function of the SCN^- concentration in the aqueous phase. The extraction of SCN^- into hexone as HSCN was determined in the following manner. Solutions containing 1 M KSCN and nitric acid at various concentrations were shaken with equal volumes of hexone. The concentration of SCN^- or HSCN in each phase was determined by titrating each phase with Ag^+ using Fe^{+++} as an indicator. Thiocyanic acid is a strong acid thus we can write the reaction: $\text{H}^+ + \text{SCN}^- = \text{HSCN}_{\text{hexone}}$

$$K_c = \frac{(\text{HSCN})_{\text{hexone}}}{(\text{H}^+)_{\text{aq.}} (\text{SCN}^-)_{\text{aq.}}}$$

or

$$K_c = \frac{E}{(\text{H}^+)_{\text{aq.}}}$$

where E is the extraction coefficient and equal to

$$\frac{(\text{HSCN})_{\text{hexone}}}{(\text{SCN}^-)_{\text{aq.}}}$$

The extraction coefficients and distribution constants will be found in Table 3.

Table 5

The Distribution of Thiocyanate between Hexone and Water

Expt.	Conc KSCN moles/liter	Conc HNO ₃ moles/liter	Extraction Coefficient	μ	$\frac{E}{(H^+)_{aq}} = K_c$ *
1	1	0.00	Very Small	1	----
2	1	0.20	0.217	1.02	7.78
3	1	0.40	0.482	1.06	7.14
4	1	0.60	0.829	1.1	7.15
5	1	0.80	1.21	1.20	5.76
6	1	1.00	1.61	1.29	5.29

* The extraction coefficients were plotted against the nitric acid concentrations, and a smooth curve was drawn which best fitted the experimental points. The constant K_c was calculated using the values of E obtained from the curve. The constants have been corrected for the change in concentration of H^+ due to the extraction of HNO_3 .

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Table 3 shows that the concentration of thiocyanate ion in the aqueous phase is quite dependent upon the nitric acid concentration. The thiocyanate extraction increases with the nitric acid concentration until at 1.0 M HNO_3 about 60% of the thiocyanate is extracted into the hexone. It can also be seen from Table 3 that the values of K_e are not constant but tend to get smaller at the higher nitric acid concentrations. It does not seem likely that this variation in K_e is due to the change of the ionic strength. Also, no simple and reasonable physical interpretation of the variation of K_e in terms of weakness of electrolytes, polymerization, etc., seems possible. Therefore, it is presumed that the variation is due to the change in the nature of the electrolyte. That is, at low nitric acid concentrations the solution consists mainly of potassium thiocyanate while at high nitric acid concentrations the solution consists mainly of potassium nitrate.

It is also evident from Table 3 that since the extraction of thiocyanate is small at low nitric acid concentrations, it would be profitable to extract uranium from solutions which have small nitric acid concentrations. For example, to obtain approximately equal uranium extractions there would be required roughly two and a half times as much potassium thiocyanate at 1 M HNO_3 as at 0.40 M HNO_3 .

IV. The Solubility of Thorium Sulfate in Various Extraction Solutions

The solubility of thorium sulfate in various extraction solutions has been studied. In reference(1) it was shown that the presence of sodium sulfate in the extraction solution reduced the amount of thorium extracted into the hexone. This indicates that a thorium sulfate complex has formed which is not extracted by hexone. Therefore, it is to be expected that if all the thorium were complexed by sulfate ion, the extraction of thorium into hexone would be very small. To determine the highest concentration of sodium sulfate which could be used in the extraction, solutions were made up which contained identical concentrations of $\text{Th}(\text{NO}_3)_4$, $\text{UO}_2(\text{NO}_3)_2$, HNO_3 , etc., but which contained different concentrations of sodium sulfate. These solutions were then placed on a shaker for several days. It was necessary to shake the samples for a long period of time since it was known that thorium sulfate solutions tended to supersaturate badly. The absence of a solid after long shaking was interpreted to mean that the concentration of $\text{Th}(\text{SO}_4)_2$ aq. was below that which is necessary for the precipitation of thorium sulfate. Three series of experiments were performed. The solutions of the first series contained 0.504 M $\text{Th}(\text{NO}_3)_4$, 0.0974 M $\text{UO}_2(\text{NO}_3)_2$, 0.10 M HNO_3 , 1.00 M KSCN , and 0.90 M NH_4NO_3 . The volume of both the hexone layer and aqueous layer was ten milliliters. The sodium sulfate concentration was varied in steps of about 0.02 M from 0.527 M to 0.429 M. In every experiment a precipitate formed which indicated that each was initially supersaturated with respect to thorium sulfate.

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In the second series solutions were made which contained 0.504 M $\text{Th}(\text{NO}_3)_4$, 0.0974 M $\text{UO}_2(\text{NO}_3)_2$, 0.50 M HNO_3 , and 1.00 M KSCN. The volume of both layers was again ten milliliters. Three concentrations of sodium sulfate were used, namely 0.40 M, 0.349 M, and 0.300 M. A precipitate formed at 0.40 M sodium sulfate. At 0.35 M sodium sulfate the precipitation was so slight that the solid appeared as a film. No precipitation occurred at 0.300 M sodium sulfate. Therefore, if the extraction were carried out at 0.5 M $\text{Th}(\text{NO}_3)_4$, the maximum concentration of sodium sulfate which could be used is about 0.35 M.

The third series of experiments performed contained 0.252 M $\text{Th}(\text{NO}_3)_4$, 0.0974 M $\text{UO}_2(\text{NO}_3)_2$, 0.50 M HNO_3 , and 1.00 M KSCN. The volume of the hexone phase (and the aqueous phase) was ten milliliters. The sodium sulfate concentrations were 0.25 M, 0.225 M, 0.200 M, 0.175 M, and 0.150 M. It was found that no precipitation occurred at 0.200 M, 0.175 M, or 0.150 M sodium sulfate. At 0.225 M sodium sulfate very slight precipitation occurred. So little solid formed that the solution looked clear when first inspected. A precipitate formed at 0.25 M sodium sulfate. Therefore, the maximum concentration of sodium sulfate which could be used if the extraction were performed at 0.25 M $\text{Th}(\text{NO}_3)_4$ would be 0.225 M.

In reference (1) two preliminary experiments were reported in which the sodium sulfate concentration was equal to the thorium nitrate concentration, i.e., about 0.5 M. If these solutions had been shaken for an hour or so precipitation of thorium sulfate would have been observed. Further, had the sodium sulfate concentration been low enough to prevent the precipitation of thorium sulfate, the percentage of thorium extracting into the hexone would have increased.

V. The Distribution of Protoactinium and Fission Elements between Hexone and Aqueous Thiocyanate Solutions.

An experiment on the distribution of protoactinium between hexone and water in the presence of thiocyanate ion was performed. In this experiment ammonium nitrate was substituted for uranium and thorium nitrates since the extraction of any thorium or uranium daughter activities would complicate the interpretation of the results. A small concentration of thorium nitrate was present in the solution however since the protoactinium stock used in the experiment was prepared by dissolving a small portion of irradiated thorium "carbonate" in nitric acid. In this experiment 1 ml of hexone was shaken with 1 ml of a solution which contained 1.2 M NH_4NO_3 , 0.20 M HNO_3 , ~ 0.01 M $\text{Th}(\text{NO}_3)_4$, 0.00987 M Na_2SO_4 , 0.501 M KSCN and about 60,000 c/m of a protoactinium stock. It was found that 4.4% of the total activity in the aqueous phase was extracted into the hexone.

Since the protoactinium stock solution was prepared from irradiated thorium "carbonate", the tracer solution will contain some fission products. If some of the fission products were extracted, the amount of protoactinium extracted as reported above would be too high. Thus the reported extraction would be an upper limit of the amount of protoactinium which is extracted into the hexone. The value of the protoactinium extraction as reported above is the result of only one experiment. Since the distribution of protoactinium is likely to be somewhat irreproducible, the above experiment is only an indication of the amount of protoactinium which is likely to be extracted into hexone.

To determine the main fission activities which are extracted into hexone from a nitric acid-potassium thiocyanate solution the following experiment was performed. A 10 ml sample of hexone was shaken with 10 ml of a solution containing 1 M KSCN, 0.504 M $\text{Th}(\text{NO}_3)_4$, 0.485 M Na_2SO_4 , 1 M HNO_3 , and ~ 0.04 M UH which was obtained by dissolving a bombarded uranium slug in nitric acid. The β decontamination factor as measured on a Lauri'sen electroscopes was about 6.6 while the soft gamma decontamination as counted through 1.6 grams/cm² Al and 0.4 grams/cm² Pb was about 1.5. A β ray absorption curve was taken, and it was found that the absorption curve which was obtained was identical with the β ray absorption curve of zirconium. Zirconium therefore appears to be the main fission element which is extracted into the hexone from a potassium thiocyanate-nitric acid solution. It may be noticed that the aqueous solution in this experiment was supersaturated with respect to thorium sulfate, however, precipitation was not observed before the solutions were aliquoted. In any event the experiment is sufficient in that it gives the order of magnitude of the decontamination factors for the fission elements and reveals the identity of the main fission element which is extracted into the hexone.

VI. Separation of Uranium from Thorium by Extraction into Hexone as $\text{UO}_2(\text{SCN})_2$

It was found that a greater percentage of the thorium could be complexed with SO_4^{2-} without precipitation of $\text{Th}(\text{SO}_4)_2(\text{s})$ if 0.25 M $\text{Th}(\text{NO}_3)_4$ were used in the extraction solution instead of 0.50 M $\text{Th}(\text{NO}_3)_4$. Since a greater fraction of the thorium can be complexed at 0.25 M $\text{Th}(\text{NO}_3)_4$, and since the sulfate complex is not extracted into the hexone, it would be desirable to use 0.25 M $\text{Th}(\text{NO}_3)_4$ in the extraction solution so that a greater separation between uranium and thorium could be obtained.

Two experiments have been performed at 0.25 M $\text{Th}(\text{NO}_3)_4$. The conditions and results of the experiments will be found in Table 4.

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Table 4

The Separation of Uranium from 0.25 M Thorium
Nitrate Solutions

Fixed Conditions:

0.252 M $\text{Th}(\text{NO}_3)_4$
0.2 M HNO_3
0.224 M Na_2SO_4
0.0974 M $\text{UO}_2(\text{NO}_3)_2$
10.0 milliliters aqueous phase
10.0 milliliters hexone

Expt.	Conc KSCN moles/liter	% U as ana- lyzed in R_2O phase	% U analyzed in hexone phase	% Th analyzed in hexone phase
1	0.501	35	63	0.14 *
2	0.25	64.7	35	0.015 *

* The thorium extraction was performed under slightly different conditions in that identical solutions were prepared except that ammonium nitrate was substituted for uranyl nitrate. An ionium tracer was added to the solution and the distribution was measured by determining the amount of ionium in each layer.

Table 4 shows that at 0.5 M KSCN the thorium extraction is about 0.14% when the thorium nitrate concentration is 0.25 M. In a counter current extraction column there would be required six theoretical plates to obtain 99% of the uranium if equal volumes of hexone and aqueous solution were used. The amount of uranium which is extracted into the hexone in experiment 2 is quite low, and thus would require a much larger number of theoretical plates to extract 99% of the uranium.

Although a better separation of uranium from thorium is obtained at 0.25 M $\text{Th}(\text{NO}_3)_4$, extraction solutions containing 0.50 M $\text{Th}(\text{NO}_3)_4$ could be used to good advantage by installing a stripper column of two or three theoretical plates. Thus under conditions where 90% of the uranium is extracted with 3-5% of the thorium, 99% of the uranium could be extracted with two theoretical plates, and the thorium which is extracted could be removed by a stripper column of two or three plates.

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