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by Atomic-Absorption Spectrophotometry

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DETERMINATION OF SELECTED RARE EARTHS IN URANIUM ALLOYS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

by

R. D. Gardner, A. L. Henicksman, and W. H. Ashley

ABSTRACT

Scandium, yttrium, holmium, erbium, thulium, ytterbium, and lutetium, at concentrations of 0.01 to 0.1 wt% in uranium-matrix alloys, are determined by atomic-absorption spectrophotometry in a perchloric acid solution of the alloy without separation. The presence of uranium enhances the absorbances of the rare-earth elements and eliminates interferences by other elements. The measurement's relative standard deviation at the 0.1-wt% level is 1%, except for lutetium for which it is 5%. At the 0.01-wt% concentration level, each element except lutetium and yttrium is measured with a relative standard deviation no greater than 3%. For lutetium and yttrium, the relative standard deviations are 10 and 8%, respectively.

I. INTRODUCTION

Use of the nitrous oxide-acetylene flame¹ in atomic-absorption spectrophotometry has made determination of most of the rare-earth elements relatively straightforward. Recent books such as Slavin's² give some details on determination of each of the elements, and Kinnunen and Lindsjö^{3,4} and Van Loon, Galbraith, and Aarden⁵ report more detailed studies of some of these elements in minerals. As with other elements that are difficult to atomize, the absorbances of the rare earths are sensitive to the other constituents of the sample solution. Sodium³ and lanthanum⁶ are among the additives recommended for eliminating this sensitivity. We⁶ found uranium to be a generally satisfactory "radiation buffer." We undertook this study to find the best conditions for determining selected rare earths in uranium alloys without prior separations, and to learn what precision could be expected in such determinations.

II. RECOMMENDED PROCEDURE

A. Special Apparatus

Atomic absorption spectrophotometer, Varian Techtron AA-4, with 1M-5 amplifier module and DI-30 digital indicator, or its equivalent.

Lamps, hollow-cathode, for erbium, holmium, lutetium, scandium, thulium, ytterbium, and yttrium. HCN series from Varian Techtron.

B. Reagents

Hydrochloric acid, 12M, reagent grade.

Hydrogen peroxide, 30%, reagent grade.

Metal standard solutions, approximately 1 g/liter. Accurately weighed portions of freshly ignited oxides of the various metals were individually dissolved in nitric acid and diluted to 100 ml with water.

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Nitric acid, 15*M*, reagent grade.

Perchloric acid, 70%, reagent grade.

Uranium solution 200 g/liter. Pure uranium metal was dissolved in hydrochloric acid, uranium (III) and uranium (IV) were oxidized with hydrogen peroxide, and the solution was diluted with water to the appropriate volume.

C. Sample Preparation

Alloy samples are ordinarily received in the form of turnings, and the portions taken for analysis should be carefully inspected to ensure that foreign material has not been introduced during machining or sampling. If cutting oil is present, the sample should be washed sequentially with water, ethanol, and acetone, and allowed to dry at room temperature. The 1-g sample size and 25-ml final solution volume are usable for all seven elements in the 0.01- to 0.1-wt% range. For higher concentrations of some of the elements, a more dilute solution is preferable. At the 0.01-wt% level, scale expansion will be needed for most of the elements, but a more concentrated sample solution is not recommended.

D. Operations

1. To a weighed 1-g sample in a covered 100-ml beaker, add 1 ml of 12*M* HCl, 1 ml of H₂O₂, and 2 ml of 70% HClO₄. Warm on the hot plate to remove excess H₂O₂.

2. Prepare two calibration solutions in the same way, starting with either 1 g of pure uranium metal or a uranium solution. To one of these add a volume of the metal standard solution of the element sought, to give the

concentration expected in the sample. Use the second solution as a blank.

3. Transfer each solution to a 25-ml volumetric flask and dilute to volume with water.

4. Using the appropriate hollow-cathode lamp and the instrument settings shown in Table I, adjust the absorbance of the instrument to zero. The settings given are specifically for the Techtron AA-4, and are mostly from the instruction manual. If another instrument is used, refer to the operator's manual for appropriate conditions.

5. Aspirate in sequence the blank, the calibration solution, the sample solutions, the calibration solution, and the blank, verifying the base line with water before each reading, and record the absorbances. Repeat the sequence three or four times. Average the readings for each solution, and subtract the absorbance of the blank from those of the sample and calibration solutions.

6. Calculate the concentration of the element in the sample.

$$\text{Element sought, wt\%} = (100 AB)/CD$$

where

A = grams of element in calibration solution,

B = net absorbance of sample solution,

C = net absorbance of calibration solution,

and

D = grams of sample taken.

III. EXPERIMENTAL

A. Anion Effects

Kinnunen and Lindsjö^{3,4} reported very little effect on the absorbance of the rare earths from the kind or concentration of acid in the sample solution. Cattrall and Slater,⁷ working only with yttrium, found a greater effect

TABLE I
RECOMMENDED INSTRUMENT SETTINGS FOR TECHTRON AA-4

Element	Wavelength (Å)	Lamp Current (mA)	Slit (μm)	Burner Height (mm)	N ₂ O ₂ -C ₂ H ₂ Flame
Sc	3912	7	50	12	rich
Y	4102	10	50	12	rich
Ho	4104	10	25	11	mod. rich
Er	4008	8	50	11	mod. rich
Tm	3718	8	100	14	rich
Yb	3989	5	100	15	mod. rich
Lu	3360	20	50	13	very rich

even though the variation in concentration was less. They recognized that the effect depends somewhat on the flame conditions and the location of the beam in the flame. We tried for maximum absorbance in our flame conditions and location, and for a high acid concentration that would minimize effects of small variations in concentration. To determine optimum acid conditions, we evaporated aliquots of each metal standard solution, containing about 1 mg of the metal, to incipient dryness, dissolved the residue in one of the various acids being tested, and diluted the solution to a volume of 10 ml. To some of the solutions, we added 200 mg of uranium before the evaporation to incipient dryness. The hydrochloric, nitric, and perchloric acid concentrations were each about 5%, and the sulfuric and phosphoric acid concentrations were about 2.5% in the final solutions. The solutions were aspirated into the flame as described under "Operations." The measured absorbances are shown in Table II.

The absorbance of each element is greatest in the presence of perchloric acid, and uranium further enhances the absorbance. Cattrall and Slater⁷ also noticed an enhancing effect from perchloric acid above a certain concentration. They attributed this effect to a higher flame temperature produced by the oxidizing action of the

perchloric acid, but they did not make any temperature measurements. We offer no explanation of the effect, but we found that a further increase of 50% in the perchloric acid concentration, to 7.5%, did not increase the absorbance. The enhancement by perchloric acid was not affected by the presence of chloride or nitrate ions, but it was quenched by the presence of sulfate or phosphate ions. Fluoride ions always interfered because of the insolubility of rare-earth fluorides.

B. Cation Effects

We studied a few other metals for possible interference. These included some other rare earths, aluminum, and some elements common to the alloys for which the procedure was developed (see Table III). We included aluminum because Kinnunen⁸ had found that it caused serious interference in his procedure which used sodium to suppress ionization. In each case, the amount of the element we investigated was 10 times that of the element being measured and 1% of the amount of uranium present. The results, Table III, show that for the concentrations we tried, the effect of the uranium was strong enough to obscure the effects of the other elements.

TABLE II
ABSORBANCES OF THE RARE EARTHS IN VARIOUS ACIDS

Rare Earth	HCl	HNO ₃	HClO ₄	H ₂ SO ₄	H ₃ PO ₄
Sc	0.400	0.396	0.579	0.428	0.334
Sc + U	0.479	0.479	0.776	0.277	0.393
Y	0.118	0.092	0.157	0.076	0.085
Y + U	0.087	0.073	0.294	0.054	0.071
Ho	0.234	0.222	0.261	0.230	0.254
Ho + U	0.234	0.253	0.411	0.165	0.231
Er	0.221	0.219	0.272	0.229	0.252
Er + U	0.201	0.205	0.408	0.152	0.203
Tm	0.299	0.298	0.321	0.332	0.329
Tm + U	0.403	0.403	0.453	0.330	0.354
Yb	0.354	0.352	0.357	0.349	0.335
Yb + U	0.390	0.404	0.443	0.353	0.385
Lu	0.065	0.060	0.090	0.050	0.060
Lu + U	0.050	0.050	0.150	0.040	0.040

TABLE III
EFFECTS OF VARIOUS CATIONS ON ABSORBANCE

Rare Earth (1 mg)	Element Added (10 mg)	Rare Earth Found (%) ^a No Uranium	Rare Earth Found (%) ^a With Uranium
Sc	La	123	99.5
Sc	Yb	121	101.2
Ho	Dy	138	100.5
Ho	Er	131	100.7
Tm	Mo	109	100.3
Tm	Ni	115	100.0
Tr	Ir	100	99.4
Tr	Al	89	100.2

^aRelative to the rare earth taken.

Uranium contributes a slight background absorbance at the working wavelengths of all these elements. The blank, prepared and used as directed, corrects for this effect.

IV. RELIABILITY

We prepared two solutions, each containing 1 g of uranium in 25 ml of solution as in the "Recommended Procedure." To one solution, we added all of the rare earths being studied, each in the amount of 1 mg per 25 ml, or 0.1 wt% with respect to the uranium present. To the other solution, we added 0.1 mg of each, or 0.01 wt% relative to the uranium. We analyzed each solution six times for each element, each time calibrating the absorbance with a solution containing only the element being determined and uranium. The results, Table IV, show that the relative standard deviation is no greater than 1% in measuring 0.01 or 0.1% of scandium, thulium, or ytterbium, or 0.1% of holmium or erbium, and no greater than 2.7% in determining 0.1% of holmium or erbium in uranium alloys. The relative standard deviations were between 4.8 and 10.6% in determining 0.01 or 0.1% of lutetium or 0.01% of yttrium.

In this Laboratory, many uranium alloys have been analyzed for rare earths with apparently satisfactory re-

sults. The rare earths most commonly encountered have been lutetium, thulium, yttrium, and scandium in the 0.1 to 1.0% range. Additional alloying elements frequently present are nickel and either rhodium or iridium. Mixtures of rare-earth oxides have also been analyzed. In such cases, we add uranium to the sample solution to eliminate the rare earths' effects on each other.

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REFERENCES

1. M. D. Amos and J. B. Willis, "Use of High-Temperature Pre-Mixed Flames in Atomic Absorption Spectroscopy," *Spectrochim. Acta*, **22**, 1325 (1966).
2. W. Slavin, *Atomic Absorption Spectroscopy* (Interscience Publishers, New York, 1968).
3. J. Kinnunen and O. Lindsjo, "Determination of Rare Earths in Phosphate Rocks by Atomic Absorption Flame Photometry," *Chemist-Analyst* **56**, 25 (1967).
4. J. Kinnunen and O. Lindsjo, "Determination of Rare Earths in Phosphate Rocks by Atomic Absorption Flame Photometry II," *Chemist-Analyst* **56**, 76 (1967).
5. J. C. VanLoon, J. H. Galbraith, and H. M. Aarden, "Determination of Yttrium, Europium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, and Lutetium in Minerals by Atomic Absorption Spectrophotometry," *Analyst* **96**, 47 (1971).
6. R. D. Gardner, A. L. Henicksman, and W. H. Ashley, "The Determination of 0.01 to 1.0% of Titanium, Zirconium, Hafnium, Niobium, Tantalum, Molybdenum, and Tungsten in Uranium Alloys by Atomic Absorption Spectrophotometry," Los Alamos Scientific Laboratory report LA-4529 (October 1970).
7. R. W. Cattrall and S. J. E. Slater, "Atomic Absorption Determination of Yttrium in Nitrous Oxide-Acetylene Flame," *Anal. Chim. Acta*, **56**, 143 (1971).

TABLE IV
RECOVERY AND PRECISION OF DETERMINATION OF RARE-EARTH
METALS IN URANIUM

<u>Element</u>	<u>Concentration (%^a)</u>	<u>Found (Ave %)</u>	<u>Rel. Std. Dev. (%)</u>
Sc	0.01	99.0	0.9
Sc	0.1	99.6	0.8
Y	0.01	101.9	8.4
Y	0.1	100.6	1.2
Ho	0.01	99.9	2.7
Ho	0.1	100.5	0.5
Er	0.01	100.8	2.1
Er	0.1	100.3	0.7
Tm	0.01	98.9	0.9
Tm	0.1	100.4	0.8
Yb	0.01	99.3	0.4
Yb	0.1	100.8	0.6
Lu	0.01	98.6	10.6
Lu	0.1	101.2	4.8

^aRelative to the uranium present.