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**DETERMINATION OF TRACE IMPURITIES IN URANIUM HEXAFLUORIDE
BY AN INDUCTIVELY COUPLED ARGON PLASMA SPECTROMETER**

by

B. W. Short, H. S. Spring, R. L. Grant
Chemical Analysis Department
Technical Division

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SUMMARY

A procedure has been developed to determine 21 trace impurity elements in uranium hexafluoride, using inductively coupled argon plasma emission spectrometry (ICAP). The method consists of a liquid-liquid extraction to separate uranium from the trace impurities with a mixture of tri-(2-ethyl-hexyl)-phosphate (TEHP) and heptane. The raffinate containing the elements is subsequently analyzed by ICAP.

The impurity elements which can be analyzed by this method are: Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Sb, Sn, Ti, V and Zn.

INTRODUCTION

The Portsmouth Gaseous Diffusion Plant receives uranium as UF_6 for enrichment in uranium-235 and the UF_6 must be analyzed to determine if it meets specifications as a feed material.¹ In addition to uranium and uranium-235 assay, the UF_6 must be analyzed for several metallic impurities. Analytical procedures which may be used for the specification analysis of UF_6 are described and generally, three or more of these procedures are required to determine the metallic impurities in UF_6 .² Several carrier distillation procedures³⁻⁷ have been used at GAT for the determination of trace non-volatile impurities in U_3O_8 generated from the pyrohydrolysis of UF_6 . In our present procedure a mixture of silver chloride and lithium fluoride is used as the carrier along with DC arc excitation. The sensitivities for most elements are satisfactory; however, a higher degree of precision is desired.

The carrier distillation procedure is subject to large inherent errors due to sample variations and variable excitation conditions. When spectrographic analysis is coupled with photographic recording of spectral data, the analysis is subject to additional errors. Due to these errors in the carrier distillation spectrographic procedure, a chemical concentration method using partition chromatography followed by a spectrographic analysis was tried and found to be very time consuming.⁹ In order to improve this analysis, it was decided to use the ICAP method of analysis which eliminates many of the errors associated with the carrier distillation method.

A single method has been developed to determine 21 metallic impurities in UF_6 using the ICAP. In the method, a portion of the U_3O_8 generated from the pyrohydrolysis of UF_6 for uranium analysis is dissolved in nitric acid. The uranium is separated from the impurity elements by extraction using a mixture of tri-ethyl-hexyl-phosphate (TEHP) and heptane.⁹ The raffinate containing the metals is then analyzed using an inductively coupled argon plasma spectrometer.

EXPERIMENTAL

Apparatus

1. Inductively Coupled Argon Plasma Spectrometer - Jarrell-Ash Mark III AtomComp
2. Computer - Digital 1103-L
3. Teletype - Digital DecWriter III
4. Peristaltic Pump - Gilson - Minipuls 2
5. 50 ml Polytetrafluorethylene (PTFE) Beakers and Lids
6. 125 ml Separatory Funnels
7. 50 ml Graduated Analysis Tubes with Caps

Reagents

1. Nitric Acid (concentrated)
2. Nitric Acid - 8M: Dilute concentrated nitric acid with an equal volume of distilled water
3. Tri-2-ethyl hexyl-phosphate (TEHP) - Technical Grade
4. Heptane - Reagent Grade
5. TEHP-Heptane Mixture (1:1 V/V) - 25 ml of TEHP is added to 25 ml heptane in a 125 ml separatory funnel. Seventy-five milliliters of 8M nitric acid is then added to the separatory funnel which is then stoppered and shaken by hand for two minutes. The layers are allowed to separate and the acid layer (bottom) is discarded.
6. Reference Solutions - Prepared by the serial dilution of a commercial stock solution (Spex Industries) in 25 percent nitric acid.

PROCEDURE

A weighed portion of U_3O_8 containing 2 grams of uranium is transferred to a 50 ml PTFE beaker. Ten milliliters of concentrated nitric acid is added to the sample and the beaker is covered with a PTFE lid. The sample is heated to 100°C and digested for 5-10 minutes. After dissolution, 10 ml of deionized water is added and the solution is allowed to cool. The sample is then transferred to a 125 ml separatory funnel and 50 ml of the TEHP-heptane mixture is added to the funnel. The separatory funnel is stoppered and shaken for two minutes and the layers are allowed to separate. The aqueous (bottom) layer is transferred to a second 125 ml separatory funnel containing 50 ml of the TEHP-heptane mixture. The separatory funnel is stoppered and shaken for one minute and the layers are allowed to separate. The aqueous layer is then drawn off into a graduated analysis tube and diluted to 40 ml with deionized water. The tube is then capped and shaken. The solution containing the impurity metals is analyzed by ICAP using the following instrumental parameters:

Gas Flow:	Coolant 21 L/min Plasma 0.6 L/min Nebulizer 0.4 L/min
RF Power:	Forward 1100W Reverse <10W
Observation Site:	16 mm above working coil
Integration Time:	2 x 7 sec on-line 1 x 7 sec on-background
Nebulizer:	Fixed cross flow Solution uptake rate 1 ml/minute

A reagent blank and U_3O_8 standards should be carried through the entire procedure.

RESULTS AND DISCUSSION

Separation of Uranium

Uranium is a spectral interference in the determination of metals by ICAP; therefore, it must be separated from the impurity elements. Several uranium solutions containing from 10 to 250 ppm of uranium were analyzed by ICAP for spectral interferences at the wavelengths of the desired elements and it was found that solutions containing less than 100 ppm of uranium did not interfere. In considering separation procedures for uranium, it was decided that liquid-liquid extraction would effectively separate the uranium from the elements of interest. Three extractants, amyl acetate, tri-n-butyl phosphate, and tri(2-ethyl-hexyl) phosphate (TEHP) were tried and TEHP was chosen because of its high uranium selectivity and stability in nitric acid.

The extraction efficiency for uranium with TEHP-heptane is about 99.9 percent for a single extraction. With two grams of uranium a dual extraction is needed to lower the uranium concentration below 100 ppm and eliminate spectral interferences.

It was found that Nb, Ta, W, and Zr partially extract with TEHP-heptane; therefore, these elements cannot be determined with the given procedure.

Selection of Analytical Wavelengths

The analyte lines were selected on the basis of their spectral intensities and their freedom from spectral interferences. The line selection process was facilitated by the list of prominent lines observed in the ICAP¹⁰ and through consultation with Jarrell-Ash. The wavelengths of the selected analytical lines used in the spectrometer are shown in Table I.

TABLE I: ANALYTE EMISSION LINES USED FOR ANALYSIS

<u>Element</u>	<u>Wavelength (nm)</u>	<u>Element</u>	<u>Wavelength (nm)</u>
Al	308.22	Mg	279.55
B	249.77	Mn	257.61
Ba	493.41	Na	589.00
Be	234.86	Ni	231.60
Bi	223.06	Pb	220.35
Ca	393.33	Sb	217.58
Cd	228.80	Sn	189.99
Co	228.62	Ti	334.94
Cr	205.55	V	292.40
Cu	324.75	Zn	213.86
Fe	259.94		

Precision and Accuracy

The precision of the ICAP method for the determination of trace impurities in U_3O_8 was evaluated by analyzing a U_3O_8 containing the desired elements in significant concentration. Eight determinations were made on eight separate days. These results are shown in Table II.

TABLE II: ANALYSIS OF LABORATORY CONTROL U_3O_8

Element	$\mu g/gU^*$	Element	$\mu g/gU^*$
Al	64 $\pm$ 8	Mg	10.4 $\pm$ 0.8
Ba	61 $\pm$ 3	Mn	4.9 $\pm$ 0.5
Be	4.9 $\pm$ 0.4	Na	78 $\pm$ 8
Bi	4.9 $\pm$ 0.3	Ni	69 $\pm$ 4
Ca	53 $\pm$ 3	Pb	46 $\pm$ 3
Cd	0.6 $\pm$ 0.1	Sb	29 $\pm$ 4
Co	0.7 $\pm$ 0.1	Sn	28 $\pm$ 6
Cr	47 $\pm$ 3	Ti	3.3 $\pm$ 0.6
Cu	7.8 $\pm$ 0.9	Zn	13 $\pm$ 3
Fe	43 $\pm$ 2		

* Mean and standard deviation based on eight separate determinations.

The results show that the precision is about ± 10 percent for a single determination.

To check accuracy two synthetic U_3O_8 standards were prepared by adding known amounts of each element at two concentration levels to the U_3O_8 and analyzed by the ICAP method. The results of these analyses are shown in Table III.

TABLE III: ANALYSIS OF SYNTHETIC U_3O_8 STANDARDS

Element	Sample No. 1		Sample No. 2	
	Added, ppm	Found, ¹ ppm	Added, ppm	Found, ¹ ppm
Al	10	11	50	58
B	5	6	25	27
Ba	10	9.6	50	50
Be	1	1	5	5.1
Bi	10	11	50	53
Ca	10	10	50	55
Cd	1	0.9	5	6
Co	5	5	25	26
Cr	10	10	50	53
Cu	10	9.4	50	51
Fe	10	7.1	50	58
Mg	10	11	50	52
Na	10	10	50	53
Ni	10	10	50	53
Pb	10	8.8	50	56
Sb	10	9.7	50	51
Sn	1	0.7	5	6
V	1	0.6	5	5
Zn	10	11	50	53

¹Values represent the average of four separate determinations of the same aliquot.

The recovery of the metals at the two concentration levels was satisfactory indicating that the extraction and ICAP measurement were acceptable.

Certified UF_6 standards for trace metals were not available; therefore, three U_3O_8 standards certified by the New Brunswick Laboratory for trace metals were analyzed to determine the accuracy of the procedure. Each standard was carried through the dissolution and extraction and four spectrographic measurements were made on the raffinates. The results are shown in Table IV. The ICAP results agree very well with the certified values. Although the levels of the trace metals in these uranium standards are much higher than those usually found in UF_6 , the data demonstrate that the proposed procedure is accurate at these concentration levels.

TABLE IV: ANALYSIS OF CERTIFIED STANDARDS

Element	Standard #1		Standard #2		Standard #3	
	Certified Value, ppm	ICP* Results, ppm	Certified Value, ppm	ICP* Results, ppm	Certified Value, ppm	ICP* Results, ppm
Al	210	200 ± 24	54	47 ± 6	14	11 ± 2
B	5.2	5 ± 0.5	2.2	1.8 ± 0.3	**	
Ba	**		**		**	
Be	4	3.9 ± 0.4	2	1.8 ± 0.2	1	0.9 ± 0.1
Bi	50	50 ± 3	10	9 ± 0.6	5	4 ± 0.3
Ca	25	26 ± 2	10	10 ± 1	5	4 ± 0.3
Cd	5	5 ± 0.5	1.3	1.1 ± 0.1	0.6	0.5 ± 0.1
Co	18	19 ± 5	9	10 ± 2	2	2.2 ± 0.1
Cr	95	102 ± 6	24	24 ± 1	0.3	0.2 ± 0.1
Cu	51	50 ± 6	5	5.2 ± 0.6	1.4	1.4 ± 0.2
Fe	520	530 ± 20	66	60 ± 3	22	25 ± 1
Mg	100	104 ± 7	20	20 ± 1	4	3.6 ± 0.3
Mn	54	49 ± 5	12	10 ± 1	6	5 ± 0.6
Na	400	400 ± 40	40	44 ± 4	8	10 ± 1
Ni	110	111 ± 7	24	23 ± 2	6	5.5 ± 0.4
Pb	50	50 ± 4	10	9.5 ± 0.7	2	1.8 ± 0.2
Sb	12	10 ± 2	3	2.3 ± 0.4	**	
Sn	20	19 ± 5	5	4 ± 1.2	1	0.8 ± 0.2
Ti	**		**		**	
V	45	44 ± 8	11	10 ± 2	5	4 ± 0.9
Zn	200	207 ± 38	20	18 ± 4	10	8 ± 2

* Value represents the average of 4 separate determinations of the same aliquot.

**No certified value given.

Detection Limits

The detection limits are defined as the concentration required to give a signal equal to three times the standard deviation of ten consecutive seven-second exposures of the blank. Table V gives the detection limits of each element on µg/gU basis.

TABLE V: DETECTION LIMITS

<u>Element</u>	<u>µg/gU</u>	<u>Element</u>	<u>µg/gU</u>
Al	0.4	Mg	0.04
B	0.2	Mn	0.02
Ba	0.01	Na	0.6
Be	0.006	Ni	0.2
Bi	0.2	Pb	0.6
Ca	0.04	Sb	0.6
Cd	0.06	Sn	0.2
Co	0.1	Ti	0.02
Cr	0.1	V	0.2
Cu	0.02	Zn	0.02
Fe	0.06		

CONCLUSION

The data presented show that the ICAP method can be a useful method for analyzing trace metals in UF₆. The detection limits for most elements are lower than other existing methods with improvements in both accuracy and precision with less time being spent per analysis.

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