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LOS ALAMOS of the NEW MEXICO
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THE X-RAY ABSORPTION EDGE DETERMINATION OF PLUTONIUM IN URANIUM-PLUTONIUM-MANGANESE ALLOYS

by

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ABSTRACT

Plutonium in uranium-plutonium-manganese alloys is determined using an x-ray absorption edge method in which the intensities of the secondary x-rays of niobium and molybdenum transmitted through the sample solution are measured. These secondary x-rays are generated by irradiating a niobium-molybdenum metal target with x-rays from a tungsten-target x-ray tube and are transmitted through an absorption cell filled successively with water, suitable standards, and the sample solution. The L III absorption edge for plutonium at 0.686 A. occurs between the $K\beta_1$ line for niobium and the $K\alpha$ line for molybdenum at 0.666 and 0.710 A., respectively. Measured transmitted intensities of these lines are related to plutonium concentrations using accepted absorption principles. The method is applicable to the determination of plutonium concentrations in the range between 30 and 100% with relative standard deviations in the range between 0.91 and 0.55%. Only radon, radium, neptunium, and americium have absorption edges between the x-ray lines used for analysis and cause interference.

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INTRODUCTION

A rapid and precise analytical method was required for determining greater than 30 percent of plutonium in ternary alloys of uranium-plutonium-manganese which are being considered as possible fuels in the LAMPRE program. X-Ray absorption edge techniques are well suited for determinations of this type because they do not require separations that are necessary in usual chemical methods of analysis. In addition, x-ray absorption edge methods, being less susceptible to interference by other elements, are preferred over x-ray fluorescence methods for determination of major constituents. In x-ray absorption edge analysis, the intensities for two x-ray energies, one located on each side of a suitable absorption edge of the element being determined, are transmitted through a cell of suitable path length filled successively with water, a blank solution containing major impurity elements expected in the sample, a solution of known plutonium content, and the sample. Transmitted intensities are related to concentration using the equation:

$$\text{Concn., mg./ml.} = k_1 \log (I_1^o/I_1) - k_2 \log (I_2^o/I_2) \qquad (1)$$

In this equation I_1^o and I_2^o are transmitted intensities through water at wavelengths λ_1 and λ_2, respectively; I_1 and I_2 are transmitted intensities through the blank, known solution, or sample solutions at the respective wavelengths; and k_1 and k_2 are constants. Values for k_1 and k_2 are determined from the blank and known solutions.

Plutonium has an L III absorption edge at 0.686 angstroms. From a consideration of x-ray energies, a molybdenum-technetium secondary target emitting strong Kα x-ray lines at 0.710 and 0.674 angstroms would be the most advantageous choice. However, technetium is rare and radioactive. Therefore, another element emitting an x-ray at an energy slightly greater than the energy of the plutonium L III edge was sought. Ruthenium was considered, but the wavelength of its Kα line (0.644 angstrom) is too short. This wide separation in wavelength of the molybdenum and ruthenium lines would greatly reduce the selectivity of the method, and lower concentrations of the matrix elements could cause interference. For these reasons niobium, having a $K\beta_1$ x-ray line at 0.666 angstrom, was selected although the intensity of its x-ray is only 20 percent of that of a Kα line in the same wavelength region.

CAUTION

Any work involving the handling of plutonium-containing material should be done under approved conditions and in laboratories designed for adequate protection of the worker. Rules such as those recommended by the Health Division of the Los Alamos Scientific Laboratory for safe handling of such materials should be rigidly followed.

The high operating voltages of the x-ray equipment and the generated x-rays are potential hazards requiring care in operation and adequate shielding and safety interlocks to protect the worker. Regular monitoring to detect stray x-rays in the vicinity of the equipment should be frequently and routinely performed.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical, Ainsworth Model BCT or similar instrument.

Niobium-molybdenum alloy disc, approximately one inch in diameter.

Sample cell, polystyrene, 1.0-cm. path length and 1.5-cm. path length.(2)

Syringe, hypodermic, 5.0-ml., with 15-gauge, 3.5-cm. stainless steel hypodermic needles.

X-ray spectrograph, Philips Electronics Corporation or similar instrument, equipped with lithium fluoride analyzing crystal, tungsten-target x-ray tube, scintillation detector with associated electronic circuitry, and modification for absorption edge analysis.(2) In addition, the original power supply to the detector was replaced with a Baird-Atomic, Model 312 A, high-voltage d.-c. power supply.

Reagents

Hydrochloric acid, 38%, reagent grade.

Manganese solution, 100 mg. of manganese per ml. Dissolve 10.000 grams of pure manganese metal with 70% nitric acid, and dilute with distilled water to 100.0 ml. in a volumetric flask.

Nitric acid, 70%, reagent grade.

Plutonium solution, 20 mg. of plutonium per ml. Dissolve 5.000 grams of freshly polished high purity plutonium metal with approximately 50 ml. of 38% hydrochloric acid. Dilute with distilled water to 250.0 ml. in a volumetric flask.

Uranium solution, 100 mg. of uranium per ml. Wash 11 to 12 grams of uranium metal turnings in dilute nitric acid, rinse in methyl chloroform, and dry in air. Slowly dissolve 10.000 grams of the cleaned uranium metal turnings by adding successive small volumes of 70% nitric acid, and dilute with distilled water to 100.0 ml. in a volumetric flask.

SAMPLING

Samples of uranium-plutonium-manganese alloy are generally received in the form of turnings, rods, or chunks. Samples selected for analysis should weigh approximately 200 milligrams and contain greater than 60 milligrams of plutonium.

X-RAY OPERATING CONDITIONS

X-ray tube: Tungsten target, Machlett FA 60
Potential: 50-kv
Current: 40-ma
Counter: Scintillation
Counter voltage: 680
Scaler input signal: Fixed count
Rate meter scale factor: Off
S-P scale factor: 8
Count register: 1,000
Scaler scale factor: 8, 16, 32, 64, or 128
Analyzing crystal: LiF (2d = 4.028 A.)

RECOMMENDED PROCEDURE

Accurately weigh a sample of approximately 200 mg. of the alloy into a calibrated 10.0-ml. volumetric flask, and slowly add 4.0 ml. of 38% hydrochloric acid to sustain dissolution at a moderate rate. When dissolution is complete, dilute the solution to volume with distilled water. Using aliquots of the known solutions of manganese, plutonium, and uranium, prepare 10.0-ml. solutions containing: (a) 150 mg. (1.5 ml.) of uranium, 50 mg. (0.5 ml.) of manganese, and 4.0 ml. of 38% hydrochloric acid; and (b) 50 mg. (0.5 ml.) each of uranium and manganese, 100 mg. (5 ml.) of plutonium, and 4.0 ml. of 38% hydrochloric acid. Dilute each solution to volume with distilled water. Using the absorption cell having a 1.0-cm. path length, measure successively the transmitted intensities of the $K\alpha$ x-ray line for molybdenum and the $K\beta_1$ x-ray line for niobium through water, known solution (a), known solution (b), and the sample, accumulating a minimum of 128,000 counts at each x-ray line. Correct all measured count times for coincidence loss by subtracting 4.0 seconds per million counts accumulated. Calculate the intensity of each line using the equation:

$$\text{Intensity, counts/sec.} = \frac{\text{counts accumulated}}{\text{seconds, corrected}} \tag{2}$$

With power to the x-ray tube turned off, determine the noise level of the counter circuitry and subtract this from all intensity measurements. Determine the ratio of intensity transmitted through water to the intensity transmitted through each solution at each of the two wavelengths using the appropriate equation:

$$R_1 = \text{ratio (Nb } K\beta_1) = \frac{\text{corrected counts/sec., water}}{\text{corrected counts/sec., sample}} \qquad (3)$$

$$R_2 = \text{ratio (Mo } K\alpha) = \frac{\text{corrected counts/sec., water}}{\text{corrected counts/sec., sample}} \qquad (4)$$

Using a table of five-place logarithms, determine the logarithm of each ratio. Determine the values for k_1 and k_2 from data for blank and known solutions (a) and (b), then determine the plutonium content of the samples using the equation:

$$\text{Concn. Pu, mg./ml.} = k_1 \log R_1 - k_2 \log R_2 \qquad (5)$$

which is essentially the same as Equation (1). (For the blank and known solutions, the concentrations are known, and k_1 and k_2 are calculated; using the calculated values for k_1 and k_2, the concentration is calculated for the sample.) Determine the plutonium content of the sample using the equation:

$$\text{Concn. Pu, percent} = \frac{\text{concn. Pu, mg./ml. x 1,000}}{\text{sample weight, mg.}} \qquad (6)$$

RELIABILITY

Standard samples of uranium-plutonium-manganese alloy were not available for analysis. Therefore, the reliability of the method is based upon analysis of solutions prepared to contain known concentrations of uranium, plutonium, and manganese. Fourteen determinations of a blank (no plutonium) and each of three plutonium concentrations were made. The total of the three elements was 200 milligrams in each determination. Relative standard deviations of 0.5 to 0.9 percent were obtained (Table I).

Table I

Precision of the X-Ray Absorption Edge Method for Determining Plutonium in Uranium-Plutonium-Manganese Alloys

Pu, mg./ml.	Pu*, %	Standard deviation, mg./ml.	Relative standard deviation, %
0.00	0.0	0.02	----
6.00	30.0	0.06	0.91
10.00	50.0	0.05	0.50
20.00	100.0	0.11	0.55

*Based upon total of 200 mg. of the three metals in each case.

Elements having an absorption edge between the Kα x-ray line for molybdenum and the Kβ_1 line for niobium are expected to cause a positive bias in the concentration of plutonium found. These elements are radon, radium, neptunium, and americium. Radon and radium are too rare to warrant further consideration. Neptunium and americium are possibilities that must be considered, and any sample suspected of containing significant concentrations (greater than approximately 0.2 percent) of these elements should be analyzed radiochemically. The concentrations determined in this manner can be subtracted directly from the measured plutonium concentration because the mass absorption coefficients of these two elements at the two wavelengths are approximately equal to the respective absorption coefficients of plutonium.

Interference in x-ray absorption edge methods also is caused by variations in the absorption by the matrix. The magnitude of the matrix effect is related to the k_1/k_2 by the equation:

$$k_1/k_2 = (\lambda_2/\lambda_1)^n \tag{7}$$

where λ_1 and λ_2 are the wavelengths of the x-ray lines used and n, which is a number dependent on the matrix elements, generally has a value of approximately 2.3 to 3.(1) For the Kβ_1 x-ray line for niobium and the Kα line for molybdenum, k_1/k_2 is predicted to vary in the range of 1.16 to 1.22. Measured values for k_1/k_2 in the presence of various matrix elements (Table II) indicate that the experimental values are higher than predicted. These high values may be attributed to overlap of the $K\beta_1$, β_2 doublet for niobium which was not considered in the calculation of the theoretical range of values. The observed spread in values for k_1/k_2 indicates that elements expected in the sample as major constituents should be added to known solutions.

Table II

Determination of k_1/k_2 in the Presence of Various Elements

Element	Atomic number	(μ/ρ)*	X-Ray region where analytical line occurs	Experimental k_1/k_2
Ca	20	18.6	Below K Edge	1.223 ± 0.010
Mn	25	34	Below K Edge	1.221 ± "
Zn	30	58	Below K Edge	1.203 ± "
Sr	38	107	Near K Edge	1.226 ± "
Y	39	114	Near K Edge	1.237 ± "
Nb	41	18.6	Between K and L III Edges	1.217 ± "
Mo	42	20	Between K and L III Edges	1.207 ± "
Cd	48	29	Between K and L III Edges	1.211 ± "
I	53	38.5	Between K and L III Edges	1.211 ± "
Ce	58	49.5	Between K and L III Edges	1.205 ± "
Bi	83	138	Near L I Edge	1.195 ± "
Th	90	91	Between L II and L III Edges	1.200 ± "
U	92	125	Between L II and L III Edges	1.187 ± "

*Mo Kα(3)

The method was applied to the determination of plutonium in mixtures prepared to simulate samples of uranium-plutonium-manganese alloys containing greater than 30 percent of plutonium and various amounts of uranium and manganese. Cells having 1.0- or 1.5-centimeter path lengths were used in these determinations. The results of single determinations (Tables III and IV) indicate that recoveries are within the 95 percent confidence limits of the method. The cell having the shorter path length (1.0-centimeter) is recommended because it enables a more rapid analysis without loss in precision or accuracy.

Table III

X-Ray Absorption Edge Spectrographic Determination of Plutonium in the Presence of Uranium and Manganese
(1.0-cm. cell)

Pu concn., %	Mn concn., %	U concn., %	Pu recovered, %	Error, percent relative
0.00	100.0	0.0	-0.08	----
30.00	70.0	0.0	30.0	0.0
	30.0	40.0	29.6	-1.3
	0.0	70.0	29.8	-0.7
50.00	50.0	0.0	49.7	-0.6
	25.0	25.0	49.9	-0.2
	0.0	50.0	50.0	0.0
80.00	20.0	0.0	79.6	-0.5
	10.0	10.0	80.0	0.0
	0.0	20.0	79.6	-0.5

Table IV

X-Ray Absorption Edge Spectrographic Determination of Plutonium in the Presence of Uranium and Manganese
(1.5-cm. cell)

Pu concn., %	Mn concn., %	U concn., %	Pu recovered, %	Error, percent relative
0.00	100.0	0.0	0.05	----
30.00	70.0	0.0	30.4	1.3
	30.0	40.0	29.7	-1.0
	0.0	70.0	30.3	1.0
50.00	50.0	0.0	49.8	-0.4
	25.0	25.0	50.1	0.2
	0.0	50.0	49.9	-0.2
80.00	20.0	0.0	79.6	-0.5
	10.0	10.0	79.2	-1.0
	0.0	20.0	79.0	-1.2

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