

RD82+8C218

-c2

RECD JAN 14 1955

CANADA
DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

**THE DETERMINATION OF URANIUM IN
URANIUM CONCENTRATES
USING ETHYL ACETATE**

by

R. J. GUEST and J. B. ZIMMERMAN

RADIOACTIVITY DIVISION



Price 25 cents

Technical Paper No. 8

1954

CANADA
DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

THE DETERMINATION OF URANIUM IN URANIUM CONCENTRATES USING ETHYL ACETATE

by

R. J. GUEST and J. B. ZIMMERMAN

RADIOACTIVITY DIVISION



Price 25 cents

Technical Paper No. 8

1954

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.



THE DETERMINATION OF URANIUM IN
URANIUM CONCENTRATES
USING ETHYL ACETATE

R. J. GERT and J. R. ZIMMERMAN
ANALYTICAL DIVISION



CONTENTS

	Page
Introduction	1
Reagents and Apparatus	2
Procedure	3
Experimental	6
Results and Discussion	15
Summary and Conclusions	16
References	16

TABLES

Table 1 - Effect of Acidity on the Extraction	7
Table 2 - Extraction of Ions other than Uranium by Ethyl Acetate	9
Table 3 - Effect of Contaminants on Uranium Recovery	10
Table 4 - Use of a Wash Solution during the Extraction Procedure	11
Table 5 - Comparative Results of Uranium Determinations by Different Laboratories Using Different Methods .	12
Table 6 - Extraction of Thorium by Ethyl Acetate at Different Acidities	13
Table 7 - Comparison of Procedures for Eliminating the Effect of Thorium	14
Table 8 - Comparison of Regular Ethyl Acetate Method with the Water Stripping Method	15

ILLUSTRATIONS

Figure 1 - Effect of Concentration of Salting Solution on the Extraction of Uranium by Ethyl Acetate - Quantity of Aluminum Nitrate Salting Solution (130°C) Required per 5 ml Sample Solution	18
Figure 2 - Effect of Concentration of Salting Solution on the Extraction of Uranium by Ethyl Acetate - Concentration of Aluminum Nitrate Required to Salt 5 ml of Sample	19

CONTENTS

Page
Introduction
Research and Development
Literature Review
Methodology
Results and Discussion
Conclusions

TABLES

Table 1: Description of the research design
Table 2: Demographic characteristics of participants
Table 3: Descriptive statistics of the dependent variables
Table 4: Results of the ANOVA test
Table 5: Results of the regression analysis
Table 6: Results of the mediation analysis
Table 7: Results of the moderation analysis
Table 8: Results of the path analysis

FIGURES

Figure 1: Conceptual model of the research
Figure 2: Results of the mediation analysis
Figure 3: Results of the moderation analysis
Figure 4: Results of the path analysis

Abstract

A method is described for the determination of uranium in high grade uranium material. Uranium is separated from contaminants by means of an ethyl acetate extraction using aluminum nitrate as a salting agent. The uranium is then determined colorimetrically by the sodium hydroxide-hydrogen peroxide method. The procedure is accurate, rapid and easily adaptable to routine work.

Abstract

A method is described for the determination of organic nitrogen in urine. The method is based on the determination of nitrogen in the urine by means of an alkaline extraction using nitrogen gas as a carrier gas. The nitrogen is then determined colorimetrically by the indophenol reaction. The procedure is simple and accurate. The procedure is accurate, rapid and easily adaptable to routine work.

CHEM
MADE IN
BO

THE DETERMINATION OF URANIUM IN URANIUM CONCENTRATES
USING ETHYL ACETATE

by

R. J. Guest and J. B. Zimmerman
Radioactivity Division

INTRODUCTION

Classical methods of determining uranium in ores and solutions usually employ a preliminary chemical separation before final determination of the uranium volumetrically or colorimetrically.

Recently, fluorophotometric methods were developed (1, 2) which permit determination of uranium in many types of material without prior chemical separation. However, with some material, i. e. material containing high manganese, iron or other quenchers, a preliminary chemical separation is necessary before a fluorophotometric method can be applied.

Material high in uranium content, i. e. greater than 5% uranium oxide, usually requires less preliminary treatment than material with a low uranium content but nevertheless, a separation is almost always necessary before a volumetric or colorimetric finish can be employed. Usually, one or more of such standard procedures as (a) hydrogen sulphide separation, (b) cupferron separation, (c) ammonium or sodium carbonate separations and (d) mercury cathode separation are required (3). Such separations are, of course, time-consuming.

A fluorophotometric method for determining uranium in high grade material has been described (1) and is in use in this laboratory. Although a preliminary separation is seldom required in this method, it is difficult to attain consistently a precision of better than 1.5% - 2.0% and a precision greater than this is required in some cases.

A number of organic solvents for uranyl nitrate have been reported (4), and separations based on the use of some of these solvents have been described (5, 6, 7). In this laboratory diethyl ether-nitric acid has been used in conjunction with the cellulose column for some time (8). This method, while not as lengthy as many other separation procedures, possesses all the hazards involved in using ether.

The extraction of uranium by means of ethyl acetate from a nitric acid solution heavily salted with aluminum nitrate has been used in this laboratory (9) as a preliminary separation prior to a fluorimetric finish. The separation is rapid and results are reproducible. In an attempt to obtain greater precision and accuracy in uranium assays on uranium concentrates it was decided to investigate the possibility of developing a method using an ethyl acetate extraction and a colorimetric or volumetric finish.

Volumetric methods for determining uranium which have been used in this laboratory employ potassium dichromate as a titrant after reduction of uranium VI to uranium IV by means of a Jones reductor (10, 11), lead reductor (12) or stannous chloride solution (13).

A number of colorimetric methods for determining uranium have been described (11, 14, 15). A method that has been used successfully in this laboratory is the sodium hydroxide-hydrogen peroxide method. As this colorimetric procedure detects milligram quantities of uranium, it is applicable to the detection of uranium in concentrates. Because of this and due to the speed and simplicity of the procedure, its application after an ethyl acetate extraction was investigated.

REAGENTS AND APPARATUS

Reagents

Aluminum nitrate salting solution

Place 400 gm of reagent grade (Mallinckrodt) aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in a 600 ml beaker and dissolve the salt in a minimum amount of water. Concentrate the solution by boiling until a boiling point of 130°C is reached. Cover the beaker with a watch glass. If this solution is not to be used immediately, reheat to about 120°C just before using. Dilute the solution before allowing it to cool to room temperature.

Aluminum nitrate wash solution

Add 100 ml of aluminum nitrate salting solution (B. P. 130°C) to 73 ml of distilled water and 4 ml of concentrated nitric acid.

10% sodium hydroxide solution

Dissolve 200 gm of reagent grade sodium hydroxide in distilled water and dilute to 2 liters.

30% hydrogen peroxide (reagent grade)

Ethyl acetate (Merck, reagent grade)

1:1 nitric acid (V/v)

1:1 hydrochloric acid (V/v)

1:1 sulphuric acid (V/v)

5% nitric acid

Dilute 50 ml of concentrated nitric acid to 1000 ml with distilled water.

10% nitric acid

Dilute 100 ml of concentrated nitric acid to 1000 ml with distilled water.

Apparatus

Beckman DU Spectrophotometer

60 ml separatory funnels (Squibb, pear-shaped)

N_o 0 rubber stoppers - Boil twice in ethyl acetate and once in 5% nitric acid before using.

PROCEDURE

Place an appropriate quantity (1-5 gm) of the sample in a tared weighing bottle, stopper the bottle and weigh the bottle and contents immediately. Carry out a moisture determination on a separate sample if uranium is to be calculated on a dry weight basis.

Bring the sample into solution in one of three ways:- (1) nitric acid treatment, (2) multiacid treatment, (3) sugar carbon-sodium peroxide fusion.

For the nitric acid treatment, dissolve the sample in a suitable quantity of nitric acid and transfer the solution and insoluble residue into an appropriate volumetric flask and make up to volume. Regulate the dilution so that the aliquot chosen for extraction will contain between 10 and 30 mg of uranium oxide if the final dilution for the colorimetric finish is to be 250 ml. Adjust the acidity of the sample solution to about 5% in nitric acid.

If nitric acid treatment is not sufficient, treat the sample with hydrochloric acid, nitric acid, perchloric acid and finally sulphuric acid. If necessary, add a few drops of hydrofluoric acid. Fume the sample to dryness and leach the residue with nitric acid, finally transferring the solution and residue to an appropriate volumetric flask and adjusting to 5% in nitric acid as in the single acid treatment.

If the sample is refractory use the sugar carbon-sodium peroxide fusion method described by Muehlberg (16), although in some cases this method has led to low results and should not be used as a general procedure. After dissolution of the sample in this manner transfer the acidified solution to an appropriate volumetric flask and dilute so that the final solution is 5% in nitric acid.

Aliquot solution samples directly or dilute as required for an ethyl acetate extraction. If the sample is aliquoted directly for an extraction, add 5 drops of concentrated nitric acid per 5 ml aliquot of sample and standards before extraction. Where samples are diluted before aliquots are taken for extraction, adjust the acidity so that the final volume is 5% in nitric acid.

The Ethyl Acetate Extraction

Place aliquots (usually 5 ml) from samples and from previously prepared standard uranium solutions (2 gm/l U_3O_8 to 6 gm/l U_3O_8 in 5% nitric acid) into 60 ml separatory funnels. Choose the standards so that they cover the range into which the samples are expected to fall. Add, by means of a graduated pipette, 6.5 ml of aluminum nitrate solution per 5 ml of sample solution. The aluminum nitrate salting solution should be added while hot (greater than $100^{\circ}C$). Cool the solution to room temperature and add 20 ml of ethyl acetate. Stopper the separatory funnels with pretreated rubber stoppers. Shake the mixture for 45-60 seconds. Occasionally crystallization will take place in the separatory funnel near the stopcock. In such a case place the lower part of the separatory funnel into a beaker of hot water until the solidified portion dissolves.

After the layers have separated, drain off the aqueous (lower) layer. Occasionally a cloudiness will appear at the boundary of the aqueous and organic layer. This cloudy portion should not be drained off. Add 10 ml of aluminum nitrate wash solution to the funnel and again shake the mixture for 45-60 seconds. Drain off the aqueous layer, once again being careful to retain the cloudy portion at the boundary in the funnel. Rinse inside the stem of the separatory funnel with a stream of water from a wash bottle.

Complete the determination by one of two procedures:

1) The colorimetric finish with removal of ethyl acetate by evaporation

Drain the organic layer into a clean 250 ml beaker and rinse the separatory funnel and stopper thoroughly with ethyl acetate (10-15 ml from an all glass wash bottle). Add 15-20 ml of distilled water to the organic extract and place the mixture on a low temperature hot plate. Evaporate the solution to 5-10 ml, taking care that the sample does not bake. A small amount of silicone grease is sometimes carried through with the ethyl acetate and may cause retention of uranium in the beaker if the sample is taken to dryness.

Add enough 10% sodium hydroxide solution to neutralize the solution and dissolve any precipitated aluminum hydroxide and then add 10 ml in excess per 100 ml final volume. Add 1 ml of 30% hydrogen peroxide per 100 ml final volume. Transfer the solution to a volumetric flask of appropriate size and dilute to volume. Read the absorbance on the Beckman DU spectrophotometer at 370 m μ against a reagent blank. Compare the absorbances of the samples against the absorbances of the standard uranium solutions.

2) The colorimetric finish with water stripping of uranium from the ethyl acetate layer

Add 15 ml of water to the separatory funnel containing the ethyl acetate, stopper the flask and shake the mixture for about 45 seconds. After washing off the stopper with a little water, drain the aqueous layer into a volumetric flask of suitable size and wash the separatory funnel and ethyl acetate layer 4 or 5 times with 5 ml portions of water by means of a wash bottle. Combine the aqueous fractions.

To the volumetric flask containing the aqueous fractions add 10% sodium hydroxide solution until the solution is neutralized and the precipitated aluminum hydroxide redissolves. A larger amount of aluminum is usually present in this procedure than in the previous one, so a greater amount of sodium hydroxide is required. Add 20 ml excess of 10% sodium hydroxide and 1 ml of 30% hydrogen peroxide per 100 ml final volume. Dilute the solution to volume and continue as in procedure 1 (above).

The Removal of Interfering Thorium

After an ethyl acetate extraction the uranium solution is freed of ethyl acetate by either of the above procedures. If the water stripping procedure has been used the uranium fraction is collected in a 250 ml beaker. In either case add enough 10% sodium hydroxide solution to neutralize the solution and

redissolve precipitated aluminum hydroxide. Then add 10 ml excess of 10% sodium hydroxide solution and 1 ml of 30% hydrogen peroxide per 100 ml final volume. Filter the solution through an 11 cm 41H filter paper (Whatman), collecting the filtrate in a volumetric flask of suitable size. Wash the paper and precipitate once with 5 ml of a solution of 10% sodium hydroxide containing 0.5 ml of 30% hydrogen peroxide. Redissolve the precipitate by washing the paper with a few ml of 10% nitric acid solution, collecting the washings in the original beaker. Neutralize the solution with 10% sodium hydroxide solution and add 5 ml in excess. Add 0.5 ml of 30% hydrogen peroxide and filter off the precipitate on the original filter paper, washing as before and collecting the filtrates in the original volumetric flask. If the precipitate on the paper is coloured yellow this step should be repeated. Make the solution in the volumetric flask up to volume and read the absorbance on the spectrophotometer. Carry standards through the same procedure as the samples.

EXPERIMENTAL

A series of standard uranium solutions was made up by dissolving M. S. S. T. uranium oxide (U_3O_8) in nitric acid and making the solutions up to volume in volumetric flasks. The acidity of the solutions was 5% in nitric acid. Appropriate aliquots of these solutions were transferred to volumetric flasks and colour development carried out by the sodium hydroxide - hydrogen peroxide method.

Similar aliquots of the standard solutions were extracted with ethyl acetate using aluminum nitrate as a salting agent. The effect on the extraction of pH, shaking time and varying amounts of salting agent was investigated. After evaporation of the ethyl acetate, the uranium content of the synthetic samples was determined by the sodium hydroxide - hydrogen peroxide method. A brief comparison of several colorimetric and volumetric finishes was made.

Extraction tests were carried out on synthetic solutions containing common contaminating ions and the results tabulated. The method was then applied to actual samples and the results compared with known values obtained by other methods. A procedure for the removal of interfering thorium was developed. Finally, the use of a technique employing water stripping of uranium from the ethyl acetate layer was investigated.

Extraction of Uranium with Ethyl Acetate and the Effect of the Salting Agent

A series of aliquots of standard uranium solutions such that 5 ml contained from 5 mg to 100 mg of uranium oxide were extracted with 20 ml of ethyl acetate. The quantity of aluminum nitrate salting agent required to give complete extraction of uranium was first determined.

It is shown in Figure 1 that at least 5.5 ml of aluminum nitrate solution, so concentrated that it boils at 130°C, is required to give complete extraction of 25 mg of uranium oxide (U_3O_8) contained in 5 ml of solution. The most convenient way found to express the amount of aluminum nitrate added was in terms of the boiling point of its concentrated solution. Figure 2 indicates that to extract completely 25 mg of uranium oxide from 5 ml of solution with 6.5 ml of aluminum nitrate salting solution, the boiling point of the salting solution must be at least 126°C. It can be seen from these figures that the amount of salting agent added is critical. The use of a ratio of 6.5 ml of salting solution, boiling point 130°C, to 5 ml of sample solution was adopted as standard procedure.

Tests indicated that at least 35 mg of uranium oxide can be extracted quantitatively with 20 ml of ethyl acetate. The relationship is linear and results are reproducible with excellent precision. A procedure using two extractions with ethyl acetate was tried but did not appear to present any advantage over the method using one extraction.

An attempt was made to extract quantities of uranium oxide greater than 35 mg but results obtained were not always consistent. It is believed that this inconsistency is at least partially due to errors in instrument reading at high absorbances. Brief tests indicated that errors from this source can be minimized by using the method of differential colorimetry (17). It is planned to carry out further investigations along this line.

If desirable, smaller quantities of ethyl acetate than 20 ml can be used. The larger amount has been used in this laboratory to minimize the error caused by possible loss of a small amount of ethyl acetate during the extraction.

Effect of Acidity on the Extraction of Uranium

Quantitative extraction of uranium was obtained on samples varying from 1.5% to 11.0% in nitric acid using the described procedure (Table 1). It has been found convenient to use an acidity of 5% in nitric acid for most of the work carried out in this laboratory.

Table 1

Effect of Acidity on the Extraction

<u>Acidity in nitric acid</u> %	<u>Uranium present,</u> mg U_3O_8	<u>Uranium found,</u> mg U_3O_8
1.5	25.0	25.1
6.0	25.0	25.2
11.0	25.0	25.0

Effect of Shaking Time on the Extraction of Uranium

Little difference in the extraction of uranium was found under the conditions of the procedure by shaking the mixture for periods of time varying from 20 to 60 seconds. The deviation in recovery of 25 mg of uranium oxide using 6% acidity and shaking time of 20, 40 and 60 seconds was approximately 1%.

Final Determination of Uranium Colorimetrically and Volumetrically

Although the sodium hydroxide-hydrogen peroxide colorimetric method was used in most of this work for final determination of uranium after the extraction, a number of other finishes were tried briefly. Two colorimetric methods, one using thiocyanate (14) and the other using thioglycolic acid (15), are 2-3 times as sensitive as the sodium hydroxide-hydrogen peroxide method. However, the latter method showed greater reproducibility and is preferred in this laboratory.

Standard volumetric techniques, such as titration with potassium dichromate after reduction of uranium VI to uranium IV, were tried briefly. Reduction was carried out by both the lead reductor method (12) and the stannous chloride method (13). However, before using either reduction method, it was necessary to add sulphuric acid and take the samples to fumes to remove nitric acid. These volumetric methods are lengthier than the sodium hydroxide-hydrogen peroxide method and do not appear to offer any advantages in precision.

It was decided, therefore, that because of its speed and reproducibility the sodium hydroxide-hydrogen peroxide method was the most promising of the methods tried for the final determination of uranium after an ethyl acetate extraction.

Extraction of Ions Other Than Uranium

In order to determine whether or not a number of common contaminants likely to be found in high grade uranium material are extracted with ethyl acetate, solutions containing these contaminants were made up and appropriate aliquots put through the extraction procedure. The organic extract was washed with a wash solution containing a ratio of 6.5 ml of salting agent to 5 ml of 5% nitric acid solution. This step is necessary to compensate for mechanical retention of the contaminating ion during separation of the organic and aqueous layers. The amount of contaminant found in the ethyl acetate layer was then determined by standard procedures. Of the ions tested only thorium was found to be extracted under the conditions of the procedure (Table 2). Aluminum was found in variable amounts.

Table 2

Extraction of Ions other than Uranium by Ethyl Acetate

Contaminant added	Amount of contaminant added, mg	Amount of contaminant found, mg
Vanadium	10	< 0.1
Iron	10	< 0.01
Molybdenum	10	< 0.01
Copper	10	< 0.1
Arsenic	20	< 0.01
Phosphorus (as P ₂ O ₅)	20	< 0.01
Cobalt	10	< 0.05
Calcium	10	< 0.01
Magnesium	10	< 0.1
Manganese	10	< 0.1
Aluminum	800 (approx) as salting agent	1.4
"	"	7.0
"	"	1.6
Thorium	3.8	> 0.3

Application of the Method to Synthetic Samples

Synthetic solutions containing uranium and various contaminants were made up and appropriate aliquots carried through an ethyl acetate extraction, washing the organic extract with the aluminum nitrate wash solution. After evaporation of the ethyl acetate, uranium was determined by the sodium hydroxide-hydrogen peroxide method. When the ratio of contaminant to uranium was 2 to 1, or greater in several cases, none of the contaminants tested appeared to affect uranium recovery. Single determinations were carried out in all cases and individual deviations are considered to be experimental (Table 3).

Preponderant ratios of iron and copper to uranium were added in two cases, tests 3 and 5. In each case two washings with aluminum nitrate were carried out. This is a precautionary measure when the sample is highly contaminated. If appreciable quantities of copper or iron are present in the colorimetric finish they will catalyse the breakdown of the hydrogen peroxide, values being low in the presence of copper and high in the presence of iron.

Tests 19, 20 and 21 were carried out on synthetic solutions containing uranium and a number of contaminants in the approximate ratios expected to be found in high grade uranium samples met with in this laboratory. From results tabulated in Table 3 it can be seen that amounts of common contaminants met with in high grade uranium samples should not cause difficulty.

Table 3

Effect of Contaminants on Uranium Recovery

Test	Contaminant added	Amount of contaminant added, mg	Uranium added, mg U ₃ O ₈	Uranium found, mg U ₃ O ₈
1	Vanadium	10	5.00	5.02
2	Iron	10	5.00	5.14
3	Iron	88	8.00	7.98
4	Copper	10	5.00	4.94
5	Copper	120	8.00	7.95
6	Cobalt	10	5.00	4.90
7	Calcium	10	5.00	5.10
8	Magnesium	10	5.00	5.02
9	Calcium + Magnesium	12 Ca + 20 mg	5.00	4.93
10	Nickel	5	5.00	5.03
11	Cerium III	15	5.00	4.98
12	Manganese	10	5.00	5.10
13	Thorium	10	5.00	4.92
14	Chromium	9	5.00	4.82
15	Arsenic	16	5.00	4.97
16	Arsenic	36	5.00	4.95
17	Molybdenum	8	5.00	5.02
18	Molybdenum	18	5.00	5.00
19	Synthetic A - Multi-contaminant			
		(1)	6.25	6.30
20	Synthetic B -	" "	(2) 20.00	20.11
21	Synthetic C -	" "	(3) 4.00	4.08

(1) 4.0 mg arsenic, 1.5 mg copper, 0.5 mg phosphorus, 0.6 mg iron, 0.06 mg nickel, 0.1 mg vanadium, 0.1 mg molybdenum, 0.1 mg chromium per 6.25 mg uranium oxide.

(2) 0.5 mg vanadium, 0.5 mg iron, 0.4 mg molybdenum, 1.0 mg copper, 5.0 mg arsenic, 2.0 mg phosphorus, 0.5 mg cobalt per 10.0 mg uranium oxide.

(3) 0.5 mg vanadium, 9.2 mg iron, 0.4 mg molybdenum, 10.0 mg copper, 15.0 mg arsenic, 10.0 mg phosphorus, 1.0 mg cobalt per 4.0 mg uranium oxide.

Use of a Wash Solution during the Extraction of Uranium

During the separation of the organic and aqueous layers in the ethyl acetate extraction there is some mechanical retention of contaminants. It was found essential, therefore, to wash the ethyl acetate layer with a solution to reduce the amount of impurities retained. Accordingly, a wash solution was made up consisting of the same ratio of aluminum nitrate, water and nitric acid as found in the sample extraction. This solution has proven to be most satisfactory. If the amount of contaminant is very high it may be necessary to carry out a second washing. In practice this has not been found necessary when analysing samples of over 5% uranium oxide. The effectiveness of the wash solution is illustrated in Table 4.

Table 4

Use of a Wash Solution during the Extraction Procedure

Sample	Contaminant present	Number of washings	Uranium present, mg U ₃ O ₈	Uranium found, mg U ₃ O ₈
Synthetic (1)	Multi-contaminant ⁽¹⁾	-	6.25	5.96
"	"	1	6.25	6.30
"	"	-	12.5	10.8
"	"	1	12.5	12.6
Synthetic (2)	None	-	25.0	25.1
"	"	1	25.0	25.1
Synthetic (3)	88 mg Iron	1	8.00	7.95
"	"	2	8.00	8.00
Synthetic (4)	120 mg Copper	1	8.00	colour fading
"	"	2	8.00	7.95

(1) 4.0 mg arsenic, 1.5 mg copper, 0.5 mg phosphorus, 0.6 mg iron, 0.06 mg nickel, 0.1 mg vanadium, 0.1 mg molybdenum, 0.1 mg chromium per 6.25 mg uranium oxide.

Application of the Method to High Grade Uranium Concentrates and Solutions

The method was applied to a series of high grade uranium concentrates and solutions and the results compared with values obtained by other laboratories and by fluorophotometric methods in this laboratory. A representative group of comparative results is shown in Table 5. The possibility of applying this procedure to lower grade uranium material is suggested by values obtained on a number of relatively low grade samples. Comparative results on several of these samples are included in Table 5.

Table 5

Comparative Results of Uranium Determinations by Different Laboratories Using Different Methods

Sample R-No.	Sample type	Low grade fluorimetric, % U ₃ O ₈	High grade fluorimetric, % U ₃ O ₈	Ethyl acetate colorimetric, % U ₃ O ₈	Lab. A % U ₃ O ₈ ⁽¹⁾	Lab. B % U ₃ O ₈ ⁽²⁾	Lab. C % U ₃ O ₈ ⁽³⁾
10509	Product	-	11.8	11.9	-	11.9	-
10510	"	-	9.58	9.66	-	9.68	-
10513	"	-	33.8	33.9	-	34.0	-
11403	"	-	11.4	11.4	-	11.5	-
11404	"	-	9.99	9.87	-	9.80	-
11396	"	-	43.1	42.9	-	43.4	-
12224	"	-	11.7	11.7	-	11.7	-
12225	"	-	10.6	11.0	-	10.9	-
12233	"	-	41.7	42.0	-	42.0	-
10475	"	-	43.5	43.5	43.4	-	-
10477	"	-	42.9	43.1	43.1	-	-
10479	"	-	43.6	43.9	44.0	-	-
10481	"	-	42.8	42.6	42.2	-	-
10483	"	-	41.3	41.1	41.0	-	-
10485	"	-	44.6	45.0	44.7	-	-
10487	"	-	41.6	41.8	41.3	-	-
10489	"	-	9.73	9.80	9.87	-	-
10072	"	-	77.1	74.9	-	-	74.7
11237	"	-	75.1	75.3	-	75.8	75.9
12046	"	-	73.3	74.2	-	73.8	73.0
11374	Ore	0.66	0.66	0.63	-	-	-
12231	Solution	1.75 gm/1	-	1.75 gm/1	-	1.82 (gm/1)	-
11397	"	1.92 gm/1	-	2.00 gm/1	-	2.06 (gm/1)	-
11750	"	0.036 gm/1	-	0.04 gm/1	-	-	-
-	"	1.84 gm/1	-	1.87 gm/1	-	-	-
11751	"	0.068 gm/1	-	0.08 gm/1	-	-	-

(1) Laboratory A - H₂S - cupferron - volumetric finish (2) Laboratory B - H₂S - cupferron volumetric finish (3) Laboratory C - no separation - colorimetric finish.

Interference of Extracted Thorium in
the Colorimetric Finish

During the procedure a portion of the thorium present is extracted along with the uranium. During the colorimetric finish thorium precipitates and causes cloudy solutions and, therefore, high values. The amount of thorium extracted appears to vary according to the acidity of the sample. Table 6 shows the extraction of thorium at three different acidities and the recovery of uranium under the same conditions. In each case uranium was separated from thorium according to method (B) described below.

Table 6

Extraction of Thorium by Ethyl Acetate at Different Acidities

Sample	Acidity in nitric acid, %	Thorium present, mg ThO ₂	Thorium found, mg ThO ₂	Thorium extracted, %	Uranium present, mg U ₃ O ₈	Uranium found, mg U ₃ O ₈
Synthetic	1.5	7.6	5.0	66.0	10.50	10.38
"	5	7.6	5.9	77.6	10.50	10.56
"	10	7.6	6.25	82.4	10.50	10.56

Two methods of eliminating the effect of thorium in the colorimetric finish have been tried. One method (A) is simply to centrifuge the cloudy solution before reading its absorbance. A second method (B) is to filter off the thorium precipitate on 41H filter paper, redissolve the precipitate with acid, add excess sodium hydroxide and hydrogen peroxide and filter off the thorium precipitate again. Where the thorium content is higher than that of uranium it may be necessary to repeat this step (Method B).

The filtrates are caught in a volumetric flask of suitable size, diluted to volume and the absorbance read on the spectrophotometer. A comparison of results obtained by these two procedures is shown in Table 7. It can be seen that the deviation between the two procedures is about 1%. For most work, therefore, it should be sufficient to centrifuge the solution before the colorimetric reading. If the amount of thorium present is considerably higher than the amount of uranium in the sample, it would probably be advisable to use the longer method (B).

Table 7

Comparison of Procedures for Eliminating the Effect of Thorium

Sample R-number	Thorium present, % ThO ₂	Method (A) uranium found, % U ₃ O ₈	Method (B) uranium found, % U ₃ O ₈	High grade fluorimetric uranium found, % U ₃ O ₈
A 204	6-8	44.7	44.3	-
A 325	1-3	12.0	11.9	-
A 540	1-3	9.81	9.84	-
11608	6-8	41.5	41.9	42.0
12491	65-70	25.3	27.6	27.8
11774	0.5-1.0	68.0	-	67.7
2.50 mg U ₃ O ₈	3.8	2.46 mg	-	-
10.50 mg U ₃ O ₈	7.6	-	10.56 mg	-

Stripping of Uranium from the Ethyl Acetate

Layer by means of Water

The possibility of using a water stripping technique to remove uranium from the ethyl acetate layer has been investigated with considerable success. After the aluminum nitrate layer has been drawn off, 15-25 ml of water is added to the ethyl acetate and the mixture shaken for about 1 minute. The aqueous layer is drawn off into an appropriate volumetric flask, the separatory funnel and contents are rinsed several times with water from a wash bottle and the washings added to the volumetric flask. Sodium hydroxide and hydrogen peroxide are then added directly to the volumetric flask and the colorimetric finish carried out.

This technique considerably shortens the method as it is not necessary to transfer the solutions to beakers and evaporate the ethyl acetate. It is, also, much simpler to recover the ethyl acetate by means of a water stripping technique. Because of the larger amount of aluminum carried through with the uranium while using this procedure, it has been found necessary to increase the amount of sodium hydroxide in the colorimetric finish. If an adequate amount of sodium hydroxide is not present, breakup of hydrogen peroxide and gradual deterioration of the coloured complex takes place. Comparative results using the regular ethyl acetate method and the water stripping procedure are shown in Table 8. Tests carried out on the ethyl acetate layer after water stripping indicated that less than 0.03% of the uranium present was retained.

Table 8

Comparison of the Regular Ethyl Acetate Method
with the Water Stripping Method

Sample R-number	Sample type	Ethyl acetate method (regular), % U ₃ O ₈	Ethyl acetate method with water stripping, % U ₃ O ₈	Laboratory (B) ⁽¹⁾ % U ₃ O ₈
10638	Product	72.3	72.6	-
10513	"	33.9	33.9	34.0
11404	"	9.87	9.75	9.80
12225	"	11.7	11.8	11.7
A 121	"	7.83	7.77	-
A 137	"	46.0	45.9	-
A 101	Solution	4.52 gm/1	4.50 gm/1	-
A 126	"	4.88 gm/1	4.81 gm/1	-
A 612	Product	75.3	75.4	-
A 703	"	13.3	13.4	-
A 720	"	12.0	12.1	-
A 684	"	64.7	64.8	-
A 593	"	7.70	7.55	-

(1) Laboratory B - H₂S - cupferron - volumetric finish.

RESULTS AND DISCUSSION

The work described here shows that the ethyl acetate-colorimetric method is very satisfactory for determining uranium in high grade uranium material. This method is rapid and has proven to be well suited for routine work. After dissolution of the sample a trained technician can carry out twenty determinations in a seven hour day.

Because of the high accuracy usually required on uranium assays in uranium products it has been found advisable to run standards with each series of sample determinations. It is customary in this laboratory to use a ratio of one standard to four samples but this ratio may be varied according to the accuracy required.

The standard deviation expressed as percentage of the mean has proven to be less than 0.5% for the extraction procedure and colorimetric finish. For the complete procedure including handling and dissolution of solid samples, the standard deviation expressed as percentage of the mean has been found to be less than 1%. This compares very favourably with other methods for determining uranium in uranium concentrates.

It is essential that an adequate amount of aluminum nitrate salting agent be present if reproducible results are to be obtained. This salting agent should be added while hot or trouble may be found from crystallization in the separatory funnel. It is necessary in almost all cases to wash the ethyl acetate layer once with the aluminum nitrate wash solution. A second washing may be required on highly contaminated samples but this is rarely necessary on uranium concentrates.

The procedures described for removal of thorium and for water stripping of the uranium have proven satisfactory for all samples on which they have been used. Further work is being carried out to verify their suitability for general application.

SUMMARY AND CONCLUSIONS

The extraction of uranium by means of ethyl acetate has been investigated and a procedure described for the application of this extraction procedure to uranium determinations on high grade material. Uranium is finally determined colorimetrically by the sodium hydroxide-hydrogen peroxide procedure. The method compares very favourably in speed, precision and accuracy with other uranium methods tested. Because of its speed and simplicity the method is particularly applicable to routine analysis for uranium.

REFERENCES

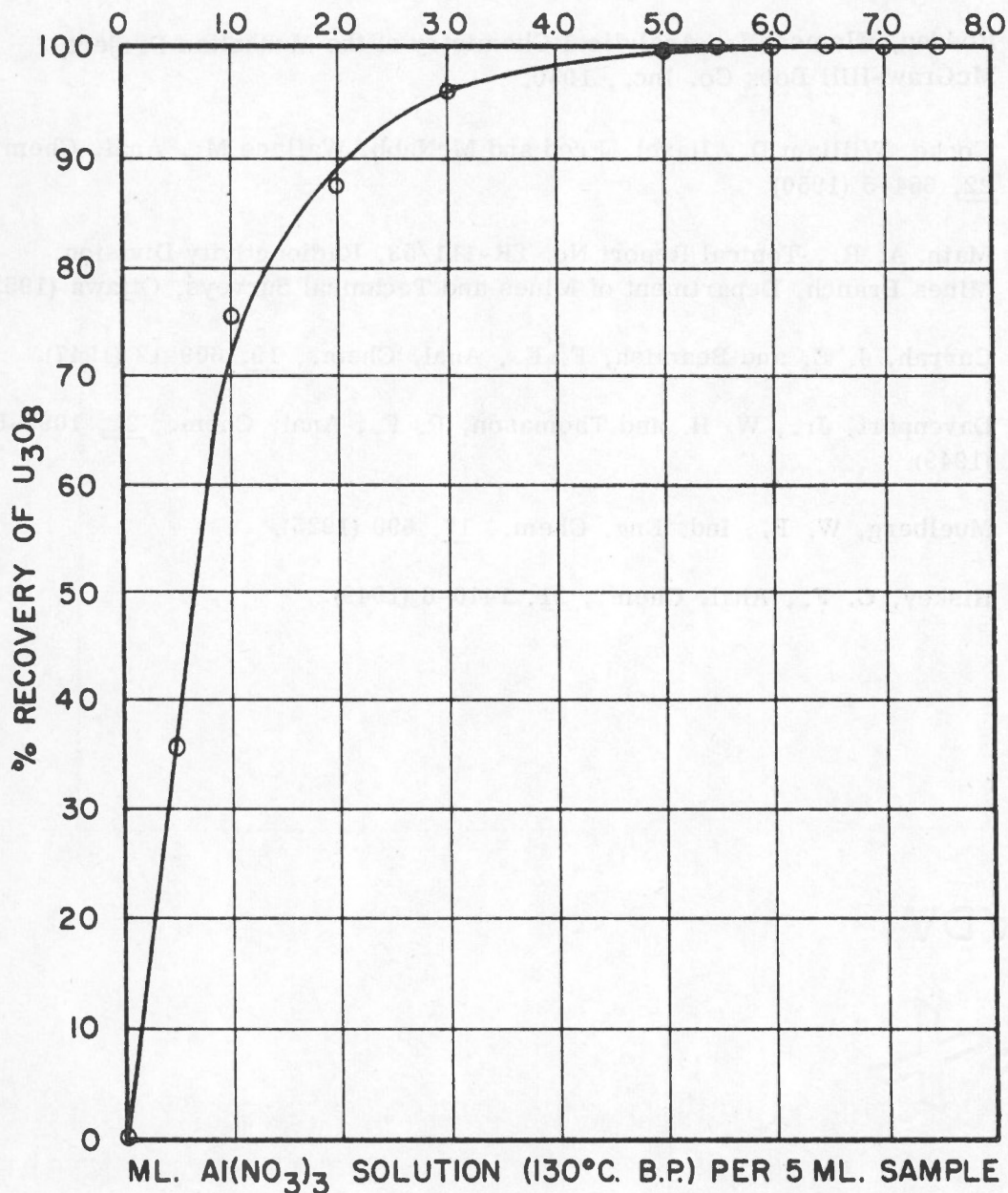
- (1) Zimmerman, J. B., Rabbitts, F. T. and Kornelsen, E. D., Mines Branch Technical Paper No. 6, Department of Mines and Technical Surveys, Ottawa (1953).
- (2) Zimmerman, J. B., Mines Branch Memorandum Series No. 114, Department of Mines and Technical Surveys, Ottawa (1951).
- (3) Rabbitts, F. T., Mines Branch Memorandum Series No. 109, Department of Mines and Technical Surveys, Ottawa (1951).
- (4) Yaffe, L., Canadian J. Research, 27B, 638-45 (1949).
- (5) Cripps, F. H., Scientific Report CRL/AE 73, Chemical Research Laboratory, Teddington (1950).
- (6) Grimaldi, F. S. and Levine, Harry, A. E. C. D. - 2824, U. S. Geol. Survey (1950).
- (7) Ryan, W. and Williams, A. F., Analyst, 77, 293-6 (1952).
- (8) Rabbitts, F. T., et al., Mines Branch Memorandum Series No. 105, Department of Mines and Technical Surveys, Ottawa (1951).

- (9) Zimmerman, J. B. and Guest, R. J., Topical Report No. TR-96/52, Radioactivity Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa (1952).
- (10) Heaney, Robert J. and Rodden, Clement J., M. D. D. C. -901, U. S. A. E. C. (1946).
- (11) Rodden, Clement J., Analytical Chemistry of the Manhattan Project, McGraw-Hill Book Co. Inc., 1950.
- (12) Cooke, William D., Haxel, Fred and McNabb, Wallace M., Anal. Chem., 22, 654-5 (1950).
- (13) Main, A. R., Topical Report No. TR-111/53, Radioactivity Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa (1953).
- (14) Currah, J. E. and Beamish, F. E., Anal. Chem., 19, 609-12 (1947).
- (15) Davenport, Jr., W. H. and Thomason, P. F., Anal. Chem., 21, 1093-5 (1949).
- (16) Muelberg, W. F., Ind. Eng. Chem., 17, 690 (1925).
- (17) Hiskey, C. F., Anal. Chem., 21, 1440-6 (1949).

STANDARD URANIUM SOLUTION-ADDED AS URANYL NITRATE.

25 MG. U_3O_8 PER 5 ML. SAMPLE.

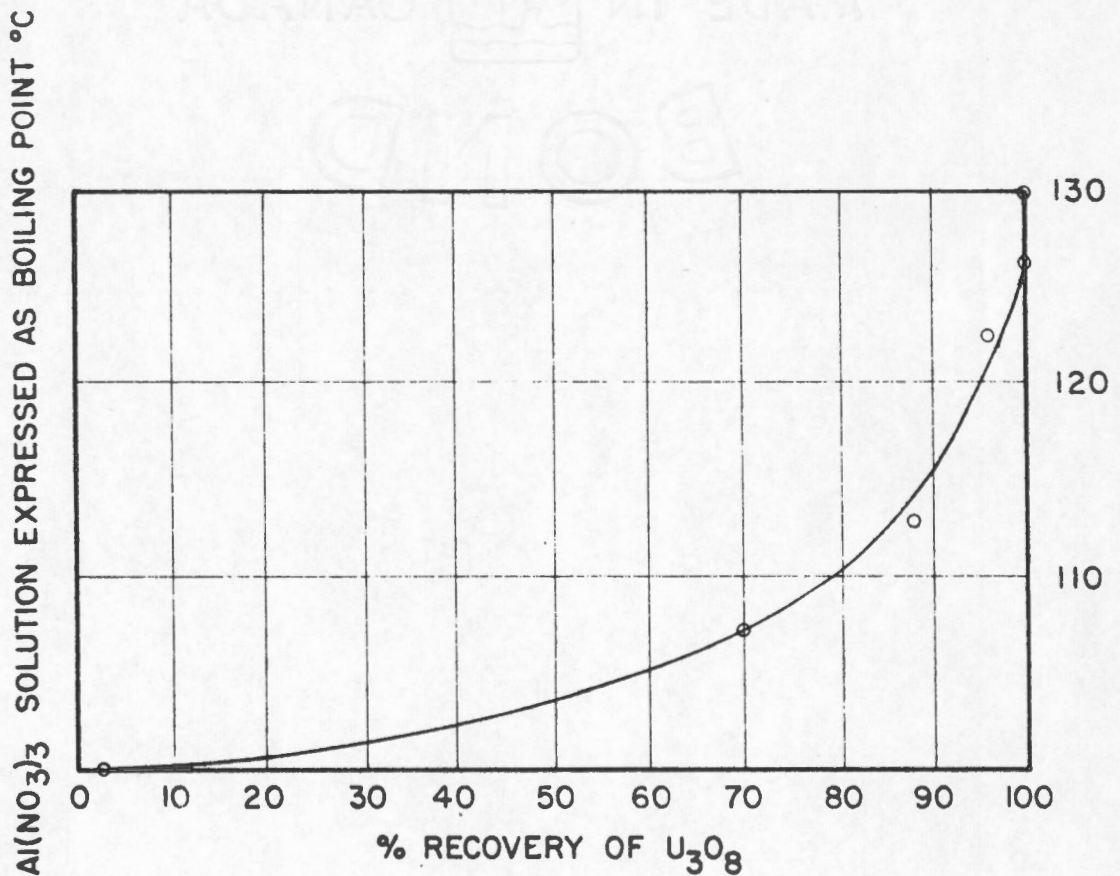
45-60 SECONDS SHAKING TIME-WITH 20 ML. ETHYL ACETATE.



EFFECT OF CONCENTRATION OF SALTING SOLUTION ON THE EXTRACTION OF URANIUM BY ETHYL ACETATE - QUANTITY OF ALUMINUM NITRATE SALTING SOLUTION (130°C) REQUIRED PER 5 ML. SAMPLE SOLUTION.

FIGURE I

STANDARD URANIUM SOLUTION - ADDED AS URANYL SULPHATE.
25 MG. U_3O_8 IN 5 ML. SAMPLE PLUS 6.5 ML. SALTING AGENT.
45-60 SECONDS SHAKING TIME WITH 20 ML. ETHYL ACETATE.



EFFECT OF THE CONCENTRATION OF SALTING SOLUTION ON THE EXTRACTION OF URANIUM BY ETHYL ACETATE—CONCENTRATION OF ALUMINUM NITRATE REQUIRED TO SALT 5 ML. OF SAMPLE.

FIGURE 2.

STANDARD URANIUM SOLUTION - ADDED AS URANYL SULPHATE
25 MG. U₃O₈ IN 5 ML. SAMPLE PLUS 6.5 ML. SALTING AGENT
45-60 SECONDS SHAKING TIME WITH 50 ML. ETHYL ACETATE

MADE IN CANADA

BOND



PERCENT RECOVERY OF U₃O₈

EFFECT OF THE CONCENTRATION OF SALTING SOLUTION ON THE
EXTRACTION OF URANIUM BY ETHYL ACETATE - CONCENTRATION
OF ALUMINUM NITRATE REQUIRED TO SALT 5 ML. OF SAMPLE

FIGURE 5

