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Curium Process Development

III-7 EMISSION SPECTROGRAPHIC DETERMINATION OF METALLIC IMPURITIES IN CURIUM OXIDE AND MIXED CURIUM-AMERICIUM OXIDE

by

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ABSTRACT

Semiquantitative emission spectrographic methods were developed for the determination of impurities in curium oxide and mixed curium-americium oxide. Twenty-one elements (Ag, Al, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, and Zn) are determined by a gallium oxide carrier technique. Zirconium is determined by a total burn method with a direct current arc. The methods are estimated to be accurate to within a factor of two.

FOREWORD

This report is one in a series that describes the development of separations processes for purifying ^{244}Cm produced in Savannah River reactors. The series is being issued under the general title *Curium Process Development.* Following the general title, a roman numeral designates the subject area of the report and an arabic numeral designates the series report number in that subject area. A subtitle describes the content of each report. Subject areas foreseen for this series are:

I. General Process Description
II. Chemical Processing Steps
III. Analytical Chemistry Support
IV. Equipment Development and Testing

Reports issued in this series include:

I. *General Process Description* by I. D. Eubanks and G. A. Burney (USAEC Report DP-1009).

II-1. *Separation of Americium from Curium by Precipitation of* $K_3AmO_2(Co_3)_2$ by G. A. Burney (USAEC Report DP-1109).

III-1. *Analytical Techniques for Characterizing Solvent* by R. Narvaez (USAEC Report DP-1010).

III-2. *Identification of Solvent Degradation Products* by D. L. West and R. Narvaez (USAEC Report DP-1016).

III-3. *Analytical Control* by E. K. Dukes (USAEC Report DP-1039).

III-4. *Evaluation of Potential Hazards from Chlorination of Amines and Ammonia* by D. L. West, M. L. Hyder, G. A. Burney, and W. E. Prout (USAEC Report DP-1142).

III-5. *Quantitative Determination of Diethylbenzene in Air* by B. Tiffany (USAEC Report DP-1230).

III-6. *Characterization of Emulsions Formed in Curium Solvent Extraction* by D. A. Brown and A. L. Marston (USAEC Report DP-1215).

IV. *Equipment Development and Testing* by A. A. Kishbaugh, H. Bull, III, G. W. Gibson, Jr., and L. F. Landon (USAEC Report DP-1146).

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INTRODUCTION

Curium is produced in Savannah River reactors by irradiating target elements of plutonium.[1] Because of its high specific power of 2.65 watts per gram, ^{244}Cm is a useful radioisotopic power source. In addition, ^{244}Cm and ^{243}Am, are precursors in the reactor production of ^{252}Cf, an isotope with numerous proposed uses.[2]

Several kilograms of curium produced at Savannah River have been purified,[3] with curium oxide or a mixed oxide of curium and americium as the final product. Curium for heat source use must be relatively free of common metallic impurities to minimize the problems of incompatibility with encapsulating materials at high operating temperatures. Curium or mixed curium-americium oxide of lower purity may be acceptable for neutron irradiation to produce transcurium isotopes, provided the impurities do not have undesirable nuclear or metallurgical properties.

This report describes the development of an emission spectrochemical method for determining aluminum, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, silicon, silver, sodium, tin, zinc, and zirconium in curium oxide and mixed curium-americium oxide. A spectrochemical method developed for determining tantalum has been reported previously.[4] Spectrochemical methods have also been developed for determining americium in high-purity curium oxide, and for determining the americium/curium ratio in mixed oxide.[5]

BACKGROUND

The emission spectra of most of the actinides are so rich in lines that the arcing of even milligram quantities will essentially obscure even the strongest lines of most metallic impurities (Figure 1). For this reason, some separation technique must be used before or during the emission spectrographic determination of trace quantities of metallic impurities in curium oxide and mixed curium-americium oxide. Solvent extraction,[6,7] ion exchange,[8] and carrier distillation[9] techniques have been used for separating various actinides from metallic impurities. Solvent extraction and ion exchange techniques are time-consuming and not sufficiently general in application.

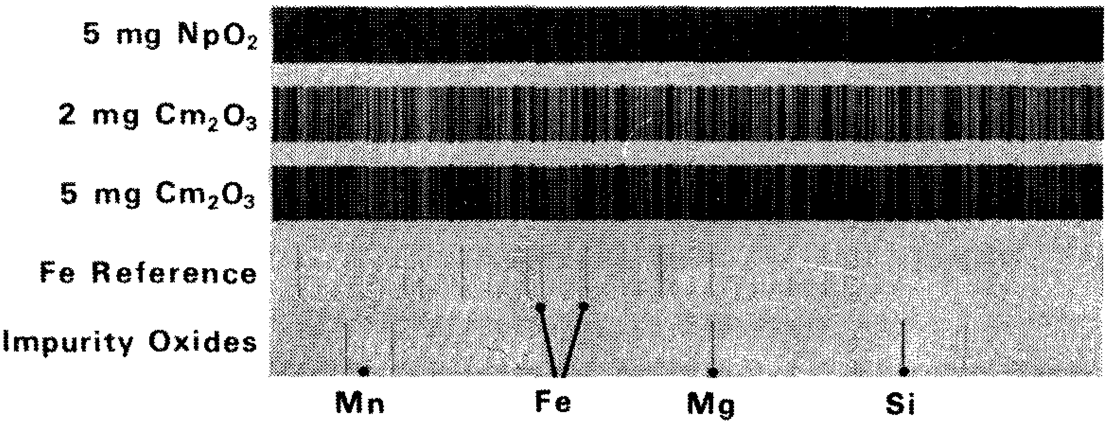

FIG. 1 ARC SPECTRA IN THE 2850Å Region

The carrier distillation method was originally used in the emission spectrographic determination of metallic impurities in uranium base materials. This technique is based on the fractional distillation of impurity metal oxides at 2200 to 2800°C from a graphite cup electrode containing the sample mixed with gallium oxide. The gallium oxide serves as the carrier during arcing of the sample in much the same way that water is the carrier in steam distillation. In the analysis of curium oxides, the carrier distillation technique is used to determine those metallic impurities whose oxides boil at temperatures below the boiling point of curium oxide. Silver chloride and sodium fluoride have also been used as carriers, but they could not be used in this application because the determination of sodium and silver in curium oxide was required.

EQUIPMENT

A Bausch & Lomb Dual Grating Spectrograph is close-coupled to a glove box train as shown in Figure 2. The first three glove boxes are used for sample preparation; the fourth box is used for arcing the sample electrodes. Both gratings in the spectrograph are illuminated simultaneously, permitting the exposure of two 2 in. x 10 in. glass plates containing the same or different sensitized emulsions. For the carrier-distillation method described in this report, the "Kodak"* Spectrum Analysis No. 3 emulsion is used for photographing the ultraviolet region and "Kodak" Spectroscopic Emulsion No. 103 aF is used for the visible region. The sensitive lines emitted by potassium at 7664.9 and 7699.0Å are photographed on "Kodak" Spectroscopic Emulsion No. 1N. The sample spectra are compared with the spectra of a graded

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* Registered trademark of Eastman Kodak Co.

series of standards on an Applied Research Laboratories Spectroline Scanner, Model 22,000 densitometer.

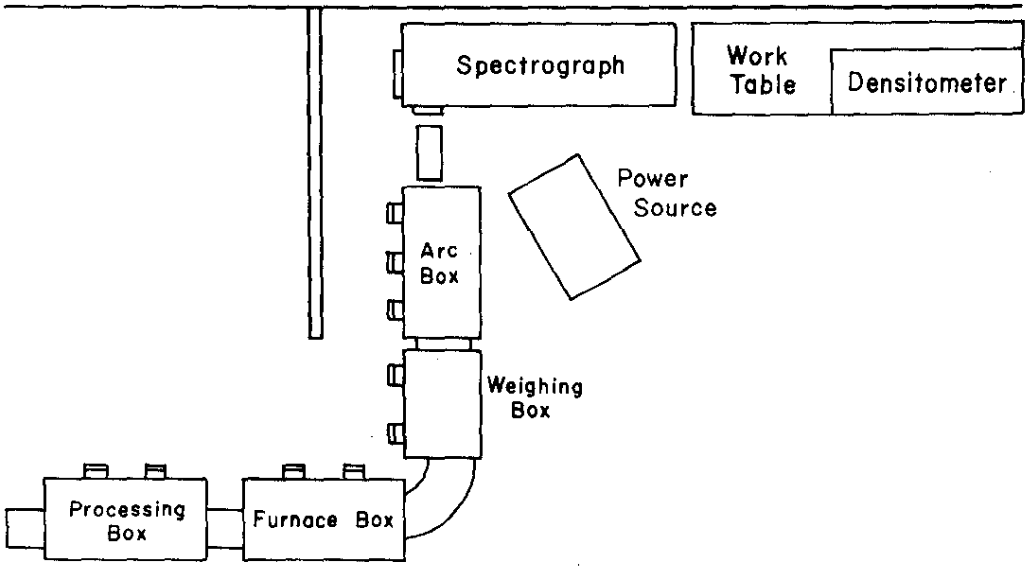

FIG. 2 SPECTROGRAPHIC LABORATORY

PREPARATION OF STANDARDS AND STANDARD PLATES

The relatively pure Ga_2O_3 used for preparing standards and analyzing samples was further purified by the method of Hoffman.[10] The impurity concentrations in Ga_2O_3 before and after purification are shown in Table I. Standards were prepared from "Spec-Pure"* or reagent-grade chemicals. Pure neptunium oxide was used as a stand-in for curium oxide in the preparation of standards because pure curium oxide was not available. Weighed quantities of the impurity element compounds were ground with purified gallium oxide in a titanium carbide mortar and pestle. Subsequent dilutions were made with gallium oxide to cover the concentration range 1-1000 ppm of impurity elements. For moving plate studies and the preparation of standard plates of the graded series of standards, 5 milligrams of neptunium oxide was mixed with 25 milligrams of each standard. Because zirconium determination is based on a total burn method, 5 milligrams of curium oxide was mixed with 25 milligrams of each gallium oxide standard for preparation of the zirconium standard plate.

In moving plate studies the volatilization rates of the impurity element oxides were determined. The photographic plates were moved

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* Registered trademark of Johnson and Matthey Chemical Co.

to a new position every 20 seconds, and the light emitted from the volatilized excited species was photographed (Figure 3). This study showed which elements could be determined by the carrier distillation method with adequate sensitivity, and, for a certain set of conditions, when the arc should be discontinued to avoid volatilizing interfering quantities (0.2 to 1 mg) of curium. The volatilization rates of some of the impurity element oxides are shown in Figure 4. The volatilization rates correlate with the boiling points of the impurity oxides as shown in Table II. Because of the refractory nature of its oxide, zirconium impurity could not be determined by the Ga_2O_3 carrier method; a total burn method was used instead.

The excitation and exposure conditions for determining 19 impurity elements by the carrier distillation method and for determining potassium and zirconium are given in Table III. The spectra of a graded series of standards are shown in Figure 5.

TABLE I

Metallic Impurities in Ga_2O_3

Element	Impurity Concentration, ppm Before Purification	Impurity Concentration, ppm After Purification	Element	Impurity Concentration, ppm Before Purification	Impurity Concentration, ppm After Purification
Ag	5	<1	Mn	<2	<2
Be	<2	<2	Mo	<1	<1
Bi	<1	<1	Na	<2	<2
Co	<2	<2	Ni	<2	<2
Cr	<1	<1	Pb	7	<1
Cu	12	0.5	Sb	<5	<5
Fe	<20	<20	Si	<5	<5
Li	<0.1	<0.1	Sn	<2	2
Mg	5	<5	Zn	<20	20

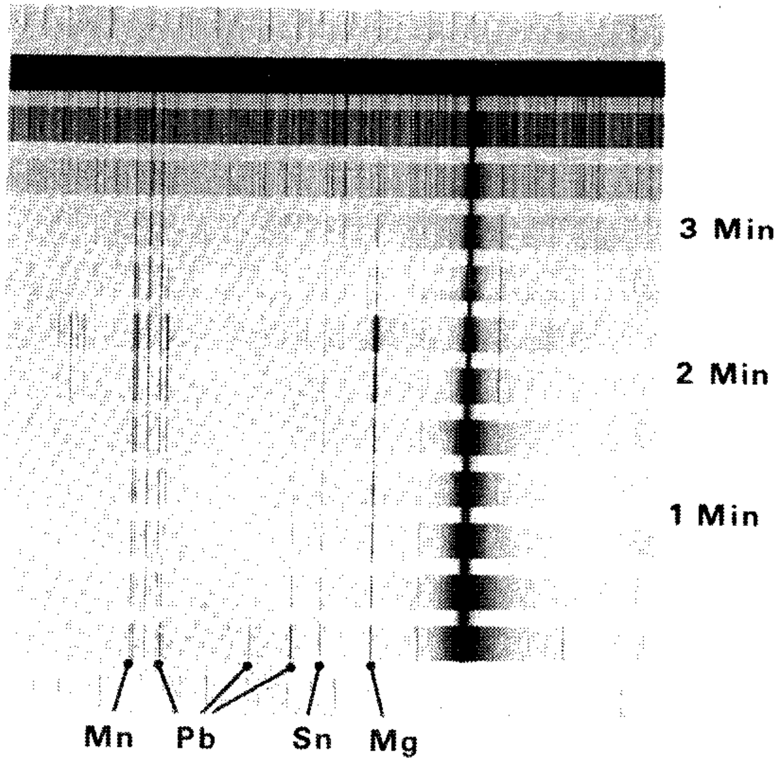

FIG. 3 MOVING PLATE STUDY OF THE 2850Å REGION

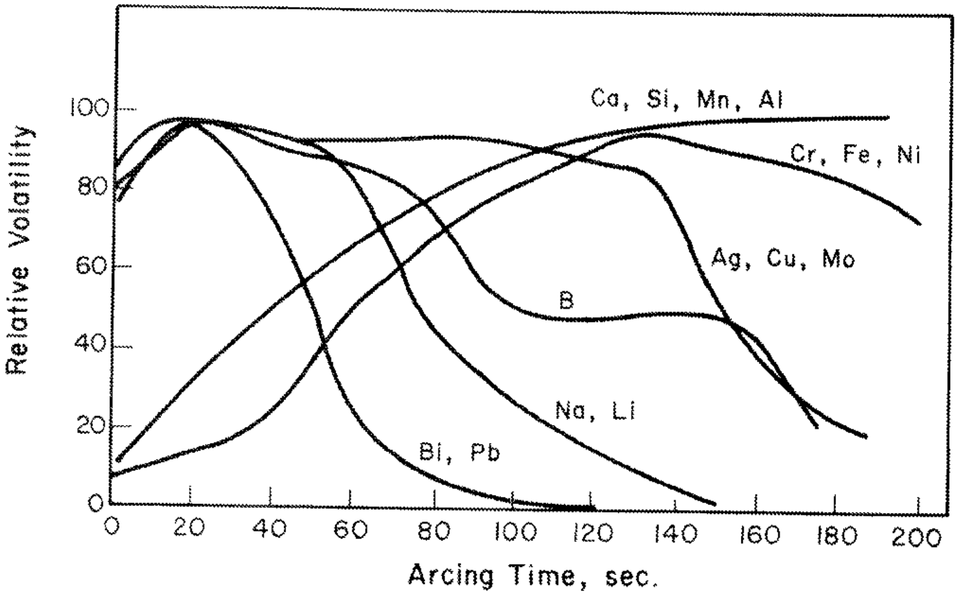

FIG. 4 VOLATILIZATION OF SOME IMPURITIES WITH Ga_2O_3 CARRIER

TABLE II

Boiling Points of Some Metallic Oxides

Compound	Boiling Point, °C	Compound	Boiling Point, °C
Li_2O	1000	Ga_2O_3	-
MoO_3	1428	MgO	2700
CdO	1500	CaO	2850
Bi_2O_3	1500	Cr_2O_3	3000
PbO	1475	MnO	4050
ZnO	1950	La_2O	4200
B_2O_3	2145	Cm_2O_3	~4000
Al_2O_3	2210	ZrO_2	4300
SiO_2	2230	Ta_2O_5	~4500

TABLE III

Excitation and Exposure Conditions for Carrier Distillation and Total Burn Methods

	Carrier Distillation		Total Burn
	19 Elements	Potassium	Zirconium
Current (closed circuit), amps	12.7	12.7	12.7
Volts	~130	~130	~130
Slit Width, microns	20	20	20
"A" Grating Setting, Å	2480-3460	7200-8100	2480-3460
"B" Grating Setting, Å	4200-6150	-	-
Electrode Gap, mm	4	4	4
Anode (lower electrode)	Met. Bay. 1278.2	Met. Bay. 1278.2	Met. Bay. 1278.2
Cathode (upper electrode)	UCP 1837B	UCP 1837B	UCP 1837B
Preburn, sec	0	0	190
Exposure, sec	190	90	150
Photographic Emulsion	S.A. 3, 103 aF	1N	S.A. 3

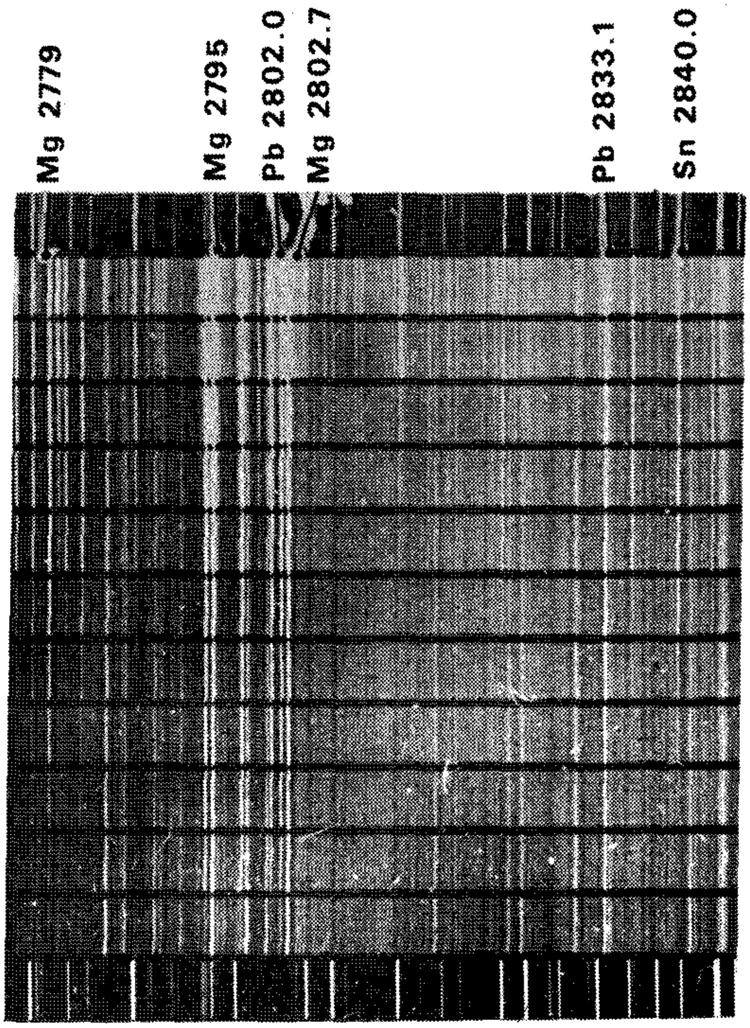

FIG. 5 STANDARD PLATE FOR VISUAL ESTIMATION IN THE 2850Å REGION

ANALYSIS OF SAMPLES

In the analysis of pure curium oxide or mixed americium-curium oxide, the samples are converted to the sesquioxide by heating at 850°C for 0.5 hour in a small platinum dish in a quartz-lined furnace. Twenty-two milligrams of the converted sample plus 110 milligrams of Ga_2O_3 are weighed and ground in a titanium carbide mortar to attain a uniform mixture. Thirty milligrams of the mixture is transferred to a graphite electrode. Duplicate exposures are made for those impurities determined by the carrier distillation methods using the conditions listed in Table III. After the completion of the 190-second burn cycle for the carrier distillation step, the plate is moved to a new position and the arcing is continued for an additional 150 seconds. During this latter time the 5 milligrams of curium oxide is completely volatilized, and the zirconium and curium spectra are photographed. The zirconium emission line at 3438.2Å is free of spectral interference and has adequate sensitivity for determining zirconium at concentrations as low as 150 parts per million in curium oxide. The impurity elements determined, their analytical lines, and their detection limits are shown in Table IV.

The precision of duplicate determinations by these emission spectrographic procedures is approximately ±25%; however, because the varying quantities of impurities in the sample affect the volatilization rates of all impurities, no greater claim for accuracy than a factor of two can be made.

TABLE IV

Spectrographic Determination of Impurities in 5 mg of Curium Oxide

Impurity	Wavelength, Å	Limit of Detection, ppm
Ag	3280.7	10
Al	3082.2-3092.7	25
B	2497.7	25
Bi	3067.7	10
Ca	4226.7	25
Cd	3261.1	5
Co	3453.3	50
Cr	4254.3	10
Cu	3247.5	10
Fe	3020.6, 2562.9, 2527.4	50
Li	6103.6	5
Mg	2802.7	10
Mo	3132.6	10
Mn	2794.8	10
Na	5890.0	25
Ni	3050.8	50
Pb	2833.1	10
Si	2516.1	50
Sn	2840.0, 3262.3	50
Zn	3302.6, 3345.0	250
K	7664.9-7699.0	5
Zr	3438.2-2568.9	150

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