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DETERMINATION OF LOW CONCENTRATIONS
OF URANIUM IN OILS AND ORGANIC
LIQUIDS BY X-RAY EMISSION

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

*prepared for the U.S. ATOMIC ENERGY COMMISSION
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ABSTRACT

An improved method has been developed for determining the concentration of uranium in organic liquids by X-ray emission. The method is applicable to uranium concentrations in the range of 10 to 2,000 micrograms per milliliter.

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SUMMARY

X-ray emission affords a rapid means for analyzing various materials for uranium. However, the established laboratory procedure for the analysis of organic liquids suffered from poor precision and lack of sensitivity. A method has been developed that eliminates these objections and reduces standardization time. This method consists of diluting the sample with diethylene glycol dibutyl ether (dibutyl Carbitol) containing a known amount of 1,3,5-tribromobenzene as an internal standard and analyzing by X-ray emission. The bromine $K\alpha_1$ line is used as the internal standard for U_{La_1} . The new procedure is valid over a concentration range of 10 to 2,000 μg s U/ml in various liquid organics and has a relative limit of error (0.95) of ± 2.5 percent for a single analysis.

INTRODUCTION

The Y-12 Plant Laboratory^(a) analyzes a wide variety of organic liquids for uranium. These liquids include diethylene glycol dibutyl ether (dibutyl Carbitol) and tributyl phosphate (TBP) from extraction processes, lubricating oils, such solvents as perchloroethylene and trichloroethylene, and mixtures of oils and chlorinated solvents used as machine coolants. The established procedure⁽¹⁾ for determining low concentrations of uranium in these materials by X-ray emission utilizes an aqueous solution of yttrium as an internal standard. This solution has to be physically mixed with the sample in an inert powder since the aqueous and organic phases are not miscible. Because it is difficult to make the resulting mixture homogeneous, precision is relatively poor. An investigation was therefore in order to find a more suitable means for adding the internal standard. When attempts to add the yttrium in an organic form proved unsatisfactory, a substitute internal standard was sought. Of the several possibilities, bromine appeared to be the most attractive. Pish and Huffman⁽²⁾ successfully used bromine as an internal standard for thorium and uranium, but limited their work to the analysis of tributyl phosphate. Experimentation showed that a Carbitol solution of 1,3,5-tribromobenzene provided a satisfactory medium for adding bromine to all the various types of organic liquids received by the laboratory.

(a) The Oak Ridge Y-12 Plant is operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

METHOD FOR URANIUM DETERMINATION BY X-RAY EMISSION

EQUIPMENT

X-Ray Emission Spectrometer

The spectrometer is equipped with a molybdenum target tube, a lithium fluoride analyzing crystal, a scintillation detector and associated counting equipment, and a 1 3/8-inch-diameter Teflon sample cup.

Balance

An analytical balance is used.

Flasks

Volumetric flasks of 50, 100, 250, and 500-milliliter capacity are needed.

Pipettes

Use volumetric pipettes of 5, 10, 20, and 25-milliliter capacity.

REAGENTS

The following reagent-grade solutions are needed: diethylene glycol dibutyl ether (dibutyl Carbitol), nitric acid, 1,3,5-tribromobenzene, and tributyl phosphate (TBP). In addition, USP Grade trichloroethylene and high-purity (0.999+) uranium metal are required.

PREPARATION OF STANDARD SOLUTIONS

Stock Solutions

The necessary stock solutions have the concentrations and methods of preparation as follows:

Solution	Concentration (μ gs U/ml)	Preparation Procedure
1	10,000	Five grams of uranium metal dissolved in dilute nitric acid, evaporated to near dryness, then redissolved in 500 milliliters of Carbitol.
2	5,000	Two and one-half grams of uranium metal prepared in the same manner as Solution 1.
3	1,000	One-half gram of uranium metal prepared in the same manner as Solution 1.
4	100	Twenty-five milliliters of Solution 3 made to 250 milliliters with Carbitol.

Internal Standard

The internal standard is prepared by dissolving 1.9 grams of 1,3,5-tribromobenzene in 1,000 milliliters of diethylene glycol dibutyl ether.

"A" Working Standards for Carbitol, Oils, and Tributylphosphate

The "A" working standards have the concentrations and methods of preparation as follows:

Concentration (μ gs U/ml)	Preparation Procedure
2,000	20 Milliliters of Stock Solution 1.
1,000	10 Milliliters of Stock Solution 1.
500	10 Milliliters of Stock Solution 2.
250	25 Milliliters of Stock Solution 3.
100	10 Milliliters of Stock Solution 3.
50	5 Milliliters of Stock Solution 3.
10	10 Milliliters of Stock Solution 4.

Pipette each standard into a 100-milliliter volumetric flask, add 20 milliliters of the internal standard, dilute to volume with diethylene glycol dibutyl ether, and mix thoroughly.

"B" Working Standards for Chlorinated Solvents and Coolants

Note: Prepare these standards fresh every time samples of this type are analyzed. Use the same schedule as for the "A" working standards. Pipette each standard into a 100-milliliter volumetric flask, add 50 milliliters of trichloroethylene, 20 milliliters of the internal standard, then dilute to volume with diethylene glycol dibutyl ether and mix thoroughly.

INSTRUMENT PARAMETERS

Instrument parameters have been determined and are as follows:

Excitation	50 kv - 15 ma
Crystal	LiF
Detector Voltage	900
Course Gain	64
Fine Gain	5.5
Upper Level	1.30
Lower Level	0.075
Time	50 seconds
Goniometer	26.14° 2 θ (U_{La_1})
	28.70° 2 θ (Bkg)
	29.93° 2 θ ($BrKa_1$)

CALIBRATION PROCEDURE

Proper calibration is accomplished by observing the following steps:

1. Set the X-ray generator for 50 kv and 15 ma and allow a few minutes for the X-ray beam to stabilize.
2. Set the pulse height analyzer to the proper conditions for uranium.
3. Rinse the Teflon sample cup with the standard, then pour about 10 milliliters of the standard into the cup and cover the cup with a Teflon cover. Position the specimen in the X-ray beam.
4. Count at $26.4^{\circ} 2\theta$ (U) for 50 seconds, $28.70^{\circ} 2\theta$ (Bkg), and $29.93^{\circ} 2\theta$ (Br) for 50 seconds.
5. Obtain the net counts for 50 seconds for U and Br by subtracting the background (c/50 sec) from the gross peak (c/50 sec).
6. Calculate the intensity ratio: $R = \frac{U \text{ c/50 sec}}{Br \text{ c/50 sec}}$
7. Count all standards and calculate a factor.

FACTOR CALCULATION

Calculate the relationship between the intensity ratio and concentration of standards. The equation should be of the form: $Y = mX + b$ where: Y represents the concentration in $\mu\text{gs/ml}$, X the intensity ratio, m the slope of the calibration curve, and b the intercept of the calibration curve.

SAMPLE PREPARATION

Samples are prepared as follows:

1. Tare a clean 50-milliliter volumetric flask.
2. Pipette 25 milliliters of the sample into the tared volumetric flask. Note: On some samples, such as heavy oils, it may be necessary to pour the sample into the volumetric flask through a funnel because of its high viscosity.
3. Obtain the gross weight.
4. Add 10 milliliters of the internal standard.
5. Dilute the sample to volume with Carbitol and mix thoroughly.

SAMPLE ANALYSIS

Analysis of the sample is accomplished as follows:

1. Follow Steps 1 through 6 of the **CALIBRATION PROCEDURE**.
2. For Carbitol, oil, and TBP samples, use the "A" working standards calibration curve. (Prepare a blank for the TBP samples by pipetting 25 milliliters of tributyl phosphate and 10 milliliters of the internal standard into a clean, 50-milliliter volumetric flask, then dilute to volume with diethylene glycol dibutyl ether and mix thoroughly.)
3. For chlorinated solvents and coolants, use the "B" working standards calibration curve.

CALCULATION

Calculation of the uranium concentration can be accomplished by using the equation:

$$C = \frac{(R \times F) + I}{W} \times V$$

where:

C represents the concentration of uranium in grams per gram of sample,

R the U_{La1}/Br_{Ka1} intensity ratio,

F the slope of the calibration curve,

W the sample weight in grams, and

V the volume of the volumetric flask.

For tributylphosphate samples, calculate the apparent uranium concentration in the TBP blank by using the equation and then subtracting this value from the calculated sample result to obtain the uranium concentration of the sample.

DISCUSSION

The established method for determining low concentrations of uranium in organics uses an aqueous solution of yttrium as an internal standard. Yttrium is an ideal internal standard for uranium and is currently being used in several other procedures requiring the determination of uranium concentrations. However, physical mixing of an aqueous internal standard with an organic is not practical because it is not possible to obtain a homogeneous solution from the two phases, and the inhomogeneity will increase with time.

Using an organic form of yttrium was suggested and investigated. The internal standard selected was yttrium acetate dissolved in Carbitol. Results of these investigations showed vast improvements in accuracy, precision, and the detection limit, but it was found that

yttrium acetate, which had to be synthesized in the laboratory and dissolved in Carbitol, was not stable for long periods of time.

Table 1
URANIUM IN CARBITOL STANDARDS

Standard Concentration (μg s U/ml)	Analytical Results (μg s U/ml)			
	Day 1	Day 2	Day 3	Day 4
2,000	1,965	1,972	1,964	1,995
1,000	996	1,003	985	1,017
500	500	501	500	500
250	251	248	247	252
100	105	103	99	98
50	47	53	46	47
10	10	9	10	11

It was then decided to investigate the use of bromine as the internal standard since organic bromides are not likely to appear in samples being analyzed for uranium. The organic compound 1,3,5-tribromobenzene was selected and dissolved in Carbitol for use as a possible internal standard.

The X-ray fluorescence spectrometer used in this investigation was calibrated using synthetic standards prepared on a metal-to-metal basis following the proposed procedure. Each series of standards were then analyzed by this method for four different days. The resulting data are presented in Tables 1 and 2.

Using 1,3,5-tribromobenzene as an internal standard proved to be a much faster and more accurate method than the existing procedure. With this internal standard, the organic solution is completely homogeneous and it is possible to prepare standards and samples well in advance, except for those liquids containing chlorine. Within a few hours after adding the bromine internal standard to chlorinated organic liquids, the uranium-to-bromine intensity ratio begins to change significantly and continues to change over a period of several days. The cause of this phenomenon has not been

Table 2
URANIUM IN TRICHLOROETHYLENE STANDARDS

Standard Concentration (μg s U/ml)	Analytical Results (μg s U/ml)			
	Day 1	Day 2	Day 3	Day 4
2,000	2,008	1,981	2,040	2,015
1,000	1,055	978	995	958
500	500	500	500	500
100	102	100	102	93
50	50	49	52	53
10	11	10	10	10

Table 3
CARBITOL LABORATORY CONTROL SAMPLE
(Concentration: 758 μg s U/ml)

Date	Concentration, Old Method (μg s U/ml)	Date	Concentration New Method (μg s U/ml)
7-01-71	688	10-12-71	761
7-06-71	699	10-26-71	757
7-08-71	725	10-28-71	775
7-20-71	681	11-04-71	766
7-22-71	708	11-09-71	765
7-27-71	791	11-11-71	776
7-29-71	759	11-16-71	782
8-03-71	812	11-18-71	746
8-05-71	753	11-23-71	749
8-10-71	698	11-30-71	766
8-12-71	750	12-02-71	751
8-17-71	718	12-07-71	762
8-19-71	705	12-09-71	762
8-24-71	737	12-14-71	781
8-26-71	719	12-16-71	770
8-31-71	732	12-21-71	771
9-02-71	703	12-28-71	766
9-14-71	744	12-30-71	762
9-16-71	738	1-04-72	758
9-21-71	716	1-06-72	766
9-23-71	701	1-11-72	772
9-28-71	679	1-13-72	774
9-30-71	791	1-18-72	781
10-05-71	727	1-20-72	764
10-07-71	764	1-27-72	771
Mean	729		766
LE (0.95) of Mean	± 14		± 4
Absolute LE (0.95) of a Single Analysis	± 72		± 19

investigated thoroughly, but it is probably due to a slow reaction between the bromine and chlorine. For this reason, the internal standard should be added to chlorinated samples and standards just prior to analysis.

Estimated time savings for calibration by this new method is at least 50 percent. Calibration time is much longer with the old method as it is necessary to prepare standards every day. In addition, they can only be counted one time and both standards and samples have to be counted immediately after preparation.

As a control measure, the Quality Control Laboratory submits samples of a Carbitol batch containing 758 micrograms of uranium per milliliter with each group of production samples. Results obtained by the old and new methods on these samples over a period of three months are presented in Table 3.

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