Date of Issue: July 26, 1951 Report Number: K-789

1

APPLICATION OF TRIBUTYL PHOSPHATE EXTRACTION OF URANIUM TO WORKS LABORATORY SAMPLES

T. W. Bartlett

Work Supervised by
R. H. Lafferty, Jr.
Laboratory Division
F. W. Hurd, Superintendent

CARBIDE AND CARBON CHEMICALS COMPANY
K-25 Plant
Oak Ridge, Tennessee

Photostat Price $ 1.80
Microfilm Price $ 1.80

Available from the
Office of Technical Services
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Washington 25, D. C.

603-1

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Subject Category: CHEMISTRY-GENERAL
SPECIAL

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Author: T. W. Bartlett

ABSTRACT

A tributyl phosphate extraction procedure for the gravimetric determination of uranium is described. Carbon tetrachloride was used to remove small amounts of tributyl phosphate before precipitation in order to avoid contamination of the uranous-uranic oxide with phosphate. With samples in the range 3 to 10 grams of uranium per liter, the precision, expressed as the 95% symmetric confidence interval, was ±1% of the amount present. Several other procedures for the removal of tributyl phosphate proved to be unsatisfactory.

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The purpose of this investigation was to test tributyl phosphate extraction of uranium on Works Laboratory samples using Works Laboratory equipment and procedures. The work was exploratory in nature and was done to develop a satisfactory procedure using tributyl phosphate. No attempt was made to investigate each aspect of the procedure thoroughly.

A previous report (1) indicated that very favorable uranium distribution coefficients could be obtained with tributyl phosphate and that iron, copper, and nickel were not extracted to any great extent. In comparison with pentaether (dibutoxytetraethylene glycol), it was reported that tributyl phosphate offers the advantages of economy and availability but the disadvantage of introducing phosphate contamination.

Preliminary work confirmed that the most serious problem in connection with tributyl phosphate extraction was phosphate contamination of the oxides. Except when such contamination occurred, the preliminary results were satisfactorily precise and accurate.

The phosphate contamination was found to be due to physical transfer of small volumes of the solvent with the ammonium sulfate solution used to remove uranium from the organic phase and not to solubility of the tributyl phosphate in the aqueous layer. Considerable improvement could probably have been made by using extreme care and by discarding or re-working several of the separatory funnels which were constructed in such a way that small amounts of the solvent were trapped near the stopcock and drained off with the aqueous phase. However, it was considered preferable to develop a method of removing these traces of tributyl phosphate between the extraction of uranium from the organic phase and the ignition of the ammonium diuranate precipitate.

APPARATUS AND PROCEDURE

The Works Laboratory extraction apparatus consists of banks of open-top separatory funnels with a motor-driven stirrer for each funnel. Two funnels, one above the other, are used for each solution to be extracted. The upper funnels have two-way stopcocks to permit drainage either into the lower funnel or to a beaker.

Briefly, the "nitrate wash" procedure (2) which is fundamentally the same as the procedures used for pentaether extraction by the Uranium Analysis Section (4) and for tributyl phosphate extraction, consists of the following steps: sample preparation, extraction of uranium with the organic solvent, washing the organic phase with ammonium nitrate solution, re-extraction of the uranium into ammonium sulfate solution, ammonia precipitation, ignition of the precipitate, and weighing the uranium as uranous-uranic oxide.

Most of the work described below was done on "water media" and "acid loop" samples since a satisfactory procedure for these samples would probably be satisfactory for other samples as well. "Water media" samples vary widely in character; they contain only small amounts of organic material

but they may be basic or acidic and may contain considerable quantities of metallic impurities. "Acid loop" samples may be considered to be a special type of "water media" sample which contains very high concentrations of metallic nitrates.

The "Carbon Tetrachloride" Procedure

Of the methods used in attempts to prevent phosphate contamination, the most effective consisted of washing the ammonium sulfate solution with carbon tetrachloride prior to the precipitation of uranium. This was accomplished by draining the ammonium sulfate solution from the separatory funnel into a small beaker containing 10 to 15 ml. of carbon tetrachloride, agitating with a stirring rod, and decanting the aqueous phase into a second beaker. The successive volumes of ammonium sulfate solution from one funnel were contacted with the same volume of carbon tetrachloride so that the first volume, which contained most of the uranium, was washed into the second beaker by the second and third volumes of ammonium sulfate solution. The carbon tetrachloride was then washed once with water to minimize loss of uranium.

Data obtained by application of this technique to three water media samples and to three acid loop samples are reported in tables I and II. In addition to the carbon tetrachloride wash, two other slight changes in the above extraction procedure were made: sodium nitrate solution containing 20 g. salt per 100 ml. was used in place of ammonium nitrate solution in the preparation of the samples for extraction and the 61.5% ammonium nitrate solution was diluted with an equal volume of water before using it to wash the organic phase. Both of these changes improved the visibility of the organic-aqueous interfaces.

In the case of the acid loop samples, a further variation in procedure was introduced. Such samples are usually prepared for extraction by filtering and washing the filter paper with 3 N nitric acid; the procedure used consisted of adding nitric acid to the samples, heating to boiling, and cooling to room temperature before extraction.

Precision and Accuracy. The precision of the results on the water media samples meets the present requirement of ±2.5% of the uranium present (3). It should be noted that precision obtained in replicate determinations carried out simultaneously, as was done here, is probably better than would be obtained if the same determinations were made over a period of time as is the case in the Works Laboratory. The data on acid loop samples are insufficient to permit any positive precision statement. The obviously imprecise values obtained on sample 373019 were probably due to the low uranium concentration and the fact that a relatively small volume of sample was available (the determinations reported here were made on the solution remaining after aliquots were removed for the pentaether determinations).

An indication of accuracy is available from the data on sample 725300 which was a quality control sample. The experimental mean and 95% symmetric confidence interval was 4.92 ± 0.02 grams uranium per liter which is in satisfactory agreement with the known value of 4.91 grams uranium per liter.

TABLE I

TRIBUTYL PHOSPHATE EXTRACTION OF WATER MEDIA SAMPLES
(CARBON TETRACHLORIDE PROCEDURE)

	Grams Uranium per Liter Found		
	Sample 6131	Sample 612992	Sample 725300
	3.64	10.26	4.91
	3.66	10.28	4.91
	3.63	10.26	4.91
	3.65	10.27	4.90
	3.66	10.26	4.92
		10.27	4.91
		10.25	4.92
		10.25	4.92
		10.24	4.92
		10.19	4.93
Mean ±95% L. E.$_x$	3.65 ± 0.04	10.25 ± 0.06	4.92 ± 0.02
Mean of Works Laboratory Results	3.75	10.4	4.91
Known Value	---	---	4.91

TABLE II

TRIBUTYL PHOSPHATE EXTRACTION OF ACID LOOP SAMPLES
(CARBON TETRACHLORIDE PROCEDURE)

	Grams Uranium per Liter Found		
	Sample 373014	Sample 363019	Sample 373033
	0.14	0.031	1.78
	.14	.023	1.79
Mean	0.14	0.027	1.78
Mean of Works Laboratory Results	0.12	0.034	1.78

Purity of Oxides. Results of spectrographic analyses of the oxides obtained by the "carbon tetrachloride" procedure are presented in table III. In general, the total of spectrographic impurities was between 2000 and 3000 parts per million. The major contaminants were iron and silica, about 1000 parts per million each, and phosphorous, up to 500 parts per million.

The very badly contaminated oxide (column 3, Table III), containing 1.5% impurities, was a composite of the oxides from the determinations of uranium in the acid loop samples. The high contamination may be due to the omission of the filtering step prior to extraction or to the nature of acid loop samples. Comparable data for oxides obtained from pentaether extraction are unavailable since the oxides were sent to the Counting Section and, consequently, were not analyzed spectrographically.

Two of the oxides from sample 725300 were sent to the Counting Section to find out if the oxides were sufficiently pure for use in their procedure. No difficulty was encountered; the samples were deposited and counted satisfactorily.

TABLE III

SPECTROGRAPHIC ANALYSIS OF OXIDES OBTAINED BY THE "CARBON TETRACHLORIDE" PROCEDURE

	Parts per Million Found				
Element	Sample 6131	Sample 612992	Acid Loop Sample*	Sample 725300	
Iron	1000	1000	5000	1000	500
Silicon	1000	1000	8000	1000	1000
Phosphorous	500	150	NF	NF	NF
Copper	300	30	300	30	50
Lead	100	30	500	100	100
Tin	100	30	300	30	10
Nickel	30	NF	1000	80	30
Magnesium	10	30	100	50	50
Manganese	5	5	30	3	3
Cadmium	1	0.1	NF	NF	NF
Silver	1	1	5	1	1
Aluminum	NF	NF	300	NF	NF
Chromium	NF	NF	200	50	10

"NF" means not found.

*Composite of oxides from samples 373014, 373019, and 373033.

Disadvantage of the "Carbon Tetrachloride" Procedure. The technique of mixing the ammonium sulfate solution with carbon tetrachloride and decanting the aqueous layer is somewhat time-consuming. It is complicated by the fact that a small amount of carbon tetrachloride usually remains on the upper surface of the aqueous phase and is decanted with it, preventing clean separation. For routine use, a light solvent, such as Varsol, in a separatory funnel would probably be more convenient for removing the tributyl phosphate.

Unsuccessful Procedures

The experiments described below were conducted before the development of the "carbon tetrachloride" procedure and are included in this report primarily for the sake of completeness.

The data in table IV are the results obtained with three variations of the Works Laboratory pentaether procedure. The values are typical of the results obtained throughout this investigation before the "carbon tetrachloride" procedure was developed. About 20 to 50% of the oxides were light green or white in color and contained large amounts of phosphate; exclusive of the visibly contaminated oxides, the results were quite precise and in fairly good agreement with the pentaether results or the known value in the case of quality control samples.

The procedures mentioned in the table were as follows: the "P.E." procedure was the Works Laboratory pentaether procedure substituting tributyl phosphate for pentaether; the "25% Varsol" procedure was identical except that 75% tributyl phosphate in Varsol was used as the solvent; and the "50% alcohol wash" procedure was repetition of the "P.E." procedure except that the ammonium diuranate precipitate was washed on the filter paper with a solution containing 1 g. ammonium nitrate, 2.5 ml. ammonium hydroxide, and 50 ml. ethyl alcohol per 100 ml.

TABLE IV

RESULTS OF SEVERAL UNSATISFACTORY TRIBUTYL PHOSPHATE EXTRACTION PROCEDURES

	"P.E." (g. U/g.)	"25% Varsol" (g. U/g.)	"50% Alcohol Wash" (Total g. U)
	0.294	4.93	4.92
	.295	5.19*	4.92
	.296	4.90	5.52*
	.295	5.70*	4.92
	.295	5.47*	5.44*
	.320*	4.93	5.27*
	.298	4.90	5.19*
	.299	4.91	5.09*
	.294		4.91
	.304*		4.92
Mean	0.299	5.12	5.11
95% $L.E._x$	± 0.018	± 0.73	± 0.52
Mean of Works Laboratory Results	0.292	4.95	4.86**

*Oxides were light green or white.
**Known value.

Ammoniacal 95% ethyl alcohol was also tried for washing the precipitate with no reduction in contamination of the oxides.

An attempt to remove the tributyl phosphate by filtration prior to precipitation was made. Two of the four oxides obtained in this way were light green in color indicating high phosphate content.

The following experiments were made in attempts to shorten the extraction procedure:

1. The nitric acid solutions containing uranium and fairly large amounts of silica, which are known as "carbon leach" solutions, were extracted without prior removal of silica. Although emulsification was not a serious difficulty, this procedure was unsatisfactory because of high silica contamination of the oxides.

2. Acid loop samples were extracted as received. Iron contamination was so high that the ammonia precipitate had the appearance of hydrated ferric oxide rather than ammonium diuranate. The extreme contamination was believed to be due to extraction of iron at low acidities.

3. Several experiments were conducted using two instead of three 25 ml. volumes of tributyl phosphate for the extraction. Uranium recovery was satisfactory for water media samples but about 50% of the results on acid loop samples were definitely low.

SUMMARY

Uranium in water media samples was determined by a tributyl phosphate extraction procedure which involved washing the ammonium sulfate solution with carbon tetrachloride to remove traces of tributyl phosphate. The 95% symmetric confidence interval was approximately ±1% of the uranium present and the deviation of the mean from the known value was not statistically significant at the 95% confidence level.

When carbon tetrachloride was not used, 20 to 50% of the oxides were light green or white in color and some contained more than 0.5% phosphorous.

The ammonium nitrate solution used for washing the organic phase to remove impurities was diluted from 61.5% to about 30% ammonium nitrate in order to increase the visibility of the interface.

Unsuccessful attempts to prevent phosphate contamination of the oxides included dilution of the tributyl phosphate with Varsol, washing the ammonium diuranate precipitate with alcoholic solutions, and filtering the ammonium sulfate solution prior to the precipitation of uranium.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to R. Aiken and the other members of the Uranium Analysis Section of the Works Laboratory for their cooperation and assistance.

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