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C-55 Technology-Plutonium

M-3679 (22nd Ed., Rev 1)

Sodium Fluoride as a Spectroscopic Carrier for Plutonium Metal Analysis

by

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THE DOW CHEMICAL COMPANY

ROCKY FLATS PLANT

DENVER, COLORADO

U.S. ATOMIC ENERGY COMMISSION CONTRACT AT (29-1)-1106

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SODIUM FLUORIDE AS A SPECTROSCOPIC CARRIER
FOR PLUTONIUM METAL ANALYSIS

by

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ABSTRACT

A pyroelectric carrier distillation method, using sodium fluoride as a spectroscopic carrier has been developed for the impurity analysis of plutonium metal.

ACKNOWLEDGMENTS

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2) The authors wish to acknowledge the helpful suggestions contributed by C. W. Barrick and B. L. Bickley.

1. INTRODUCTION

The impurity analysis of plutonium metal⁽¹⁾ was formerly accomplished by two different spectrochemical methods, 1) cupferron extraction method and 2) gallium oxide carrier distillation method. The use of two methods complicated the time schedule for completing the impurity analysis, and also increased the complexity of the analysis. Of the two methods, the cupferron extraction procedure was the most time-consuming and required a meticulous technique. This method was used for the determination of aluminum, beryllium, calcium, lanthanum, lithium, magnesium, and sodium.

It had been previously found that lithium and sodium could be determined down to the required limits by the gallium oxide method; but that the other elements were not sufficiently sensitive with the gallium oxide carrier. Sodium fluoride had previously been used as a spectroscopic carrier^(2,3) for some of these elements in the impurity analysis of uranium. Consequently, a program was undertaken to evaluate sodium fluoride and other carrier salts for the determination of these elements in plutonium.

2. SUMMARY

A pyroelectric carrier distillation method using sodium fluoride as a spectroscopic carrier has been developed for the determination of five impurities in plutonium metal. The method was designed to determine those elements previously determined by the cupferron extraction method. By replacing this method with a carrier method, a savings in analysis time and material was realized.

The plutonium metal is oxidized by heat to plutonium oxide which is mixed with sodium fluoride to form an electrode charge consisting of approximately 5% sodium fluoride. A 12-ampere d-c arc is employed to excite the mixture for a period of 45 seconds using a 5-second pre-arc and a 40-second exposure. The resulting spectra are recorded on a photographic plate and the impurity concentrations are determined by visual estimation procedures using standard spectra for comparison purposes.

For the same plutonium metal samples, the analytical results obtained with the sodium fluoride method agreed favorably with those obtained with the cupferron extraction method.

3. EXPERIMENTAL

3.1 Sample Preparation

A sufficient amount of plutonium metal (>200 mg) was placed in a platinum crucible and air oxidized to PuO_2 by heating in a furnace for one hour at 800 C. Twelve milligrams of NaF carrier and 226 mg of PuO_2 were placed in a plastic vial and thoroughly mixed by shaking the vial on a Wig-L-Bug (a dental amalgamator) for one minute. Two 100-mg electrode charges were removed from the vial and loaded into pedestal electrodes, thereby giving duplicate spectra for each sample.

3.2 Standard Preparation

Since no substantial quantity of spectrographically pure plutonium oxide was available, the impurity elements were added to the sodium fluoride carrier. Nine individual standards were prepared by adding appropriate amounts of Al_2O_3 , BeO, CaO, La_2O_3 , and MgO to the NaF carrier. The standards covered an impurity range of 1 to 500 ppm based on a 1-2-5 system of concentration increments. An exception was made for beryllium, which was prepared at one-tenth of the original standard values.

The NaF- PuO_2 electrode charge was prepared in the same manner as that described for the samples. However, since the impurities were placed in the carrier, the weights of both the PuO_2 matrix and the NaF carrier were adjusted to give a

constant carrier weight of 12 mg and a fixed final weight of 238 mg for the NaF-PuO₂ mixture.

3.3 Electrode System

- 1) Lower Electrode - UCP type 2314, pedestal form, 1/4-in. diameter, graphite anode cup with a 4.5- x 8-mm crater.
- 2) Upper Electrode - UCP type 1346B, pointed 1/8-in. diameter, graphite rod, 1-1/2 in. long.

3.4 Apparatus

- 1) Spectrograph - Jarrell-Ash Duplex Fixed Position, 3.4-meter Wadsworth mount, grating instrument, having a reciprocal linear dispersion of 5.12 A/mm in the first order.
- 2) Comparator - Hilger Projection Spectrum Comparator.
- 3) Plate Processing - JAcO Plate Processing Unit.
- 4) Source Unit - JAcO Varisource.

3.5 Excitation

Source - d-c arc

Current - 12 amp

3.6 Recording

2100 - 3400A - Eastman S.A. - 1

3400 - 4100A - Eastman S.A. - 2

3.7 Exposure Conditions

Spectral Region - 2100 - 4100A Second Order

Slit Width - 30 μ

Slit Length - 1 mm
Filters - None
Pre-Arc - 5 sec
Exposure - 40 sec
Analytical Gap - 4 mm

3.8 Plate Processing

Developer - 5 min with agitation
Short Stop - 20 sec
Fixer - 5 min with agitation
Wash - 5 min with running water
Dry - Circulating warm air

3.9 Determination of Results

The analytical results were obtained by visually comparing a sample spectrum with known standard spectra and estimating each respective impurity concentration. The impurity values were reported in ppm as micrograms of the impurity element per gram of the plutonium metal sample.

The wavelengths used are listed in Table I along with the limit of detection for each element.

TABLE I

Detectability of Impurities in Plutonium Metal

<u>Element</u>	<u>Wavelength (A)</u>	<u>Limit of Detection (ppm)</u>	
		<u>NaF Carrier</u>	<u>Ga₂O₃ Carrier</u>
Al	2567.99	2	300
Be	2348.61	0.1	0.1
Ca	3933.67	2	100
La	4333.73	10	>2000
Mg	2802.70	2	2

4. RESULTS

4.1 Accuracy

Ten samples which were used in a four laboratory sample exchange program were also analyzed by the sodium fluoride carrier method. A summary of the results for the four participating installations is shown in Table II. In general, the Rocky Flats carrier results show reasonable agreement with those of the other three installations.

An additional comparison was also made on twenty-five routine metal samples which were analyzed by the cupferron extraction method and the sodium fluoride carrier method. Using Student's "t" test, no significant differences were observed at the 95% confidence limit between the individual impurity averages for the two methods.

4.2 Precision

For reproducibility data, twelve spectra of the same metal sample were recorded on two different plates. To eliminate any bias due to visual interpretation of the spectra, the analytical lines were microphotometered and their relative intensities obtained from the usual emulsion calibration curve. The coefficients of variation for the relative intensities for aluminum, calcium, and magnesium are reported in Table III. No reproducibility data is available for beryllium and lanthanum.

TABLE II

Inter-Laboratory Comparison

<u>Sample</u>	<u>Lab.</u>	<u>Al</u>	<u>Be</u>	<u>Ca</u>	<u>La</u>	<u>Mg</u>	<u>Sample</u>	<u>Lab.</u>	<u>Al</u>	<u>Be</u>	<u>Ca</u>	<u>La</u>	<u>Mg</u>
1	HW	3	ND	3	ND	20	6	HW	20	ND	13	ND	<20
	LASL	20	<.1	<5	<10	100		LASL	70	<.1	<5	35	<5
	RFP	10	<.1	2	<20	50		RFP	30	<.1	<5	<20	7
	SRP	15	<.1	<2.5	<10	75		SRP	30	<.1	<2.5	25	<2.5
2	HW	3	ND	3	ND	20	7	HW	20	ND	13	ND	<20
	LASL	40	<.1	<5	<10	100		LASL	70	<.1	<5	30	10
	RFP	20	<.1	2	<20	50		RFP	30	<.1	<5	<20	7
	SRP	20	<.1	<2.5	<10	75		SRP	45	<.1	<2.5	20	<2.5
3	HW	<3	ND	13	ND	100	8	HW	200	ND	8	ND	50
	LASL	25	<.1	7	<10	90		LASL	80	<.1	<5	10	200
	RFP	10	<.1	<2	<20	75		RFP	50	<.1	<5	<20	300
	SRP	25	<.1	2.5	<10	100		SRP	50	<.1	<2.5	<10	100
4	HW	<3	ND	13	ND	100	9	HW	20	ND	13	ND	100
	LASL	20	<.1	10	<10	90		LASL	500	<.1	<5	35	75
	RFP	15	<.1	3	<20	150		RFP	150	<.1	<5	<20	100
	SRP	15	<.1	3	<10	125		SRP	300	<.1	<2.5	25	50
5	HW	<3	ND	13	ND	100	10	HW	32	ND	8	ND	50
	LASL	20	<.1	<5	<10	90		LASL	150	<.1	<5	<10	10
	RFP	10	<.1	<2	<20	150		RFP	30	<.1	<5	<20	20
	SRP	15	<.1	<2.5	<10	100		SRP	100	<.1	<2.5	<10	5

TABLE III

Reproducibility Data for a Single Sample

<u>Element</u>	<u>Concentration (ppm)</u>	<u>Coefficient of Variation for Log I_x</u>
Al	36	7.4%
Ca	2	14.4%
Mg	18	16.3%

5. DISCUSSION

5.1 Selection of Carrier

Several halogen salts of Group I and Group II metals were tested as spectrographic carriers. Five milligrams of each salt was mixed with 90 mg of plutonium oxide and the mixture excited with a 10-ampere d-c arc for four consecutive 20-second intervals. The criteria used for selecting the most promising carrier was the ratio of line density to background density. Of all those tested, sodium fluoride had the highest ratio, with the analytical lines showing satisfactory sensitivity.

5.2 Selection of Spectrographic Conditions

Standards were prepared by grinding oxides of the impurity elements with sodium fluoride. Various ratios of NaF:PuO₂ were arced. The ratio selected was 12 mg of NaF to 226 mg of PuO₂, thereby providing for two 100-mg electrode charges. Moving plate studies at different amperages indicated that 12 amperes were necessary; 10 amperes were not enough to provide the necessary sensitivity for lanthanum.

After the establishment of the NaF to PuO₂ ratio, standards were prepared on this basis. These standards were first arced with U₃O₈ to determine if they graded properly. All of the added element lines graded well except lanthanum, which was not visible in any of the standards. The 500-ppm standard was arced at various ampere settings, but lanthanum

was not detectable in the U_3O_8 matrix. When the standards were mixed with PuO_2 and arced, lanthanum was visible down to 5 ppm. This indicated that there is a definite, and sometimes quite large, difference in the behavior of elements arced from a U_3O_8 matrix and their behavior in a PuO_2 matrix.

This method was put into operation to determine aluminum, beryllium, calcium, lanthanum, and magnesium in plutonium metal. It is estimated that three times as many samples may be run by one person using the sodium fluoride carrier method as using the two methods it replaces.

The necessity of purifying the water and hydrochloric acid which was required for the extraction procedure has also been eliminated thereby effecting a saving in time and material.

The possibility of employing sodium fluoride as a carrier for a more extended impurity analysis of plutonium metal is also under investigation.

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