LA-3159

MASTER

64
325/28-
12

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

**X-RAY FLUORESCENCE SPECTROMETRIC DETERMINATION
OF URANIUM IN NIOBIUM TRICHLORIDE**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor

Printed in USA. Price \$1.00. Available from the

Clearinghouse for Federal Scientific
and Technical Information,
National Bureau of Standards,
U. S. Department of Commerce,
Springfield, Virginia

LA-3159
UC-4, CHEMISTRY
TID-4500 (34th Ed.)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA   LOS ALAMOS   NEW MEXICO

REPORT WRITTEN: September 1, 1964

REPORT DISTRIBUTED: December 3, 1964

**X-RAY FLUORESCENCE SPECTROMETRIC DETERMINATION
OF URANIUM IN NIOBIUM TRICHLORIDE**

by

E. A. Hakkila
R. G. Hurley
G. R. Waterbury

This report expresses the opinions of the author or authors and does not necessarily reflect the opinions or views of the Los Alamos Scientific Laboratory.

Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

ABSTRACT

An x-ray fluorescence spectrometric method was developed for determining 0.1 to 6% of uranium in niobium trichloride. Samples weighing approximately 500 mg. are dissolved in nitric-hydrofluoric acids, bismuth is added to serve as an internal standard, and the solution is diluted to 10.00 ml. with distilled water. The ratio of the intensities of the $L\alpha_1$ lines for uranium and bismuth is measured and compared to intensity ratios measured for solutions of known uranium content. The relative standard deviation of a single determination varies from 12 to 1.5% for uranium concentrations in the range between 0.1 and 6.0%.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of C. F. Metz under whose supervision this work was performed.

CONTENTS

	<u>Page</u>
ABSTRACT	2
ACKNOWLEDGMENTS	2
INTRODUCTION	4
CAUTION	5
SAMPLING	6
APPARATUS AND REAGENTS	7
X-RAY OPERATING CONDITIONS	8
RECOMMENDED PROCEDURE	9
RELIABILITY.	10

INTRODUCTION

A rapid method, preferably requiring no chemical separation, was needed for determining small quantities (0.1 to 6 percent) of uranium in niobium chlorides of variable composition. X-ray fluorescence methods generally possess the speed and selectivity needed for this type of analysis and require no chemical separation. By applying an internal standard technique to x-ray fluorescence analysis, errors caused by variations in matrix composition can be minimized. For these reasons, an internal-standard x-ray fluorescence method seemed ideally suited for this determination.

Bismuth was selected for the internal standard element because it possesses an $L\alpha_1$ line at a wavelength of 1.144 angstroms which is reasonably close to the $L\alpha_1$ line for uranium at 0.911 angstrom. In addition, bismuth is readily available in pure form and has no major x-ray lines overlapping the $L\alpha_1$ line for uranium.

Selection of the solvent for the complex materials to be analyzed presented a problem. This was solved by using a combination of nitric and hydrofluoric acids. Niobium is readily soluble in hydrofluoric acid,

and the nitric acid oxidizes uranium quickly to the fluoride-soluble (VI) oxidation state. The bismuth internal standard also is soluble in the mixed acids.

This report describes the internal-standard x-ray fluorescence method developed for this particular application and the experimental work that established the reliability of method. In addition, the effects of several ions on this determination are discussed.

CAUTION

Health safety rules for the safe handling of hydrofluoric acid (e.g., as recommended by the Health Division of the Los Alamos Scientific Laboratory) should be followed at all times.

The high operating voltages of the x-ray equipment and the generated x-rays are potential hazards requiring care in operation and adequate shielding and safety interlocks to protect the worker. Regular monitoring to determine stray x-rays in the vicinity of the equipment should be common practice.

SAMPLING

Samples of niobium trichloride are received as powders which are packaged in a dry, inert atmosphere. Niobium trichloride is extremely hygroscopic, and exposure to the atmosphere should be minimized during the sampling operation. This is done by weighing the closed sample vial, quickly removing about 500 mg. for analysis, and immediately reweighing the closed vial.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical, Ainsworth, model BCT or similar instrument.

Beakers, Teflon, 50-ml. capacity.

Bottles, polyethylene, 1 oz.

High voltage d. -c. power supply, Baird-Atomic Model 312A, to replace original power supply to the counter.

Hot plate, electric, Fisher Autemp or similar instrument.

Mylar sheet, 0.25-mil thick.

Normal laboratory glassware, including borosilicate glass pipets, volumetric flasks, etc.

Sample cell, stainless steel, as supplied with x-ray spectrograph, but coated on the inside with paraffin. To prepare a window for the cell, place a 3-in. square of 0.25-mil thick Mylar sheet on the inner ring of the cell window frame, press the outer ring in place with a small mallet. Trim off excess Mylar sheet with scissors and screw the window onto the sample cell. The window must be replaced after 2 hr. of exposure in the x-ray beam.

X-ray spectrograph, Philips Electronics Corp. or equivalent, equipped with lithium fluoride analyzing crystal, tungsten-target x-ray tube, and scintillation detector with associated electronic circuitry.

Reagents

Bismuth known solution, 2.00 mg. of bismuth per ml. Dissolve 500 mg. of pure bismuth metal with nitric acid. Dilute with water to 250 ml. in a volumetric flask.

Hydrochloric acid, 38%, reagent grade.

Hydrofluoric acid, 49%, reagent grade.

Niobium known solution, 100.0 mg. of niobium per ml. Dissolve 25.00 grams of pure niobium metal with hydrofluoric acid, adding nitric acid dropwise to maintain a reasonable reaction rate. Dilute the solution with distilled water to 250 ml. in a borosilicate glass volumetric flask. Transfer immediately to a polyethylene bottle.

Nitric acid, 70%, reagent grade.

Uranium known solution, 100.0 mg. of uranium per ml. Wash 11 to 12 grams of pure uranium turnings in dilute nitric acid, rinse with methyl chloroform, and dry in air. Slowly dissolve 10.00 grams of the uranium metal turnings with nitric acid, and dilute with distilled water to 100.0 ml. in a volumetric flask. Dilute 0.10, 1.00, and 10.00 ml. aliquots of this uranium solution to 100.0 ml. volumes to obtain solutions containing, respectively, 0.10, 1.00, and 10.00 mg. of uranium per ml.

X-RAY OPERATING CONDITIONS

X-ray tube, tungsten-target.

Potential, 50 kv.

Current, 40 ma.

Counter, scintillation.

Counter voltage, 680.

Scaler input signal, Pos.

Scaler operation, Fixed count.

Rate meter scale factor, Off.

S-P scale factor, 8.

Count register, 1000.

Scaler scale factor, 2, 4, 8, or 16, to accumulate 16,000, 32,000, 64,000 or 128,000 counts, respectively.

Analyzing crystal, LiF (2d = 4.028 Å.)

RECOMMENDED PROCEDURE

Accurately weigh approximately 500 mg. of the niobium trichloride sample into a 50-ml. beaker and dissolve with 1 to 2 ml. of nitric acid containing 5 to 6 drops of hydrofluoric acid. Add 2.00 ml. of bismuth known solution (4.00 mg. of bismuth) and dilute to 10.0 ml. with distilled water. Prepare known solutions designated a, b, c, d, and e, each containing 2.0 ml. of bismuth known solution (4.00 mg. of bismuth); 2.5 ml. of niobium known solution (250 mg. of niobium); 0.5 ml. of 38% hydrochloric acid (220 mg. of chloride); and suitable aliquots of known uranium solutions to contain, respectively, 0, 0.10, 2.00, 5.00, and 30.0 mg. of uranium. Dilute each solution to 10.0 ml. For each sample solution and known solution measure the intensities of the $L\alpha_1$ x-ray lines for uranium and bismuth, accumulating a minimum of 32,000 counts at each wavelength. Determine the count rate for each measurement using the equation:

$$\text{Count rate, counts/sec.} = \frac{\text{Number of counts accumulated}}{\text{secs.}} \quad (1)$$

Determine the intensity ratio for each solution, using the expression:

$$\text{Intensity ratio, } R = \frac{\text{Counts/sec., U } L\alpha_1}{\text{Counts/sec., Bi } L\alpha_1} \quad (2)$$

Calculate the average slope of the calibration curve using equation (3):

$$\text{Slope (A)} = \frac{R(b)-R(a) + R(c)-R(a) + R(d)-R(a) + R(e)-R(a)}{\text{total mg. of U in solutions b, c, d, e}} \quad (3)$$

where a, b, c, d, and e refer to the known solutions.

Obtain the amount of uranium in each sample from the following relationship:

$$\text{Uranium, mg.} = \frac{R(s)-R(a)}{A} \quad (4)$$

where $R(s)$ refers to the intensity ratio for the sample, $R(a)$ refers to the intensity ratio for the blank (solution a), and A is the slope of the calibration curve as determined in Equation (3). Determine the concentration of uranium in each sample using the equation:

$$\text{U concentration, \%} = \frac{\text{U, mg.}}{\text{sample, mg.}} \times 100 \quad (5)$$

RELIABILITY

Niobium trichloride samples containing known amounts of uranium were not available. Therefore, the reliability of the method is based upon analyses of solutions containing known concentrations of uranium and niobium. These solutions were prepared from the known solutions (described under Reagents) to contain amounts of niobium equivalent to samples containing between 375 and 600 milligrams of niobium chloride and 0.1 to 30.0 milligrams of uranium (Table I). The wide variation in sample size was selected because of the difficulty expected in accurately weighing by difference 500-milligram samples of niobium trichloride. Fourteen determinations were made of a blank and each of seven uranium concentrations to estimate the relative standard deviation of the method.

Table I

Precision of the X-Ray Fluorescence Spectrographic Method for
Determining Uranium in Niobium Trichloride

<u>U added, mg.</u>	<u>U concn., %</u>	<u>NbCl₃ added, mg.</u>	<u>Standard deviation, mg. U</u>	<u>Relative standard deviation, %</u>
0	0	375 to 600	0.012	-
0.10	0.017 to 0.027	"	0.015	75
0.50	0.08 to 0.13	"	0.012	12
1.50	0.25 to 0.40	"	0.022	7.2
2.00	0.33 to 0.53	"	0.006	1.5
5.00	0.8 to 1.3	"	0.020	2.0
10.00	1.7 to 2.7	"	0.031	1.6
30.00	5.0 to 8.0	"	0.092	1.5

In order to determine the effects of various impurities on the reliability of this method, the elements that might cause interference were considered. Interference in x-ray fluorescence analysis may be caused by line overlap, selective absorption, or selective enhancement. Elements expected to interfere by line overlap with the $L\alpha_1$ x-ray line for either uranium or bismuth are summarized in Table II. Only first and second order lines having a relative intensity of ten or greater were considered. Elements expected to interfere by selective absorption (those elements having an absorption edge between the $L\alpha_1$ x-ray lines for bismuth and uranium) are summarized in Table III. Elements expected to interfere by selective enhancement (those elements having a $K\alpha$, $K\beta$, $L\alpha_1$, or $L\beta_1$ x-ray line between the L III absorption edges for bismuth and uranium) are summarized in Table IV.

Table II

X-Ray Lines Overlapping the $L\alpha_1$ Lines for Uranium and Bismuth

<u>Element</u>	<u>Lines</u>	<u>Diffraction angle, degrees 2θ (LiF)</u>
<u>U</u>	<u>$L\alpha_1$</u>	<u>26.14</u>
Sr	$K\alpha$	25.14
Hg	$L\gamma_1$	25.73
Pt	$L\gamma_4$	25.73
Te	$K\alpha_1$ (n=2)	25.88
Ra	$L\eta$	26.06
In	$K\beta$ (n=2)	26.11
Br	$K\beta_2$	26.14
Po	$L\beta_1$	26.46
Rb	$K\alpha$	26.58
Au	$L\gamma_1$	26.61
Ir	$L\gamma_4$	26.64
<u>Bi</u>	<u>$L\alpha_1$</u>	<u>33.02</u>
Tl	$L\eta$	32.50
Ge	$K\beta$	32.55
Ta	$L\gamma_1$	32.82
Os	$L\beta_5$	32.88
Ir	$L\beta_{2,3}$	32.81
Pt	$L\beta_4$	32.94
Ru	$K\beta$ (n=2)	33.00
Hf	$L\gamma_2$	33.00
Ir	$L\beta_1$	33.42

Table III

Elements Having Absorption Edges Between the $L\alpha_1$ Lines of Uranium and Bismuth^(a)

<u>Element</u>	<u>Edge</u>	<u>Wavelength, A.</u>
Ce	K	1.117
As	K	1.045
Se	K	0.980
Br	K	0.920
Lu	L I	1.140
Hf	L I	1.099
Ta	L I	1.061
Re	L I	0.990
Os	L I	0.956
Ir	L I	0.923
Ta	L II	1.114
W	L II	1.074
Re	L II	1.037
Os	L II	1.001
Ir	L II	0.967
Pt	L II	0.934
Os	L III	1.140
Ir	L III	1.105
Pt	L III	1.072
Au	L III	1.040
Hg	L III	1.010
Tl	L III	0.979
Pb	L III	0.950

(a) $L\alpha_1$ lines for bismuth and uranium are at 1.144 and 0.911 A., respectively.

Table IV
Elements Having X-Ray Lines Between the L III Absorption Edges of
Uranium and Bismuth^(a)

<u>Element</u>	<u>X-Ray Line</u>	<u>Wavelength, A.</u>
Sr	K α	0.875
Y	K α	0.829
Zr	K α	0.786
Nb	K α	0.750
Rb	K β	0.829
Fr	L β_1	0.840
Th	L β_1	0.765
Ra	L β_1	0.814
Pa	L β_1	0.742
Np	L α_1	0.889
Am	L α_1	0.849

(a) L III edges for uranium and bismuth are at 0.722 and 0.923 A., respectively.

Hafnium, tantalum, and strontium; tungsten and lead; and zirconium represent elements expected to show interference due to line overlap, absorption, and enhancement, respectively. In addition, the effects of iron, nickel, and molybdenum which might be present in samples, were selected for investigation. Results (Table V) indicate that interference of approximately 5 relative percent is caused by 1 percent of tantalum, 0.2 percent of strontium, or 2 percent of lead. These interferences are results of line overlap and absorption. Strontium also may interfere by enhancement, but this effect is small compared to line overlap. No interference was observed in the presence of 2 percent of either zirconium or hafnium, or 10 percent of iron, nickel, or molybdenum. No interference was assumed if the error in recovery of uranium, based upon a

Table V

X-Ray Fluorescence Spectrographic Determination of Uranium in
the Presence of Foreign Elements

Foreign element	Concentration, %	U added, %	U found, %	Error, % relative
Ta	2.0	0.00	-0.08	--
	2.0	1.00	0.88	12.0
	1.0	0.00	-0.06	--
	1.0	1.00	0.94	6.0
Hf	2.0	0.00	-0.03	--
	2.0	1.00	0.99	1.0
Sr	2.0	0.00	0.09	--
	2.0	1.00	1.62	62.0
	0.2	0.00	0.10	--
	0.2	1.00	1.06	6.0
W	2.0	0.00	-0.01	--
	2.0	1.00	0.91	9.0
	1.2	0.00	-0.04	--
	1.2	1.00	0.94	6.0
Pb	2.0	0.00	-0.04	--
	2.0	1.00	0.95	5.0
Zr	2.0	0.00	0.01	--
	2.0	1.00	0.98	2.0
Fe	1.0	0.00	-0.06	--
	1.0	1.00	0.99	1.0
	10.0	0.00	0.01	--
	10.0	1.00	1.01	1.0
Ni	1.0	0.00	-0.05	--
	1.0	1.00	1.00	0.0
	10.0	0.00	-0.01	--
	10.0	1.00	1.02	2.0
Mo	1.0	0.00	-0.01	--
	1.0	1.00	1.00	0.0
	10.0	0.00	0.00	--
	10.0	1.00	1.02	2.0

single determination, was not greater than two standard deviations of the method.

The chloride contents of the samples may differ because of variations in concentration of hydrogen chloride or niobium pentachloride.

Therefore, the effect of various chloride concentrations was investigated.

Solutions containing 0 and 1.0 percent of uranium in the presence of 438, 876, or 1300 milligrams of chloride in excess of that amount to be expected for niobium trichloride were analyzed. The results for uranium (Table VI) show that 438 milligrams of excess chloride do not have a deleterious effect but that the larger quantities cause a significant error. It is highly unlikely that variations in chloride concentrations in 500-milligram samples could be large enough to produce significant errors in uranium analyses.

Table VI

Effect of Chloride on the X-Ray Fluorescence Spectrograph Determination of Uranium

<u>Cl added, mg.</u>	<u>U added, %</u>	<u>U found, %</u>	<u>Error, % absolute</u>	<u>Error, % relative</u>
438	0	0.09	0.09	-
438	1.00	0.99 ₂	-0.00 ₈	0.8
876	0	0.18	0.18	-
876	1.00	1.21	0.21	21
1300	0	0.10	0.10	-
1300	1.00	1.35	0.35	35

This method was applied to the determination of uranium in five samples of niobium chloride. The average uranium concentrations were in the range between 0.11 and 0.38 percent, and the differences between duplicate determinations for each sample were less than two standard deviations for the method. No difficulties were experienced in these analyses.