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**A TOTAL BURN SPECTROGRAPHIC DETERMINATION
OF SILICON IN PLUTONIUM**

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INTRODUCTION

Metallic impurities in plutonium are usually determined by the carrier distillation-spectrographic method⁽¹⁾. Direct analysis of plutonium is avoided because of its complex emission spectrum which masks many of the spectral lines of the impurity elements. The carrier method eliminates plutonium spectral interference by causing the more volatile impurities to be selectively distilled from the excitation crater before plutonium volatilization occurs. A method based on fractional distillation, however, is subject to many variables which cannot all be controlled. Matrix effects furthermore, are significant in the carrier process.^(2,3,4) The rate and extent to which the impurities are distilled are a function of the matrix from which the distillation occurs. Such things as the density, particle size, and metallurgical history of the sample all contribute to the matrix effect. As a result, impurity concentrations measured by the carrier method could be in error. Such errors have been observed in this laboratory in the determination of silicon in plutonium. Silicon values appeared to be affected by the matrix by as much as a factor of forty on some samples. Comparisons of the carrier technique with other methods^(5,6) as well as comparisons among different laboratories⁽⁷⁾ have also shown wide differences.

The need for a method which is free from the variables discussed above is evident. Such a method would also serve as an independent check on the widely used carrier method. A possible solution to the problem lies in burning the sample completely in the direct current arc if plutonium spectral interference could be eliminated or minimized. According to Slavin,⁽⁸⁾ the total radiant energy emitted by an element is dependent only on the amount present provided the sample is burned to completion. Since the photographic plate is an integrating device, a measure of line density is a measure of the total energy emitted by an element and hence of

its concentration. Although other factors are involved, Slavin found surprisingly good correlation between concentration and energy as measured by the photographic plate for a wide variety of samples. Since plutonium spectral interference can be minimized by optical means, the total energy principle was investigated for the analysis of plutonium and was applied to the determination of silicon in plutonium.

SUMMARY

A total burn-spectrographic method has been applied to the determination of trace concentrations of silicon in plutonium. The sample is oxidized to plutonium dioxide, mixed with a germanium dioxide-graphite mixture containing tin internal standard, packed into cupped graphite electrodes, and burned to completion in a high amperage direct current arc. Plutonium spectral interference is minimized by optical means and by use of a less intense silicon line. The sensitivity is thereby decreased but is still sufficient to determine 25 ppm of silicon in plutonium. The precision of the method is estimated to be $\pm 8\%$ (relative standard deviation) at the 270 ppm level and $\pm 14\%$ at 40 ppm.

RESULTS AND DISCUSSION

Selection of Matrix

In applying the total energy principle, Slavin⁽⁸⁾ weighed a small amount (25 mg) of sample directly into a cupped graphite electrode for arc excitation. The weighing of such small quantities and the moving of sample-laden electrodes inside gloved boxes increase the chances for error using Slavin's technique. In addition, since plutonium standards with known impurity concentrations are not available, a procedure applicable to non-plutonium standards is desirable. The incorporation of an internal standard for quantitative analysis is also desirable. For the foregoing reasons, Slavin's total burn procedure was modified by mixing the sample with a diluent-buffer containing an internal standard. Weighing errors are thus decreased by weighing a larger amount of sample to be mixed with the diluent, weighing into electrodes is eliminated because of the presence of the internal standard which

also makes the method quantitative, and a common matrix is provided from sample to sample enabling the use of non-plutonium standards.

Many such buffer-diluents have been used for semiquantitative spectrographic methods. Germanium dioxide, used by Frisque⁽⁹⁾ and Jaycox,⁽¹⁰⁾ is a good diluent because it is rare in most samples, has a simple emission spectrum, is obtained in a high state of purity, and has a high ionization potential. In addition, the following compounds and metals with densities closer to that of plutonium dioxide were examined: Ag_2O , In_2O_3 , Sm_2O_3 , La_2O_3 , CeO_2 , ThO_2 , Bi_2O_3 , PtO , PbO , Tl_2O_3 , U_3O_8 , NiO , Nb , Ni , and Pd . Silicon contamination was found in Sm_2O_3 , La_2O_3 , CeO_2 , Bi_2O_3 , Tl_2O_3 , NiO , Nb , and Ni . Thorium oxide and uranium oxide emitted sparks during arcing making them unsafe for gloved box use. Palladium smoked strongly during arcing and coated the surfaces in the box. That left silver oxide and platinum oxide with the latter having a density closest to that of plutonium dioxide. A comparison of platinum oxide and germanium dioxide, however, showed no advantages in using the former. A 1:3 mixture of germanium dioxide and graphite used by Frisque⁽⁹⁾ and later by Smith⁽¹¹⁾ was applied to the total burn analysis of plutonium.

Selection of Silicon Analytical Line

With plutonium an additional complicating factor exists. Plutonium produces an extremely complex spectrum which interferes with the determination of many impurities, particularly at trace levels. That was the main reason for the development of the carrier method in the first place. If a minimum amount of plutonium consistent with high sensitivity were used and sufficient dispersion of the spectrograph were available, a direct burn procedure could be used.

The most sensitive silicon lines are those at 2881.60 Å and 2516.11Å. The reciprocal linear dispersion of the Bausch and Lomb Littrow spectrograph at 2881 Å is 3.8 Å/mm; at 2516 Å, 2.5 Å/mm. To take advantage of the greater dispersion at lower wavelengths, the Si 2516.11 Å line was used. In addition, plutonium spectral interference is less at the lower wavelength. Analysis of

a silicon - plutonium alloy, however, indicated plutonium spectral interference. High results at low silicon concentrations indicated that the plutonium spectrum was contributing to the darkening of the silicon line. Closer examination of the spectrogram did, indeed, reveal a plutonium line coincident with the Si 2516.11 A line. Si 2506.90 is free from plutonium interference. Although it is close to another line, presumably due to carbon, the two lines can be resolved. Si 2506.90, however, is a less sensitive line. Its use decreases the sensitivity of the method.

Selection of Internal Standard

A weak line of the matrix element or a strong line of an added element can be used as the internal standard. A weak germanium line at 2533.23 A and added scandium and tin at 2560.25 A and 2495.70 A, respectively were tested. Recovery and precision obtained on various National Bureau of Standards (NBS) standards and one New Brunswick Laboratory (NBL) standard showed that added scandium and tin both gave good results, with tin being slightly better. Sn 2495.70 A was selected as the internal standard. The data are summarized in Table I.

TABLE I

COMPARISON OF INTERNAL STANDARDS FOR SILICON DETERMINATION

Standard Analyzed	Number of Determinations	Ge 2533		Sc 2560		Sn 2495	
		Recovery, %	Relative $\sigma^{\oplus}$, %	Recovery, %	Relative $\sigma^{\oplus}$, %	Recovery, %	Relative $\sigma^{\oplus}$, %
NBS 104 ^(b)	14	74	± 15	87	± 14	104	± 12
NBS 671 ^(c)	15	86	± 18	116	± 9	100	± 9
NBS 78 ^(d)	14	92	± 12	97	± 17		
NBL 95-1 ^(e)	18	93	± 26	104	± 14		
		Ave. 86	± 18	101	± 14	102	± 11

$$(a) \text{ Relative } \sigma = \frac{100}{\bar{x}} \sigma \quad \text{where } \sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{M-1}}$$

(b) NBS 104 = burnt magnesite, 1.19% Si

(c) NBS 671 = nickel oxide, 0.047% Si

(d) NBS 78 = burnt refractory, 9.67% Si

(e) NBL 95-1 = U_3O_8 , 0.026% Si

Selection of Spectrographic Conditions

Frisque⁽⁹⁾ and Smith⁽¹¹⁾ used a 3:40 ratio of sample to germanium dioxide mix and burned thirty to forty milligrams of the resulting mixture in a 14 to 15 ampere d-c arc. To ensure complete burn of the sample, undercut electrodes were used for plutonium analysis and arced until the cup portion of the electrodes burned away. At 15 amperes, at least 180 seconds were required, but burning a large number of samples under those conditions caused a temperature rise in the arc stand gloved box. Shorter burning times and consequent cooler temperatures are preferable for working with anything as hazardous as plutonium. Applying the conditions used by Frisque and Smith to plutonium analysis, approximately 2.5 mg of plutonium are burned in the arc. By increasing the sample to germanium dioxide mix ratio, less total mix is burned, permitting shorter burning times for the same amount of plutonium. Various undercut type electrodes holding different amounts of sample and varying sample to diluent ratios were tried, but all produced approximately equal results provided that the sample was completely burned and that enough plutonium was analyzed to give good sampling.

Increasing the amount of plutonium consumed in the arc improves the precision of the analysis as shown by the data in Table II. An upper

TABLE II

PRECISION OF THE TOTAL BURN ANALYSIS OF PLUTONIUM FOR SILICON

<u>Silicon Concentration, ppm</u>	<u>Amount Pu Burned, mg</u>	<u>Determinations</u>	<u>Relative σ, %</u>
200	0.8	9	± 19
200	1.2	8	± 16
270	2.5	8	± 8
40	3.4	8	± 14

limit, however, is imposed by the darkening caused by the plutonium spectrum. Up to approximately 5 mg of plutonium may be burned without excessive spectral interference. A sample to germanium dioxide mix ratio of 1:4 was selected and 15 mg of the mixture burned at 15 amp for 150 sec. The selection of those conditions was an arbitrary one. Others may be used provided they meet the criteria of complete sample burn and consumption of enough plutonium for good sampling.

Precision and Accuracy

The method was tested by measuring the recovery of silicon on various NBS standards. The data of Table I show 100% recoveries using scandium or tin internal standards. Table I also shows that a relative standard deviation of $\pm 11\%$ was obtained on non-plutonium standards using tin internal standard. To determine the precision with plutonium, measurements were made on routine plutonium samples submitted for analysis. The data of Table II show that the precision with plutonium is as good as that obtained on NBS standards. At the 270 ppm silicon level, a relative standard deviation of $\pm 8\%$ was obtained; at 40 ppm, $\pm 14\%$. From the recoveries obtained on NBS standards, the accuracy of the method is estimated to be within its precision.

A check on the carrier method was made on one sample of plutonium. The first comparison showed disagreement but indicated that the carrier method was in error because its internal standard line was so weak. When the carrier procedure was modified by decreasing the depth of the cup to produce good internal standard lines, the agreement between the total burn and carrier methods was excellent.

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APPENDIXDETAILED EXPERIMENTAL PROCEDUREREAGENTS AND MATERIALS

Germanium dioxide	99.999% pure, Eagle-Picher Co., Miami, Oklahoma
Graphite powder	National high purity spectroscopic, grade SP-2, Union Carbide Corp., Carbon Products Div., New York, New York
Stannic oxide	Spectroscopic purity, Spex Industries, Metuchen, New Jersey
Sample electrode	National SPK L-4260 Harvey Series, Union Carbide Corp., Carbon Products Div., New York, New York
Counter electrode	National SP 9014. 1/8 in. diam. x 2 in. rods, Union Carbide Corp., Carbon Products Div., New York, New York
Spectroscopic plate	Kodak Spectrun analysis No. 1, Eastman Kodak, Rochester, New York

EQUIPMENT

Mixer - Mill	Spex Industries, Metuchen, New Jersey
Dental amalgamator	Wig L Bug made by Crescent Dental Manufacturing Co., Chicago, Illinois
Muffle furnace	Capable of operating at 800°C
Spectrograph	Bausch and Lomb Large Littrow
Arc Stand	Enclosed in gloved box
Power source	Varisource, Jarrell-Ash Co., Waltham, Massachusetts
Microphotometer	Jarrell-Ash Co., Waltham, Massachusetts

SPECTROGRAPH AND POWER SOURCE SETTINGS

Slit	10 microns
Slit height	2 mm
Wavelength region	8, 2350A to 2800A
Collimator mask	small

Current	15 amp, d-c on short circuit
Analytical gap	3 mm
Exposure	150 sec
Filter	100/50% transmission

MATRIX AND INTERNAL STANDARD MIX

Mix 2000 mg GeO_2 , 6000 mg graphite powder, and 35 mg SnO_2 in a 60 ml plastic vial with the Mixer-Mill for 5 min.

WORKING CURVE

National Bureau of Standards analyzed standards or their dilutions with graphite containing 40 to 1000 ppm silicon are used for the preparation of the working curve. Fifty mg are mixed with 200 mg of the matrix and internal standard mix for 30 sec in the Wig L Bug. The mixture is packed into graphite-cupped electrodes by forcing the cupped end of the electrode into the mix. Any excess adhering to the outside wall of the cup is removed by gentle tapping. The electrodes are then arced at 15 amp for 150 sec. The SA1 plate is developed for 3 min at 68 F, fixed, washed, and dried in the usual manner. The transmittances of the Si 2506.90A and the Sn 2495.70A lines are measured, converted into intensity ratios using the emulsion calibration curve, and a log-log plot of intensity ratio vs concentration made.

PROCEDURE WITH PLUTONIUM SAMPLES

1. Oxidize plutonium metal in a platinum crucible at 700 C for 30 min in the muffle furnace.
2. Mix 50 mg of PuO_2 with 200 mg of matrix and internal standard mix for 30 sec on the Wig L Bug.
3. Pack into graphite electrode, arc, develop, and calculate intensity ratios as described above for the standards. Using the intensity ratios, obtain silicon concentrations from the working curve.

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