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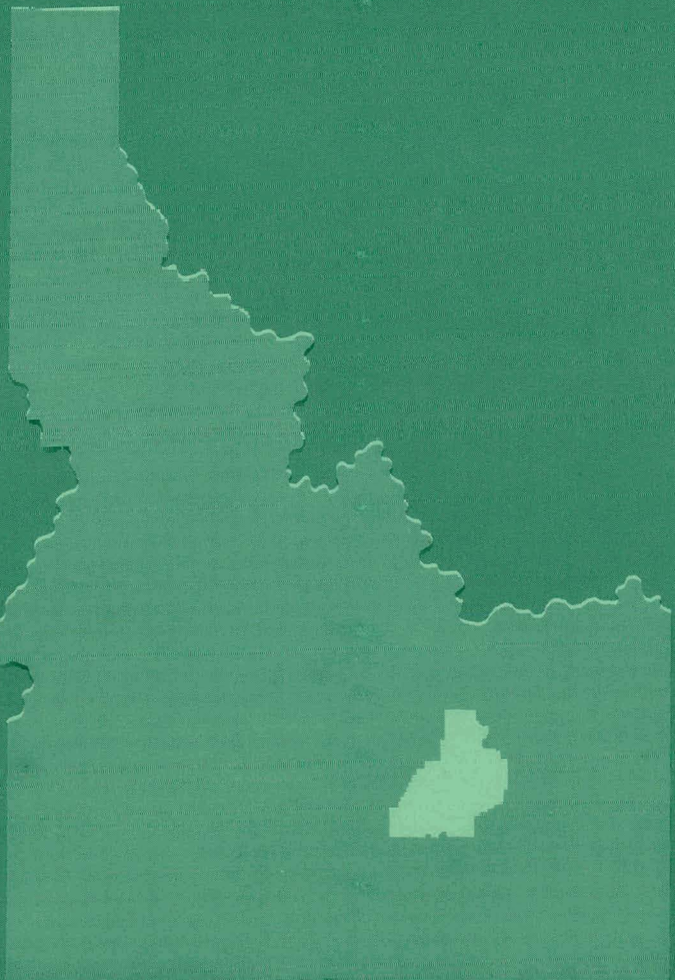

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Atomic Energy Division
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ABSTRACT

A spectrographic method using d-c arc excitation in a controlled atmosphere was developed to analyze for seven impurity elements in radioactive hafnium samples. Analysis requires as little as 35 mg. of hafnium oxide.

SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN HAFNIUM

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SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN HAFNIUM

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INTRODUCTION

An AEC contractor at the National Reactor Testing Station recently requested analysis of hafnium metal for the following impurities in the indicated concentration ranges:

Table I

Element	Expected Concentration Range In PPM
Al	25 - 400
Cu	25 - 400
Fe	60 - 1000
Lu	50 - 800
Ta	50 - 800
W	25 - 400
Zr	3000 - 50,000

Samples would be submitted either as metal chips or as weighed quantities of ground HfO_2. The maximum sample to be submitted was 50 mg. of HfO_2 which might have radiation levels up to one R/hr. at contact.

In considering the problem three points were of primary importance. The method developed must; (1) possess adequate sensitivity to obtain results for all impurities from the small sample to be submitted, (2) not require more than a slight amount of close handling of the samples outside a remote facility, (3) provide adequate containment of vaporized sample material to prevent spread of radioactive contamination. A method was developed to meet these conditions using an enclosed sample chamber with an oxygen atmosphere and d.c. arc excitation.

APPARATUS USED

1. Wig-L-Bug - Model 5A supplied by Spex Industries
2. Two torsion balances (50 and 500 mg. capacity) - Roller Smith Inc.
3. Enclosed arc chamber - Spex Industries No. 9015
4. Excitation source - Jaco Custom Varisource
5. Spectrograph - Jaco Ebert, 3.4 meter with a 15,000 line per inch grating
6. Developing Equipment: An Applied Research Laboratories temperature controlled developing machine.
7. Microphotometer: An Applied Research Laboratories comparator densitometer with recorder.

REAGENTS AND MATERIALS USED

1. High purity oxides of - Ta, Lu, Cu, W, Zr, Hf, In, Y, and Co
2. Graphite powder - National Carbon Company - SP-2 grade
3. Plastic sample vials - 1" x 1/2"
4. Upper electrodes - 2 1/2" x 1/4" pointed ASTM Type C-5 formed from National Carbon Company 1/4" x 12" high purity graphite rods
5. Lower electrodes - "Harvey Cups" - United Carbon Products performed electrode Type 101 L, ASTM Type S-13
6. Photographic emulsion - Eastman SA No. 1 - 4" x 10" plates
7. Photographic processing solutions - Eastman Developer D-19, 2% acetic acid stopbath and Eastman Rapid Liquid Fixer

PRELIMINARY INVESTIGATION

No method was found in the literature that appeared to be directly applicable to the samples in question. It is reported that good results could be obtained by d-c arc excitation of hafnium oxide samples mixed with a buffer.(1,2) This work was done with non-radioactive material and used large samples.

Because the oxide would give sample uniformity and ease of preparation of both samples and reference standards, the samples were requested as oxides. D-C arc excitation was selected as the only practical choice, since the oxides of both hafnium and some of the impurities are highly refractory. The needs for containment of vaporized sample material and for maximum sensitivity were met in part by use of an enclosed arc chamber with controlled atmosphere.(3) Hafnium oxide with the impurities added was used to prepare samples as indicated in Table II. These samples were excited as indicated to find an acceptable method.

Table II

	Samples	Electrode	Atmosphere	Excitation
1.	10 mg. HfO_2	Harvey Cup	O_2	10 amps. d.c. Arc
2.	10 mg. HfO_2 + 10 mg. Graphite	"	"	"
3.	10 mg. HfO_2 + 1.5 mg. Buffer	"	"	"
4.	10 mg. HfO_2	"	O_2 - Ar mix	"
5.	10 mg. HfO_2 + 10 mg. Graphite	"	"	"
6.	10 mg. HfO_2 + 1.5 mg. Buffer	"	"	"

Table II (Cont'd)

	Samples	Electrode	Atmosphere	E Excitation
7.	10 mg. HfO_2	Harvey Cup	Atmosphere	10 amps. d.c. Arc
8.	10 mg. HfO_2 + 10 mg. Graphite	"	"	"
9.	10 mg. HfO_2 + 1.5 mg. Buffer	"	"	"

These test exposures indicated that adequate sensitivity with acceptable line to background ratio could be obtained only with the oxygen atmosphere and with graphite mixed with the sample. With this combination a complete sample burn could be obtained in less than 60 seconds. When graphite was not added, the sample material fused and would not vaporize with the excitation conditions tested. Further investigation using combinations of the most promising conditions lead to adoption of the following procedure.

ANALYTICAL PROCEDURE

Standards are prepared as follows:

The standards will have equal weights of graphite and hafnium oxide plus impurity oxides. The first step in preparing these is to prepare a mixture of impurity oxides as shown in Table III. The oxides are placed in a plastic vial and mixed for 5 minutes on the Wig-L-Bug before using.

The second step is to mix graphite and impurity oxide mix in the proper ratio so that aliquots of it may be mixed with HfO_2 and graphite to give the desired standards. 14.5 mg. of impurity oxide mix and 237.7 mg. of graphite are placed together in a plastic vial and mixed for 5 minutes on the Wig-L-Bug. This mixture along with graphite and HfO_2 are used to prepare the standards as shown in Table IV.

Table III

Impurity Oxide Mix

Element	Analytical Range In PPM	Compound Used	Ratio of Each Impurity Element to the Total Impurities	mg. of the Element Desired	Gravimetric Factor	mg. of Oxide Used
Al	25-400	Al_2O_3	2/269	5	1.889	9.4
Cu	25-400	CuO	2/269	5	1.2517	6.3
Fe	62.5-1000	Fe_2O_3	5/269	12.5	1.4297	17.9
Lu	50-800	Lu_2O_3	4/269	10	1.1372	11.4
Ta	50-800	Ta_2O_5	4/269	10	1.2211	12.2
W	25-400	WO_3	2/269	5	1.2610	6.3
Zr	3150-50,000	ZrO_2	250/269	625	1.3508	844.0

Table IV

Standards Preparation

Standard	mg. of Graphite Impurity Oxide Mix	mg. of HfO_2	mg. of Graphite
A	126	111.58	0
B	63	114.75	58.96
C	31.53	116.33	88.44
D	15.76	117.13	103.19
E	7.88	117.52	110.54

These standards will have concentrations of the various impurity elements as shown in Table V.

Table V

Impurity Concentration PPM of Element in Hafnium Metal

Standard	Al	Cu	Fe	Lu	Ta	W	Zr
A	400	400	1000	800	800	400	50,000
B	200	200	500	400	400	200	25,000
C	100	100	250	200	200	100	12,500
D	50	50	125	100	100	50	6,250
E	25	25	62.5	50	50	25	3,125

If hafnium metal is to be analyzed the metal must be converted to the oxide. To do this, place metal chips in a clean porcelain crucible. Place the crucible in a cool muffle furnace and raise the temperature at a rate of 110°C/hr. until a temperature of 1000°C is reached. Hold it at this temperature for twelve hours or until the metal is completely oxidized. After cooling grind the oxide to 200 mesh, then proceed.(1)

Place equal weights of HfO_2 and graphite (at least 30 mg. of each) in plastic mixing vials - mix with the Wig-L-Bug for two minutes.

Standards and samples are loaded into Harvey Cup electrodes by forcing the open end of the cup to the bottom of the mixing vial several times. Sample material is well packed and remains in the electrodes as they are removed, turned upright, and placed in an electrode carrier.

Standards and samples are run according to conditions listed below:

Excitation - eight ampere d.c. arc
Atmosphere - oxygen in enclosed arc chamber supplied at the rate of 1.5 ft^3/hr.
Analytical Gap - 4 mm
Exposure - 60 seconds
Grating - 10.81° angle of incidence to give second order in the range 2550A to 3750A
Mirror - masked to 20% transmission
Slit - 30 µ
Filter - two step 50 and 100% transmission, located at the slit
Line Height - 3.8 mm
Photographic Emulsion - SA No. 1
Developing - develop 3 minutes, rinse in stopbath 20 seconds, fix for two minutes, wash in running water five minutes, then dry

The transmittances of analytical and internal standard lines (Table VI) are read for each standard and sample. The relative intensity ratios of analytical to internal standard line are determined by use of a previously prepared emulsion calibration. A working curve for each impurity to be determined is prepared from intensity ratios obtained for standards (use data from not less than triplicate shots of standards). The impurity concentrations in each sample are read directly from the appropriate curves. The average value of at least duplicate shots is used for the reported value.

Table VI

Element	Wavelength in A		Internal Standard
Ta	2653.27	-----	Hf - 2653.82 A
Lu	2911.39	-----	Hf - 2653.82 A
Zr	2945.46	-----	Hf - 2653.82 A
W	2944.44	-----	Hf - 2653.82 A
Fe	3009.57	-----	Hf - 2653.82 A
Al	3082.16	-----	Hf - 2653.82 A
Cu	3273.96	-----	Hf - 2653.82 A

PRECISION

Based on data from the standards the calculated standard deviation of a single determination for each of the several impurities determined shows a range of from ± 8 to ± 30% of the amount present. Since samples are run in duplicate and the average reported, it is believed that the standard deviation of the method ranges from ± 6 to ± 21% of the amount present for various impurities determined. The best precision was obtained for Lu and Zr and the poorest for Fe and W.

DISCUSSION

Additional development work offering possible higher precision should be carried out for future samples of this type. Sample buffer systems, other atmosphere including helium, and higher power excitation with the improved atmosphere chamber now available should be tested.

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