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Carrier-Distillation Analysis of PuO_2

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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ABSTRACT

Sample particle size is one of the parameters that must be controlled to ensure the similarity of samples and standards necessary for reliable spectrochemical analysis. In spectrochemical carrier-distillation analysis of PuO_2 , significantly greater intensities are obtained from the impurity elements when the particle size of the PuO_2 is 45 μm or less. Large PuO_2 particles, when present, reduce the intensities of the impurities and of cobalt, the internal standard. Because these intensity changes are not the same for each element, accurate spectrochemical values cannot be obtained when large PuO_2 particles are present. Proper preparation of the PuO_2 can be done easily by mortar grinding and mechanical mixing.

I. INTRODUCTION

Spectrographic analysis of PuO_2 at the Los Alamos Scientific Laboratory (LASL) involved an adaptation of the carrier-distillation technique developed by Scribner and Mullins¹ for uranium analysis. With this method, a plutonium-metal sample is ignited to PuO_2 , then ground in a mortar for 120 s. A weighed portion of a mixture of carrier compound, Ga_2O_3 , and the internal standard, cobalt as Co_3O_4 , (CIS), is added to a weighed portion of the ground PuO_2 . We use cobalt as the internal standard because during analysis it acts in a manner similar to iron, nickel, chromium, silicon, and some of the other elements of interest. The PuO_2 and CIS mixture is then ground in a mortar for 300 s, and portions are weighed into graphite electrodes, packed, vented, and arced. The resulting spectra are recorded photographically, and specific impurity contents are determined by densitometry.

In 1960, Muntz² conducted an investigation to determine the necessary conditions for substituting mechanical mixing for the 300 s of grinding the PuO_2 and CIS in a mortar. Muntz determined that the ground PuO_2 and CIS could be adequately mixed in a plastic vial containing two plastic beads using the Wig-L-Bug mixer. Muntz noted

that the initial grinding of the ignited plutonium in a mortar was important in obtaining accurate answers when using the plastic vials and the mechanical mixer.

The particle size of PuO_2 could be reduced sufficiently by grinding in a mortar, then mixing the PuO_2 plus CIS in either a mortar or a Wig-L-Bug mixer. The present work was undertaken to determine more fully the effect of particle size on the carrier-distillation analysis of PuO_2 and to explain how the difficulties of insufficient grinding can be avoided.

II. APPARATUS AND REAGENTS

A. Apparatus

Balance, keyboard, chainweight, 0.05-mg sensitivity.

Crucibles, platinum, 1.3-ml.

Electrodes, graphite, grade AGKSP, National Carbon Company.

Upper: No. L-4036

Lower: No. L-9027

Furnace, platinum-lined, capable of temperatures to 1000°C.

Mechanical mixer, Crescent Dental Manufacturing Company, Wig-L-Bug No. 3A, or equivalent.

Microphotometer, recording, Jarrell-Ash Company No. 2310, or equivalent.

Microspoon, platinum.

Mortar, titanium-carbide, 38-mm bowl.

Pestle, tungsten rod, 13-mm-diam.

Photographic emulsion, Eastman SA-1 plates.

Screens, nylon monofilament cloth, No. 100 (150 μm), No. 200 (75 μm), and No. 325 (45 μm), Spex Industries Nos. 3541, 3542, and 3543, respectively.

Spectrograph, 3.4-m, Ebert mounting with 1180 grooves/mm grating.

Venting tool, titanium.

Vials, plastic, 25.4-mm-long, 12.7-mm-diam, with 4.76-mm-diam plastic beads, Spex Industries No. 3111.

B. Reagents

Carrier-Internal-Standard. (CIS) 14.7840-g Ga_2O_3 plus 0.2160-g Co_3O_4 are mixed and ground in a mortar until the entire mixture passes through a No. 200 mesh screen.

PuO₂ Standard. A dry-mixed standard was prepared by blending known quantities of 22 metal oxides with pure PuO_2 . The PuO_2 was ground in a mortar before the metal oxides were added. The metal oxides and the PuO_2 were blended by being ground in a mortar.

PuO₂ Sample. Fifteen grams of PuO_2 were prepared by igniting chunks of plutonium metal. The entire 15 g of PuO_2 were mixed and ground in a mortar for 3750 s (25 s/100 mg of PuO_2). The PuO_2 receiving this amount of grinding was designated P_1 . A 5-g portion of P_1 was further ground in a mortar for 1750 s; the total grinding received was 60 s for each 100 mg. This 5-g portion was labeled P_2 . A second 5-g portion of P_1 was further ground in a mortar such that the total grinding received was 120 s for each 100 mg. This last 5-g portion was designated P_3 . P_1 , P_2 , and P_3 were identical materials differing only in the time of grinding in a mortar. The impurity content of the three designated portions of PuO_2 should also be identical because the original 15 g of PuO_2 were homogenized by mortar grinding before being separated into P_1 , P_2 , and P_3 . Other portions of the same parent sample of plutonium metal were analyzed repeatedly, and their impurity content was well characterized. The amount of cobalt present in the material was less than 2 ppm.

III. EXPERIMENTAL

A. Determining Particle Size Distribution in P_1 , P_2 , and P_3

Samples P_1 , P_2 , and P_3 were sieved using No. 100 (150 μm), No. 200 (75 μm), and No. 325 (45 μm) mesh screens. Table I shows the particle size distribution for P_1 , P_2 , P_3 , and the PuO_2 dry-mixed standard.

B. Analysis of Each Particle Size Group

We analyzed the three groups of particle sizes shown in Table I. One sample was composed of 150- to 75- μm particles, the second sample was composed of 75- to 45- μm particles, and the third sample was composed of particles smaller than 45 μm . For this analysis, we used the carrier-distillation technique using plastic vials and the Wig-L-Bug mixer.

Figure 1 shows the relative intensities of five elements vs the three particle size groups. Each point represents the average of six values. The data indicate that impurities in small PuO_2 particles produce greater relative intensities than impurities in larger PuO_2 particles. Table II shows the percentage increase in relative intensity for impurity elements from the largest PuO_2 particle size category (150 to 75 μm) to the smallest particle size category (smaller than 45 μm).

TABLE I
PARTICLE SIZE DISTRIBUTION FOR
 P_1 , P_2 , P_3 , AND PuO_2 STANDARD

	Particle Size Distribution (%)		
	150 to 75 μm	75 to 45 μm	Smaller than 45 μm
P_1	20	46	34
P_2	0	39	61
P_3	0	0	100
PuO_2 Standard	0	0	100

Fig. 1.

The relative intensity of the impurity elements and the internal standard, cobalt, as a function of the PuO_2 particle size.

TABLE II

INCREASE IN RELATIVE INTENSITY FOR IMPURITY ELEMENTS FROM LARGEST TO SMALLEST PuO_2 PARTICLE SIZE

Element	Increase in Intensity (%)
Fe	85
Cr	210
Ni	215
Si	280
Co ^a	117

^aInternal standard.

C. Response of Cobalt, the Internal Standard

The relative intensity of cobalt increases more than 100% from the largest PuO_2 particle samples to the smallest PuO_2 particle samples. The particle size of cobalt is constant (less than 45 μm); therefore, an explanation other than the particle size of cobalt is needed for the

variation in its relative intensity for the different PuO_2 particle sizes.

Microscopic examination of the plastic vials used in sample preparation revealed that the plastic surface was coated with embedded particles of PuO_2 .³ A possible explanation for the variation in relative intensities as a function of particle size is that the larger, more abrasive PuO_2 particles were preferentially embedding the internal standard, cobalt, into the plastic vial during sample preparation, thus reducing the amount of cobalt available to be sampled. To check on this possibility, we analyzed four pairs of plastic vials that were used to prepare PuO_2 for the carrier-distillation technique. We used the first of each pair of vials to prepare coarse PuO_2 particles and the second of each pair to prepare fine PuO_2 particles. Two electrode portions of 100 mg were taken from each vial and analyzed. Each of the four sets of duplicates from the vials used for coarse PuO_2 particles had significantly lower cobalt line intensity than the four sets of duplicates from the vials used to prepare the fine PuO_2 particles.

Next we analyzed the plastic vials for cobalt. Each of the four pairs of vials used in the above test was placed in a platinum crucible containing 200 mg of pure, cobalt-free PuO_2 . The plastic vials were melted, then ashed in a furnace. The contents of each crucible were analyzed by the carrier-distillation technique. The intensity of the cobalt lines from the four vials containing the coarse PuO_2 was equal to that from the four vials containing the fine PuO_2 . Thus, the possibility was disproved that the large, coarse PuO_2 particles were preferentially embedding cobalt into the plastic vials.

Another possible cause of the varying intensity of cobalt was that the coarse and abrasive PuO_2 particles might be picking up plastic from the Wig-L-Bug vials during sample preparation. An experiment was conducted in which coarse and fine PuO_2 was prepared for analysis using the plastic Wig-L-Bug vials. The samples were removed from the vials, placed in platinum crucibles, and heated in a muffle furnace at 500°C for 1800 s in flowing oxygen to remove any plastic present. The samples were then weighed into graphite electrodes and analyzed in the routine manner. The duplicate set of coarse PuO_2 produced significantly lower cobalt intensities than those from the set of fine PuO_2 . This experiment showed that plastic in the coarse PuO_2 was not the cause of the lower cobalt intensity.

During our investigation, the reaction of cobalt was observed under three conditions that may provide the explanation for its lower intensity with coarse PuO_2 particles. The first condition was grinding PuO_2 and CIS in a mortar for different times (Fig. 2A). The second condition was mixing PuO_2 and CIS in a vial with two plastic beads (Fig. 2B). The third condition was mixing PuO_2 and CIS in a vial without the two plastic beads (Fig. 2C).

Fig. 2.

(A) The relative intensity of cobalt as a function of seconds of mortar grinding; (B) the relative intensity of cobalt from coarse and fine PuO₂ samples prepared with two beads; and (C) the relative intensity of cobalt from coarse and fine PuO₂ samples prepared without two beads.

Figure 2A shows the response of the relative intensity of cobalt at various times of grinding coarse PuO₂ and CIS. The time is based on seconds of grinding in a mortar per 100 mg of PuO₂. The zero time of grinding consists of mixing coarse PuO₂ and CIS together in a mortar using a platinum weighing spoon. All samples were weighed into electrodes, then analyzed routinely.

As shown in Fig. 2A, grinding in a mortar up to 25 s results in a lower relative intensity for cobalt than no grinding. Further grinding of the coarse PuO₂ and CIS produces an increase in the relative intensity of cobalt.

In Fig. 2B, the relative intensity of cobalt obtained from coarse PuO₂ is much lower than that obtained from fine PuO₂. Both sizes of PuO₂ were prepared for analysis using plastic Wig-L-Bug vials and two plastic beads.

Figure 2C shows the relative intensity of cobalt obtained by preparing coarse and fine PuO₂ using plastic Wig-L-Bug vials without the two plastic beads. The relative intensity of cobalt from coarse PuO₂ is less than that from fine PuO₂.

A possible explanation for the lower relative intensity of cobalt when mixed with coarse particles of PuO₂ is the entrapment of cobalt particles (45 μ m) by the coarse PuO₂. Douglass³ found, by microscopic examination, that unground PuO₂ consisted of large irregular-shaped particles. The combination of coarse irregular-shaped PuO₂ particles, CIS, and a mechanism causing the PuO₂ particles to collide and scrape could thus entrap cobalt in the cracks and fractures of the large PuO₂ particles. In Fig. 2C, the cobalt is entrapped by the collision of the large PuO₂ particles during the shaking of the vial in the

Wig-L-Bug mixer. The mechanism in Fig. 2A is the pestle. There are two actions occurring during the grinding of PuO₂ in a mortar. One action, during the first part of the grinding, is the entrapment of cobalt as the pestle rubs the PuO₂ particles together. The second action is the reduction in particle size of the PuO₂. This second action is the more important during the last part of the grinding as the PuO₂ particle size is reduced such that both the impurity elements and the cobalt can produce higher relative intensities. The two plastic beads are the mechanism in the case shown in Fig. 2B. We agree with Muntz² that shaking PuO₂ in a Wig-L-Bug vial with two beads will mix the sample but does little grinding. Therefore, the two beads are the most effective mechanism, of the three conditions tested, for entrapping cobalt in coarse PuO₂ particles.

The data shown in Figs. 2A, 2B, and 2C seem to indicate that the principal factor causing the lower relative intensity for cobalt, using plastic vials, beads, and the Wig-L-Bug mechanical mixer, is the entrapping of cobalt by the large and irregular-shaped PuO₂ particles. Exact details of this entrapment are not now known.

D. Analysis of P₁, P₂, and P₃

The three PuO₂ materials, P₁, P₂, and P₃, were analyzed by the carrier-distillation method using plastic vials, plastic beads, and the Wig-L-Bug mixer to prepare the electrode samples. The relative intensities for iron, nickel, chromium, silicon, and the internal standard, cobalt, are plotted in Fig. 3. As the average size of the PuO₂ particles

Fig. 3.

The relative intensity of the impurity elements and the internal standard, cobalt, in P₁, P₂, and P₃.

in P_1 , P_2 , and P_3 decreases, the relative intensity of the impurity elements and cobalt increases. Table III shows the percentage increase in intensity for the five elements from P_1 to P_3 .

TABLE III

INCREASE IN RELATIVE INTENSITY
FOR IMPURITY ELEMENTS FROM P_1 TO P_3

Element	Intensity		Increase (%)
	P_1	P_3	
Fe	67	92	37
Cr	49	73	49
Ni	51	90	76
Si	40	73	80
Co	33	63	91

P_1 , P_2 , and P_3 are identical in impurity content, differing only in PuO_2 particle size distribution. Note that the percentage increase in relative intensities from P_1 to P_3 is not the same for all elements.

Figure 4 shows a plot of concentration in ppm for P_1 , P_2 , and P_3 . The concentration in ppm was obtained by plotting the ratio of the intensity of an impurity element

Fig. 4.

The concentration of impurity elements in P_1 , P_2 , and P_3 .

to the intensity of the internal standard (e.g., $I_{\text{Fe}}/I_{\text{Co}}$) vs concentration for dry-mixed standards. The concentration for an impurity element in a sample is then computed from the standard curve.

An explanation for the decrease in the concentration of iron is based on the data in Table III. The relative intensity for iron increased only 37% from P_1 to P_3 , whereas that for cobalt increased 91%. Consequently, the intensity ratio, $I_{\text{Fe}}/I_{\text{Co}}$, as well as the resulting concentration of iron, will be smaller for P_3 than for P_1 . Silicon increased in relative intensity from P_1 to P_3 about as much as cobalt; therefore, the result in concentration is only slightly less for P_3 than for P_1 .

Figure 4 indicates that the apparent trend of decreasing concentrations from P_1 to P_2 was broken for all impurity elements at P_2 and that there is a plateau of essentially equal values from P_2 to P_3 . This plateau indicates that if no large PuO_2 particles are present in the sample, a large source of error has been removed from the carrier-distillation technique.

E. Source of Large Abrasive PuO_2 Particles

The presence of large, abrasive, and refractory particles of PuO_2 depends on the size and shape of the plutonium-metal sample before ignition. Waterbury et al.⁴ studied the ignition of plutonium metal and found that turnings burned more quickly and more completely than chunks at a given temperature. We observed that turnings produce a finely powdered oxide containing no large PuO_2 particles. The PuO_2 obtained by igniting chunks of plutonium metal produces large abrasive particles. This PuO_2 must be thoroughly ground in a mortar to reduce all PuO_2 particles to less than 45 μm .

F. Analysis of PuO_2

The PuO_2 used in this study was analyzed four times by four laboratories in 1972 both spectrographically and chemically. The PuO_2 was also analyzed by atomic absorption at LASL. A compilation of these results is given in Table IV.

The concentrations of impurity elements obtained for P_2 and P_3 agree with those values given in Table IV.

IV. CONCLUSION

The relative intensities of iron, chromium, nickel, and silicon depend on the particle size of the PuO_2 being analyzed. All of the relative intensities increase with decreasing particle size. Further, the line intensity of the added internal standard, cobalt, also increases with

TABLE IV
COMPILATION OF ANALYTICAL RESULTS
OF PuO₂

Element	Average Concentration (ppm)			
	Atomic Absorption	Spectrographic ^a	Chemical ^a	P ₂ and P ₃ ^b
Fe	345	345	350	340
Si	—	30	—	30
Ni	123	135	—	140
Cr	45	45	—	50

^aBy four laboratories.

^bAverage of data plotted in Fig. 4.

decreasing PuO₂ particle size when a mechanical mixer and plastic vials with beads are used. The results in ppm are essentially equal when the particle size of the PuO₂ sample is reduced to 45 μ m or less. This particle size is similar to that of the dry-mixed standards used. Only with this sample particle size do the results from the carrier-distillation method agree with the results from independent methods of analysis.

We also observed during our investigations that greater variability was obtained when working with coarse PuO₂ than with finely ground PuO₂. This variability is undoubtedly due to the varying quantities of particle sizes in a coarse sample.

A particle size of 45 μ m or less can be obtained for refractory PuO₂ samples by 60 s of vigorous grinding in a mortar per each 100 mg of PuO₂. The analyst should check the particle size, at least once, by proving that the ground PuO₂ will pass through a No. 325 mesh screen. A mechanical mixer can then be used for further mixing of the PuO₂.

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REFERENCES

1. B. F. Scribner and H. R. Mullins, "Carrier-Distillation Method for Spectrographic Analysis and its Application to the Analysis of Uranium-Base Materials," J. Res. Nat. Bur. Std., A, 37, 379-389 (1946).
2. J. H. Muntz, Los Alamos Scientific Laboratory, unpublished data, 1960.
3. R. M. Douglass, Los Alamos Scientific Laboratory, unpublished data, 1960.
4. Glenn R. Waterbury, R. M. Douglass, and Charles F. Metz, "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate, and Oxalate," Anal. Chem. 33, 1018 (1961).