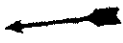


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SODIUM FLUORIDE CARRIER CONCENTRATION  
METHOD FOR DETERMINING Al, Be, Ca AND Ti IN PLUTONIUM

C. S. Homi

Introduction

Aluminum, beryllium, calcium and titanium are determined spectrochemically in plutonium using sodium fluoride as the carrier. The method employs the use of standard films for visual semi-quantitative measurements. Basic steps of control are one, two, five, ten and multiples of ten up to one thousand parts per million with a demonstrated precision of plus or minus one step.

Discussion

The procedure described in this report was developed to eliminate the long and less-accurate cupferron extraction method (1) for determining aluminum, beryllium and calcium in plutonium. The cupferron extraction method was unsatisfactory for the following reasons. Analyses of aluminum in control standards was sometimes many orders of magnitude below the standard value. The extraction method was time consuming and required the compositing of samples in order to complete the analysis in an available time. In addition, excessive handling, extractions, etc. of the sample introduced the possibility for more error and impurity contamination. Difficulty in recovering plutonium cupferrate waste and the ever-present dangers of radioactive skin contamination were other disadvantages of the method.

Aluminum and calcium are routinely determined in uranium samples using the gallium oxide carrier concentration method (2). No success has been achieved in determining these elements in plutonium using the same techniques. R. J. Kofoed, Jr. (3) found the spectral sensitivities of various elements in plutonium were suppressed by the matrix and that aluminum and calcium analyses were not reproducible. Accordingly, sodium fluoride was substituted for the gallium oxide carrier and significantly better results were obtained as shown by the data in the following table. In addition, the shortcomings noted for the cupferron method were eliminated.

<u>Element</u>	<u>Cupferron Method</u>		<u>Sodium Fluoride Carrier Method</u>	
	<u>Number of Samples</u>	<u>Accuracy</u>	<u>Number of Samples</u>	<u>Accuracy</u>
Al	12	-2.83 steps*	23	- .95 steps*
Ca	29	-0.41 steps*	20	+ .05 steps*
Be	29	-1.76 steps*	12	+ .08 steps*

\*Plus and minus steps indicate the range from a known concentration of the element. Zero steps indicate a perfect analysis.

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Standard Preparation

A high purity plutonium dioxide matrix was prepared using plutonium metal with less than 200 ppm total metallic impurities. The metal was dissolved in quartz distilled hydrochloric acid, evaporated to dryness and ignited to the oxide in a muffle furnace.

A 5000 ppm standard was prepared by adding the indicated amounts of impurities to the plutonium dioxide matrix:

$\text{Al}_2\text{O}_3$  - 18.9 mg

$\text{CaCO}_3$  - 25.0 mg

$\text{BeO}$  - 27.8 mg

$\text{TiO}_2$  - 16.8 mg

$\text{PuO}_2$  - 2159.0 mg

The salts were placed in an agate mortar and ground thoroughly. The mixture then contained 5000 ppm of each element per million parts plutonium metal. Dilutions using plutonium dioxide were carried out in the following manner: (mixing in an agate mortar)

<u>Mixture</u>	<u>Resulting Concentration</u>
800 mg 5000 std. + 1200 mg $\text{PuO}_2$ - mix	2000 ppm std.
1000 mg 2000 std. + 1000 mg $\text{PuO}_2$ - mix	1000 ppm std.
1000 mg 1000 std. + 1000 mg $\text{PuO}_2$ - mix	500 ppm std.
800 mg 500 std. + 1200 mg $\text{PuO}_2$ - mix	200 ppm std.
1000 mg 200 std. + 1000 mg $\text{PuO}_2$ - mix	100 ppm std.
1000 mg 100 std. + 1000 mg $\text{PuO}_2$ - mix	50 ppm std.
800 mg 50 std. + 1200 mg $\text{PuO}_2$ - mix	20 ppm std.
1000 mg 20 std. + 1000 mg $\text{PuO}_2$ - mix	10 ppm std.
1000 mg 10 std. + 1000 mg $\text{PuO}_2$ - mix	5 ppm std.
800 mg 5 std. + 1200 mg $\text{PuO}_2$ - mix	2 ppm std.
1000 mg 2 std. + 1000 mg $\text{PuO}_2$ - mix	1 ppm std.

Conclusions

At the 5000 ppm and 2000 ppm level, the steps for aluminum, calcium and titanium did not behave satisfactorily for use as comparison standards. Good stepping so visual comparisons could be made was observed for the standards from the detection limit to 1000 ppm which is in the normal range of the analyses.

Aluminum: Lines used were the 3082-A and 3093-A arc doublet. Both of these lines stepped down better than the arc doublet at 3944-A and 3962-A. Five parts per million aluminum was observed in the blank.

Beryllium: The beryllium doublet at 3131-A behaved satisfactorily from 5000 ppm down to 5 ppm. No blank was observed.

Calcium: The arc line at 4227-A proved to be the best line. Five parts per million was observed in the blank.

Titanium: Lines used were located at 3349-A and 3361-A. The limit of detection of the 3349-A line was 20 ppm and no blank was observed.

Equipment Used

ARL 2-meter Grating Spectrograph

ARL High-Precision Source Unit

ARL Comparator-Microphotometer

ARL Film Processing and Drying Equipment

Muffle Furnace

Torsion Balance

Reagents and Materials

Sodium Fluoride Powder

National Carbon 8 mm Craters and 1/8" Counter Electrodes

Kodak D-19 Developer

Kodak Spectrum Analysis #1 Film

Spectrographic Constants

Primary Voltage	240
Resistance	25 ohms
Discharge Amps	9
Capacitance	60 mfd
Time	2 minutes
Pre-arc	5 seconds
Filter Position	#4
Analytical Gap	2 mm
Wave-length Region	2250-4800 Å

Procedure for Plutonium Metal

1. Cut 250 mg of the metal and oxidize in a muffle furnace at  $650^{\circ}$  -  $700^{\circ}$  C.
2. Transfer 210 mg of the oxide to a Wig-L-Bug vial containing 10 mg sodium fluoride powder.
3. Grind the mixture in a Wig-L-Bug for twenty seconds.
4. Load 100 mg of the mixture into an 8 mm graphite crater.
5. Briskly tamp and vent the sample.
6. Arc the sample according to standard conditions.
7. Develop the film for three minutes at  $18^{\circ}$  C and compare spectra with standard film.

References

- (1). Nachtrieb, Normal H., Principles and Practice of Spectrochemical Analysis. New York, McGraw-Hill, 1950.
- (2). Kofoed, R. J., Jr., The Influence of the Matrix On The Carrier Distillation of Metallic Impurities From  $\text{PuC}_2$  and  $\text{U}_3\text{O}_8$ . 1958 (U. S. Atomic Energy Commission HW-54032).
- (3). Kofoed, R. J., Jr., personal communication.