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by

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THE EVALUATION OF SPECTROGRAPHIC STANDARDS FOR THE CARRIER-DISTILLATION ANALYSIS OF PuO_2

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ABSTRACT

Three plutonium metals whose impurity contents have been accurately determined are used to evaluate spectrographic standards. Best results are obtained when (1) highly impure samples are diluted, (2) the internal standard, cobalt, is used, (3) a linear curve is fitted to the standard data that bracket the impurity concentration, and (4) plutonium standards containing 22 impurities are used.

I. INTRODUCTION

Reliable analytical standards are essential for accurate results when using the carrier-distillation method¹ of analysis. To obtain accurate results, the standards must be as similar as possible to the samples with regard to physical and chemical characteristics, including density and particle size of the PuO_2 (Ref. 2). It is with chemical characteristics that problems arise. How many elements should be added to standards, and at what concentration should these elements be? For pure samples, one might want only a few impurity elements at low concentrations. For impure samples, on the other hand, one might want more impurity elements, and at higher concentrations.

To determine what type of standards would be best for the PuO_2 samples analyzed at the Los Alamos Scientific Laboratory (LASL), we decided to compare and evaluate four sets of plutonium standards, each differing either in number of impurities or in total impurity content.

II. APPARATUS AND REAGENTS

A. Apparatus

Balance: keyboard, chain-weight, 0.05-mg. sensitivity.

Crucibles: platinum, 1.3-ml.

Electrodes: graphite, grade AGKSP, National Carbon Company; upper, No. L-4036, lower, No. L-9027.

Emulsion: photographic, Eastman SA-1 plates.

Furnace: platinum-lined, capable of temperatures of 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: uranium metal, 73-mm bowl.

Pestle: uranium metal, 25-mm-diam.

Screens: nylon monofilament cloth, No. 325 (45 μm), Spex Industries No. 3533.

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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: 14.7840 g Ga_2O_3 plus 0.2160 g Co_3O_4 mixed and ground in a mortar until entire mixture passes through No. 325 mesh screen.

Chemical compounds: usually high-purity oxides, for the preparation of standards; analyzed spectrochemically for impurities and chemically for composition.

PuO_2 control samples: obtained by ignition of plutonium metals.

PuO_2 matrix: obtained by ignition of high-purity plutonium metal; analyzed spectrochemically for impurities.

III. PREPARATION OF STANDARDS

The four sets of plutonium standards used in this study were prepared from weighed amounts of the appropriate master impurity mix, pure PuO_2 , and Carrier-Internal-Standard (CIS) mix. These materials were stirred in a large uranium mortar and then were ground for 1 h. The mixtures constituted the highest-concentration standards for each of the four sets of standards. The remaining individual standards in each set were prepared by successive dilutions with pure PuO_2 and CIS mix. Each of the four sets of plutonium standards was composed of seven individual standards. These four sets were designated PS-6, PS-22, PS-30, and PS-22-UD. The number affixed to each designation indicated the number of impurity elements in that set.

The total impurity content (TIC) in each of the first three sets was lowest in individual standard 1 and increased in TIC up to individual standard 7. The PS-22-UD contained 22 impurity elements, 11 of which increased in concentration up to individual standard 7. Another 11 impurity elements decreased in concentration down to standard 7, hence the up-down (UD) designation. PS-22-UD was prepared in 2 portions of 11 impurity elements each; the portions

were then combined to obtain the UD mixture. The elements and their concentrations for each of the four sets of standards are listed in Appendix A. The internal standard, cobalt, is at 500 $\mu\text{g/g}$ in all standards.

IV. PREPARATION OF PLUTONIUM METAL SAMPLES

Approximately 30 g each of three plutonium metals were obtained from a plutonium-metal exchange program. The plutonium metals were converted to PuO_2 by ignition at 700°C for 1800 s, with oxygen flowing into a platinum-lined furnace at 60 ml/s for the last 1200 s of the ignition. The entire amount of each plutonium sample was placed in a uranium mortar and ground for 1 h. After additional mixing and shaking, a 5-g portion was taken from each of the three PuO_2 samples. Each of these portions was again ground until the entire 5 g of PuO_2 passed through a No. 325 (45- μm) mesh screen. This step ensured that the PuO_2 particle size in the samples matched that of the PuO_2 in the four sets of plutonium standards.

The three plutonium samples, used in this study as certified knowns, were designated R, P, and H metals. R metal has a relatively low TIC, P metal has an intermediate TIC, and H metal has a high TIC. Because of the high TIC in H metal, a fourfold dilution (H-4) was also prepared and analyzed.

V. STATISTICAL EVALUATION OF PLUTONIUM METALS

The statistical treatment given the three plutonium metals was reported in detail earlier.² Briefly, the analytical data were generated by six Energy Research and Development Administration (ERDA) laboratories participating in a plutonium-metal exchange program. Results from four analytical methods were statistically evaluated to produce an accurate determination of the concentrations of five metal impurities (aluminum, chromium, iron, nickel, and silicon) in each of the three plutonium metals (Table I). Each concentration is the weighted mean obtained, where possible, by pooling the means from the various analytical

TABLE I
WEIGHTED MEAN AND ITS STANDARD DEVIATION FOR EACH
IMPURITY POOLED FROM SEVERAL ANALYTICAL METHODS^a
($\mu\text{g/g}$ of plutonium metal)

Impurity	Plutonium Metals		
	H	R	P
Aluminum	176.3 $\pm$ 4.2	22.5 $\pm$ 0.5 ^b	55.3 $\pm$ 1.3
Chromium	196.7 $\pm$ 2.8 ^b	46.1 $\pm$ 0.9 ^c	48.2 $\pm$ 1.1
Iron	949.2 $\pm$ 8.8	112.7 $\pm$ 2.2	322.0 $\pm$ 4.2
Nickel	440.9 $\pm$ 4.7	102.5 $\pm$ 1.4	137.0 $\pm$ 2.1
Silicon	185.8 $\pm$ 7.7 ^d	34.5 $\pm$ 1.0	24.4 $\pm$ 0.8 ^b

^aData from all analytical methods are combined to compute the pooled weighted means and pooled standard deviations of the weighted means unless indicated by superscripts.

^bBased on emission spectroscopy.

^cBased on emission spectroscopy and atomic absorption.

^dBased on emission spectroscopy and spark source mass spectroscopy.

methods. The plus-or-minus value with each concentration represents 1 std dev of the weighted mean. The weighted mean of iron, for example, includes 227, 181, and 120 individual values (derived from the various methods) for H, R, and P metal, respectively.

VI. EXPERIMENTAL

Ten milligrams of CIS mix and 240 mg of each PuO_2 sample were transferred with two plastic beads to a plastic vial and shaken for 30 s using a Wig-L-Bug mixer. Two 100-mg portions of the PuO_2 -CIS mixture were transferred to graphite electrodes for each of the three plutonium samples R, P, and H. A fourfold dilution of the highly impure H metal was also prepared as a sample. This sample, designated H-4, consisted of 10 mg CIS mix, 60 mg H-metal PuO_2 , and 180 mg pure PuO_2 .

In addition to the portions transferred to the duplicate sample electrodes, one 100-mg portion of each of the seven individual standards from the four sets of plutonium standards was transferred to

graphite electrodes. All sample and standard electrode charges were vented and arced in an oxygen atmosphere, and the resulting spectra were recorded photographically. Two sets of standards, then the four samples (R, P, H, and H-4), and then two more sets of standards were arced. This combination of samples and standards constituted one run.

The above arrangement was repeated for a total of four runs. The positions of the four sets of standards were rotated on the photographic plates, with the four samples in the middle in all four runs. The specific impurity contents were determined by densitometry of the impurity-element (aluminum, chromium, iron, nickel, or silicon) and of the internal-standard (cobalt) spectral lines in the samples and standards. The log-intensity ratio of a given impurity to internal standard was plotted against log concentration to establish a calibration curve. Results in micrograms per gram were then obtained for samples by using the equation of the calibration curve determined by a set of PuO_2 standards. These and other calculations were carried out by a computer program.⁴

VII. DATA HANDLING

The photometry data (per cent transmittance) were stored on computer cards. This data file was the starting point for the computer program that determined equations for the calibration curves for the five impurity elements. Results in micrograms of impurity element per gram plutonium ($\mu\text{g/g}$) were obtained for each of the five impurity elements. Data from a given set of standards (e.g., PS-22) were combined from the four separate analytical runs, resulting in four data points for each concentration of a given impurity element (e.g., iron).

Sample data (duplicates from each of four runs) were analyzed using a given set of standards compiled as described above. This produced eight values for a given impurity (e.g., iron) derived from a given sample (e.g., R metal). Precision data were obtained from these eight values for each impurity in each sample. The average of these values was used for the accuracy calculations by comparison with the correct values as given in Table I.

The data file allowed us to evaluate the samples using the standards arranged in various modes. The samples were evaluated by comparison with each of the four sets of standards in three concentration ranges, 10-100 $\mu\text{g/g}$, 100-1000 $\mu\text{g/g}$, and 10-1000 $\mu\text{g/g}$. These ranges were called low-decade mode (LDM), high-decade mode (HDM), and complete-range mode (CRM), respectively (Fig. 1). The ranges were adjusted accordingly for those standards with element concentrations less than 1000 $\mu\text{g/g}$. For example, chromium ranges were LDM 12.5-125 $\mu\text{g/g}$, HDM 50-500 $\mu\text{g/g}$, and CRM 5-500 $\mu\text{g/g}$.

The first-, second-, and third-degree fits of the standard data were calculated by the computer program for each of the three modes for all four sets of standards. Finally, all calculations were done both with the internal standard, cobalt, and without any internal standard (Fig. 2). All values obtained in this study are given in Appendix B.

VIII. EVALUATION AND CRITERIA

A. Evaluation

The following evaluations were made: (1) the effect of dilution on the impure H metal, (2) the effect of the internal standard, cobalt, (3) the degree fit to

Fig. 1.

Curve A is the CRM (10-1000 $\mu\text{g/g}$), curve B the LDM (10-100 $\mu\text{g/g}$), curve C the HDM (100-1000 $\mu\text{g/g}$). Data from PS-6.

Fig. 2.

A plot of iron vs concentration. Curve A without cobalt, curve B with cobalt. Data from PS-30.

apply to standard data, and (4) the set of standards that most accurately determines the impurity elements studied.

B. Criteria

The two criteria we chose to base our conclusions on were relative standard deviation (rsd) and relative error (re). The precision (rsd) was that of the samples and of the carrier distillation method, and was little affected by any of the four sets of standards. Accuracy was a direct consequence of the standards and of how they were evaluated. Thus, although precision data are presented here, accuracy is the main basis for our conclusions of which set of standards was best. This emphasis on accuracy is justified because of the availability of the extremely well-characterized plutonium metal samples.

IX. RESULTS

A. The Effect of Dilution on the Impure H Metal

We compared results from H metal undiluted with those from H-4, using the internal standard, cobalt, in both cases. Table II shows a comparison between H metal undiluted and diluted. The rsd and re averaged from all four sets of standards are shown for each of the five impurity elements. The CRM and

a first-degree fit were used on all four sets of standards. Both the average rsd and re, and the rsd and re from each of the four individual sets of standards, showed that diluting was better than not diluting.

With only the rsd of aluminum as an exception, H metal diluted had the lowest rsd and lowest re for all the impurity elements. The overall rsd was the same (14%) for both samples, indicating good precision. The overall re, however, was about 2.5 times better for the diluted sample. We conclude that, for best results, highly impure samples should be diluted.

B. The Effect of Using the Internal Standard, Cobalt.

Table III shows a comparison of the rsd and re for the concentrations of the five impurity elements calculated with and without cobalt as the internal standard. Because we have already demonstrated that dilution results in better accuracy for impure samples, H metal undiluted was not included in this tabulation.

The results in Table III are for brevity averaged across the four sets of standards and the three samples R, P, and H-4. Except for PS-22-UD, results from each set of standards produced rsd and re that agreed with the overall average values in Table III. The overall rsd for the impurity concentrations is 34% lower with the use of cobalt, and the overall re is 75% better with cobalt than without it. In terms of this data, we conclude that using cobalt as the internal standard results in significantly more accurate and precise answers than not using cobalt.

TABLE II

RELATIVE STANDARD DEVIATION AND
RELATIVE ERROR FOR H METAL
UNDILUTED AND DILUTED

	Undiluted (%)		Diluted (%)	
	rsd	re	rsd	re
Al	11.8	58.9	26.0	22.6
Cr	16.6	41.7	15.5	30.0
Fe	12.2	50.4	6.2	17.3
Ni	18.9	23.0	15.1	16.1
Si	10.7	85.7	7.6	19.6
Overall	14.0	51.9	14.1	21.1

TABLE III

EVALUATION OF INTERNAL STANDARD

	With Co (%)		Without Co (%)	
	rsd	re	rsd	re
Al	25.0	19.5	26.2	36.9
Cr	13.3	34.5	12.3	31.1
Fe	5.1	20.2	21.9	51.8
Ni	14.3	11.9	11.0	31.7
Si	14.8	23.0	26.3	22.0
Overall	14.5	19.8	19.5	34.7

TABLE IV

**THE BEST STANDARD AND DEGREE FIT USING
THE COMPLETE RANGE MODE**

<u>Impurity Element</u>	<u>Pu Metal</u>	<u>Standard with lowest re</u>	<u>Degree Fit of Curve</u>
Fe	R	PS-30	2nd
	P	PS-30	1st
	H-4	PS-22	1st
Si	R	PS-6	1st
	P	PS-22	2nd
	H-4	PS-6	1st
Al	R	PS-22	1st
	P	PS-6	2nd
	H-4	PS-6	2nd
Ni	R	PS-22	2nd
	P	PS-22	2nd
	H-4	PS-22	2nd
Cr	R	PS-22	2nd
	P	PS-22	2nd
	H-4	PS-22	2nd

Figure 2 illustrates another advantage of the use of cobalt. Curve B, with cobalt, has an average *res* of the individual standards of 22%, whereas curve A, without cobalt, has an average *res* of 44%. Each individual standard in Fig. 2 is an average of four values. The data are from PS-30.

C. Degree Fit and the Best Set of Standards

Which degree fit should be applied to the standard data? Which one set of standards most accurately determines the impurity elements studied? These two questions are here considered together. The *re* for each impurity in each plutonium metal was noted for each set of standards and degree fit of the data, using the CRM. The 5 impurity elements in 3 plutonium samples gave 15 observations to be evaluated for each set of standards and each degree fit studied.

Table IV shows which set of standards and which degree fit gave the lowest *re* (*lre*) for these 15 obser-

vations. Of the standards, PS-22 had the *lre* 9 of the 15 times for 60%, PS-6 had the *lre* 27%, PS-30 had the *lre* 13%, and PS-22-UD had the *lre* 0 of 15 times for 0%. The second-degree fit of the data with the CRM had the *lre* 10 of 15 times for 67% of the determinations, the first-degree fit had the *lre* 33%, and the third-degree fit had the *lre* 0%. In terms of CRM and degree fit, then, PS-22 used in the CRM and fitted to a second-degree curve is the best system to use. A 14.3% average *res* and a 14.5% average *re* were achieved for the five impurity elements in the three plutonium metals using this system.

Further improvement may be attained, however, by using the best decade mode (BDM), which depends on the concentration level of the impurity in question. The BDM uses only those individual standards in a given set of standards whose concentration range brackets that of the impurity element being evaluated. Typical curves illustrating this improvement are shown in Fig. 3.

Table V shows the results when the best decade mode is substituted for the CRM. Fifteen observa-

Fig. 3.

Curve A is a 2nd-degree fit of the CRM, curve B a 1st-degree fit of the LDM, curve C a 1st-degree fit of the HDM. Data from PS-22.

tions are again considered. Because duplicate results were achieved by some standards, the total percentage is >100%. PS-22 had the lre 8 of 15 times for 53%, PS-6 had the lre 33%, PS-30 had the lre 20%, and PS-22-UD had the lre 7% of the time. The first-degree fit of the standard data produced the lre 11 of 15 observations or 73% of the time, the second-degree fit had the lre 33%, and the third-degree fit had the lre 0%. The average relative error for the five impurity elements in the three plutonium metals using PS-22 with a first-degree fit of the standard data in the BDM was 9.6%. The average relative standard deviation was 13.5%. Therefore, we conclude that for best results, PS-22 with a first-degree fit and the BDM should be used.

X. DISCUSSION

A. Cobalt and Total Impurity Content

An important concept in understanding the behavior of plutonium standards is TIC. Figure 4 shows how the TIC for each of the four sets of standards varies from individual standards 1-7. PS-22-UD is the only set that does not increase in TIC from standards 1-7.

Fig. 4.

TIC for the four sets of standards.

Figure 5 presents the relative intensity response of a constant amount of cobalt in each individual standard in all four sets. We see that the intensity of cobalt (500 μg/g) starts high in individual standards 1 and decreases to a low value in individual standards 7 for the three sets that have the highest TIC for individual standards 7. The intensity response of cobalt for PS-22-UD starts low in standard 1, rises to a peak value for standard 4 (standard 4 has lowest TIC), and decreases in value to standard 7. We conclude that the response of cobalt is inversely related

Fig. 5.

Relative intensity response of cobalt for the four sets of standards.

to the TIC in the particular standard or sample being considered.

R. L. Graff et al.⁶ of the New Brunswick Laboratory studied the response of cobalt in the gallium-oxide carrier-distillation method using a radioactive tracer technique. Using a thorium oxide matrix, they found that as the TIC increased, the volatilization of cobalt decreased. We have observed for some time, as well as in this study, that aluminum, chromium, iron, nickel, and silicon decrease in volatilization as the TIC increases. Graff et al. also found that iron, nickel, and silicon were less volatile with an increase in the TIC. They did not study aluminum and chromium.

We conclude that cobalt is an excellent internal standard precisely because it decreases in intensity as the TIC increases.

B. Diluting Highly Impure Samples

We believe that the iron signal in the undiluted H metal sample is inadequate to represent fully the high iron content. Not all the reasons for this are known. Some reasons may be (1) a cooling of the arc because of the high TIC, (2) possible self-absorption occurring in the arc, (3) the TIC and the individual concentrations differing between samples and standards, and (4) a high impurity concentration

necessitating extrapolation of the standards. Dilution of a highly impure sample overcomes these problems, as indicated in Table II.

An ideal use of standards for analyzing a sample would have one standard approximately equal to the value of the impurity in the sample, and one standard lower and one higher than the sample value. This same effect is achieved by using the BDM for the standards. Not unexpectedly, a first-degree fit of the standard data so used is superior to higher order fits (Table V).

C. The Best Set of Standards

The set of standards that ranked fourth was PS-22-UD. Its unique formulation, 11 impurities increasing in concentration with individual standards 1-7 and 11 other impurities decreasing in concentration, gave it a TIC plot different from those of the other sets of standards (Fig. 4). This in turn affected the cobalt response for PS-22-UD (Fig. 5). The carrier-distillation technique, as we use it, plots the intensity ratio (e.g., Fe/Co) vs concentration. The response of cobalt for the other three sets of standards (high intensity at standard 1 and low intensity at standard 7) favors a 45° curve for an impurity element. Because the cobalt response for PS-22-UD is different from that of the other sets (lower than the others at standard 1 and higher at standard 7), the resultant standard curve tends to be less than 45°. This causes PS-22-UD to give the least accurate results of the four sets when cobalt is used.

PS-30 was the set that ranked third. This set did not perform better because of its very high TIC, which ranges up to 2.5 times as high as those of the other sets. Another reason may be the large number of impurities (30) included in this set. Some elements are enhanced, some are suppressed in the presence of other impurity elements. With 30 elements in the standards, an unknown number of such interactions may be occurring during analysis. In any event, so many impurities in such high concentrations make PS-30 very different from most samples likely to be analyzed.

PS-6 ranked second to PS-22. These two sets of standards are nearly identical in TIC (Fig. 4). With but six impurities in PS-6, the five impurities under study are necessarily at higher concentration than are those same impurities in PS-22 (twice the con-

TABLE V
THE BEST STANDARD AND DEGREE FIT USING
THE BEST DECADE MODE

<u>Impurity Element</u>	<u>Pu Metal</u>	<u>Standard with the Irc</u>	<u>Degree Fit of Curve</u>
Fe	R	PS-30	1st
	P	PS-30	1st
	H-4	PS-22	1st
Si	R	PS-6	1st
	P	PS-22	1st
	H-4	PS-22-UD	1st
Al	R	PS-22, PS-30, PS-22-UD	1st
	P	PS-6	1st, 2nd
	H-4	PS-6	1st
Ni	R	PS-6	1st
	P	PS-22	2nd
	H-4	PS-22, PS-6	1st
Cr	R	PS-22	2nd
	P	PS-22	2nd
	H-4	PS-22	2nd

centration). However, the concentration of the five impurities under study is the same in PS-6 as in PS-30. With 24 fewer elements in PS-6, the studied impurities may not have undergone such interactions as occur in PS-30. This may explain why PS-6 ranked ahead of PS-30.

PS-22 ranked first among the four sets of plutonium standards. The TIC of PS-22 was a compromise between the high of PS-30 and the low of PS-22-UD. In the behavior of cobalt in PS-22-UD, we see that increasing TIC in a given set is advantageous. The concentration level of the five impurities studied in PS-22 was one-half that of the same impurities in PS-6. This lower concentration level is apparently an advantage, and may account for the better performance of PS-22. An additional feature of PS-22 was the presence of another 16 impurity elements, permitting the determination of 16 more impurities by using PS-22 rather than PS-6. Perhaps the additional 16 impurities in PS-22 made the set more nearly like the samples analyzed.

We offer one additional comment about PS-22-UD. Although it was rated fourth among the standards when cobalt was used as the internal standard, PS-22-UD without cobalt gave the most accurate results. We emphasize, however, that the results obtained without cobalt were decidedly inferior to those obtained with cobalt.

The explanation of why PS-22-UD should be the best standard when cobalt is not used is an interesting example of the effect of TIC. Figure 6 shows a plot of intensity ratio (Fe/Co) versus concentration (Curve A) for standard PS-22, with the values for standard PS-22-UD shown by Δ 's. Because the TIC of PS-22-UD is one-half that of PS-22 at iron concentrations of 250 and 500 $\mu\text{g/g}$, cobalt responds with greater intensity for PS-22-UD than for PS-22. This greater intensity of cobalt produces a lower intensity ratio (Fe/Co) for PS-22-UD, tending to produce a flatter curve. Also note the higher Fe/Co ratio for PS-22-UD at iron concentration 10. This results from PS-22-UD's having a higher TIC at that

Fig. 6.

Plots of iron vs concentration. Curve A with cobalt, curve B without cobalt.

standard and therefore a much lower cobalt intensity. Consequently, the Fe/Co ratio is higher for PS-22-UD at concentration 10 in Fig. 6. Curve B in Fig. 6 is a plot of intensity versus concentration (no internal standard) for PS-22, with the intensity value for PS-22-UD shown by Δ 's. Again because the TIC for PS-22-UD is less than for PS-22, the iron responds with greater intensity than it does for PS-22. This results in a curve closer to 45° for PS-22-UD without cobalt than for any of the other three standards studied. This behavior is exhibited by all five of the impurity elements studied in this report.

XI. SUMMARY AND RECOMMENDATIONS

For LASL to obtain the best results, we conclude the following: (1) dilute highly impure plutonium samples with pure PuO_2 ; (2) use the internal standard, cobalt; (3) use a first-order fit of the standard data along with the BDM; and (4) use PS-22 standards.

Any laboratory could obtain greater understanding of the particular standards it may have by the use of materials as well-characterized as the three plutonium metals analyzed in this study. The first three of the conclusions given above could be tested with any particular set of standards to obtain this greater understanding.

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APPENDIX A

IMPURITY ELEMENTS AND CONCENTRATIONS FOR THE STANDARDS*

TABLE A-I

COMPOSITION OF THE PS-22 STANDARDS ($\mu\text{g/g}$)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Al, Fe, Ni, Si	5	10	25	50	100	250	500
Ca, Cr, Mg, Na	2.5	5	12.5	25	50	125	250
Cd, Mo, Pb, Sn, V, Zn	1	2.5	5	10	20	50	100
Cu, K, Mn, Sr	0.5	1	2.5	5	10	25	50
B, Be, Bi, Li	0.25	0.5	1.25	2.5	5	12.5	25

TABLE A-II

COMPOSITION OF THE PS-6 STANDARDS ($\mu\text{g/g}$)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Fe, Si	10	25	50	100	200	500	1000
Al, Cr, Mn, Ni	5	12.5	25	50	125	250	500

TABLE A-III

COMPOSITION OF THE PS-30 STANDARDS ($\mu\text{g/g}$)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Al, Fe, Ni, Si	10	20	50	100	200	500	1000
Ta	8	16	40	80	160	400	800
Ca, Cr, Mg, Na	5	10	25	50	100	250	500
K, Ti	4	8	20	40	80	200	400
Cd, Dy, Eu, Gd, Mo, Pb, Sm, Sn, V, W, Zn, Zr	2	4	10	20	40	100	200
Cu, Mn, Sr	1	2	5	10	20	50	100
B, Be, Bi, Li	0.5	1	2.5	5	10	25	50

*Cobalt concentration in all four sets of standards is 500 $\mu\text{g/g}$.

TABLE A-IV
COMPOSITION OF THE PS-22-UD STANDARDS ($\mu\text{g/g}$)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Fe, Si	5	10	25	50	100	250	500
Mg, Na	2.5	5	12.5	25	50	125	250
Pb, V, Zn	1	2	5	10	20	50	100
Cu, Mn	0.5	1	2.5	5	10	25	50
B, Be	0.25	0.5	1.25	2.5	5	12.5	25
Al, Ni	500	250	100	50	25	10	5
Ca, Cr	250	125	50	25	12.5	5	2.5
Cd, Mo, Sn	100	50	20	10	5	2	1
K, Sr	50	25	10	5	2.5	1	0.5
Bi, Li	25	12.5	5	2.5	1.25	0.5	0.25

APPENDIX B

DATA

This appendix gives all the data obtained in this study. The ten tables give data (in $\mu\text{g/g}$) for the five impurity elements tested (aluminum, chromium, iron, nickel, and silicon) with and without the internal standard, cobalt. Results are given for R, P, H, and H-4 metals as obtained from each of the four

sets of standards. Results are given for the CRM, LDM, and HDM, with (1) first-, (2) second-, and (3) third-degree fits for each of the three modes. Each individual number given here represents an average of eight values (see Sec. VII).

IMPURITY ELEMENT - ALUMINUM

COBALT USED - NO

	R METAL				P METAL			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	11	13	4		66	53	43
	2	11	14	7		54	49	44
	3	11	14	-		23	42	--
PS-30	1	15	17	1.8		100	63	46
	2	15	17	0.2		71	63	36
	3	15	17	---		41	473	--
PS-22	1	19	17	7		76	51	56
	2	15	17	32		60	51	56
	3	--	17	--		--	61	--
PS-22-UD	1	22	21	9		72	52	50
	2	17	19	87		51	49	51
	3	19	19	--		34	70	--

	H METAL				H-4			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	226	137	248		207	176	123
	2	242	159	246		169	162	133
	3	24	103	---		89	---	---
PS-30	1	370	160	436		310	211	130
	2	419	168	448		217	209	90
	3	86	---	---		143	---	--
PS-22	1	203	109	230		253	177	169
	2	225	112	224		194	176	189
	3	---	170	---		---	202	---
PS-22-UD	1	165	96	167		243	184	158
	2	159	109	137		171	172	190
	3	54	248	---		127	226	--

IMPURITY ELEMENT - CHROMIUM

COBALT USED - NO

	R METAL				P METAL			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	79	64	58		78	63	57
	2	59	59	58		59	59	58
	3	57	56	--		56	55	--
PS-30	1	91	70	75		90	70	74
	2	73	71	72		73	71	71
	3	59	36	--		58	36	--
PS-22	1	68	59	63		67	59	62
	2	55	54	55		54	53	55
	3	--	55	--		--	55	--
PS-22-UD	1	67	58	60		67	58	59
	2	53	53	52		52	52	51
	3	54	56	91		54	55	90

	H METAL				H-4			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	252	164	286		318	256	232
	2	230	278	281		238	239	235
	3	235	227	---		228	224	---
PS-30	1	300	179	351		364	282	301
	2	352	275	355		295	286	289
	3	147	32	---		235	143	---
PS-22	1	202	155	234		271	237	252
	2	270	284	269		221	216	222
	3	---	313	---		---	222	---
PS-22-UD	1	170	132	198		269	234	240
	2	212	209	213		212	212	208
	3	234	249	---		218	223	---

IMPURITY ELEMENT - IRON

COBALT USED - NO

R METAL					P METAL				
	DF	CRM	LDM	HDM		CRM	LDM	HDM	
PS-6	1	191	96	160		462	174	626	
	2	160	108	164		614	253	619	
	3	118	103	---		327	230	----	
PS-30	1	220	106	203		575	204	877	
	2	194	132	192		930	383	964	
	3	131	107	---		411	261	---	
PS-22	1	184	112	186		412	207	569	
	2	181	115	181		589	221	603	
	3	---	139	---		---	312	---	
PS-22-UD	1	166	108	159		355	196	442	
	2	154	107	148		450	189	474	
	3	77	40	---		108	31	---	

H METAL					H-4				
	DF	CRM	LDM	HDM		CRM	LDM	HDM	
PS-6	1	629	214	1017		1510	608	1843	
	2	1048	349	896		1778	826	1859	
	3	489	311	---		1022	758	----	
PS-30	1	798	255	1481		1838	702	2527	
	2	1801	563	2007		2553	1187	2588	
	3	650	366	----		1248	844	----	
PS-22	1	544	256	844		1370	719	1765	
	2	942	279	952		1777	760	1823	
	3	---	420	---		----	1031	----	
PS-22-UD	1	463	241	634		1193	684	1431	
	2	686	229	759		1392	662	1432	
	3	120	27	---		403	135	----	

IMPURITY ELEMENT - NICKEL

COBALT USED - NO

	R METAL			P METAL			
	DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	154	103	145	197	124	206
	2	140	125	127	199	175	186
	3	69	181	---	82	272	---
PS-30	1	162	94	117	216	115	183
	2	124	98	117	182	125	180
	3	43	79	---	47	95	---
PS-22	1	136	87	125	174	105	178
	2	122	92	118	172	115	170
	3	---	33	---	---	34	---
PS-22-UD	1	119	76	95	147	89	135
	2	96	83	83	132	106	114
	3	45	129	--	52	181	---

	H METAL				H-4		
	DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	372	202	523	715	459	720
	2	560	465	666	694	614	642
	3	135	932	---	307	930	---
PS-30	1	460	195	601	772	425	617
	2	580	241	600	627	453	612
	3	55	156	---	180	352	--
PS-22	1	329	173	458	631	389	622
	2	465	219	489	602	421	590
	3	---	31	---	---	134	---
PS-22-UD	1	259	135	243	541	335	472
	2	339	214	358	467	385	403
	3	73	487	---	196	634	---

IMPURITY ELEMENT - SILICON

COBALT USED - NO

R METAL				P METAL		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	27	26	15	17	5
	2	23	24	16	16	8
	3	23	25	16	16	--
PS-30	1	41	36	23	21	10
	2	32	35	21	23	272
	3	34	35	23	23	--
PS-22	1	39	34	23	22	18
	2	36	35	22	22	17
	3	--	37	--	22	--
PS-22-UD	1	43	38	27	27	17
	2	34	36	24	25	25
	3	35	35	25	26	--
H METAL				H-4		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	217	125	168	175	76
	2	188	149	129	135	95
	3	152	396	128	155	--
PS-30	1	326	162	213	199	154
	2	325	185	185	196	388
	3	122	183	176	194	--
PS-22	1	265	162	232	189	203
	2	275	156	211	191	201
	3	--	526	--	234	--
PS-22-UD	1	222	132	242	198	164
	2	227	156	185	188	182
	3	143	86	167	171	--

IMPURITY ELEMENT - ALUMINUM

COBALT USED - YES

R METAL					P METAL				
	DF	CRM	LDM	HDM		CRM	LDM	HDM	
PS-6	1	16	18	13		61	55	54	
	2	16	18	10		59	55	54	
	3	15	19	--		59	54	55	
PS-30	1	22	23	10		89	71	60	
	2	21	23	7		74	71	56	
	3	21	18	-		74	80	--	
PS-22	1	23	22	16		73	58	63	
	2	21	22	22		64	58	63	
	3	21	21	631		63	60	56	
PS-22-UD	1	24	23	15		76	58	64	
	2	20	21	45		59	57	61	
	3	20	18	229		59	63	56	

H METAL					H-4				
	DF	CRM	LDM	HDM		CRM	LDM	HDM	
PS-6	1	270	189	274		202	191	179	
	2	272	193	278		197	213	173	
	3	283	186	---		197	187	231	
PS-30	1	404	250	421		296	243	190	
	2	412	234	430		248	245	172	
	3	407	112	---		248	279	---	
PS-22	1	260	171	281		251	203	210	
	2	278	162	277		217	205	215	
	3	270	147	---		216	213	212	
PS-22-UD	1	273	159	311		259	205	211	
	2	320	232	317		200	196	217	
	3	321	157	---		201	218	207	

IMPURITY ELEMENT - CHROMIUM

COBALT USED - YES

R METAL					P METAL			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	75	67	68		73	64	66
	2	67	64	68		65	62	66
	3	67	68	60		65	65	58
PS-30	1	76	67	69		73	65	66
	2	68	67	68		66	65	66
	3	68	67	64		66	65	62
PS-22	1	61	58	60		59	56	58
	2	58	54	62		56	52	60
	3	60	59	55		57	57	52
PS-22-UD	1	74	67	70		71	65	68
	2	65	64	67		62	62	64
	3	68	69	66		65	66	63
H METAL					H-4			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	286	219	300		295	262	266
	2	295	317	302		262	250	266
	3	324	222	483		262	264	235
PS-30	1	277	208	287		296	262	268
	2	283	213	280		267	262	266
	3	277	217	356		267	262	250
PS-22	1	205	185	213		238	227	233
	2	212	246	209		227	212	243
	3	242	181	286		232	230	212
PS-22-UD	1	272	221	312		289	263	274
	2	362	372	342		253	250	261
	3	331	213	347		265	269	257

IMPURITY ELEMENT - IRON

COBALT USED - YES

R METAL				P METAL		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	169	116	150	336	344
	2	144	143	150	326	346
	3	150	128	129	347	394
PS-30	1	162	115	144	321	326
	2	139	142	145	308	332
	3	144	147	134	326	362
PS-22	1	150	125	145	275	284
	2	144	131	155	278	294
	3	151	126	146	290	334
PS-22-UD	1	174	133	168	346	376
	2	163	179	146	379	394
	3	143	142	147	382	404
H METAL				H-4		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	751	381	914	1139	1127
	2	950	1015	911	1064	1133
	3	959	304	1299	1112	1118
PS-30	1	713	382	850	1090	1073
	2	871	1086	845	1011	1091
	3	898	1689	2156	1067	1092
PS-22	1	559	408	624	952	968
	2	628	503	566	947	1016
	3	611	335	891	994	1093
PS-22-UD	1	773	477	965	1171	1239
	2	1134	264	1770	1230	1213
	3	1843	2611	1776	1173	1243

IMPURITY ELEMENT - NICKEL

COBALT USED - YES

R METAL					P METAL			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	127	142	121		149	117	145
	2	118	106	119		141	126	143
	3	118	111	109		142	125	142
PS-30	1	134	105	114		160	122	141
	2	115	110	115		139	130	139
	3	114	111	115		138	134	140
PS-22	1	121	101	116		143	118	140
	2	114	105	122		136	125	149
	3	119	109	109		144	135	144
PS-22-UD	1	134	95	125		160	109	158
	2	117	114	120		148	144	151
	3	121	107	120		154	125	166
H METAL					H-4			
	DF	CRM	LDM	HDM		CRM	LDM	HDM
PS-6	1	399	270	435		554	440	533
	2	441	388	440		520	446	525
	3	442	205	1559		522	474	503
PS-30	1	475	301	510		590	454	511
	2	498	398	497		510	481	511
	3	482	467	1051		506	490	510
PS-22	1	395	296	432		528	440	514
	2	430	365	422		502	462	540
	3	463	610	1706		527	489	507
PS-22-UD	1	481	262	652		590	409	568
	2	752	714	718		533	518	544
	3	757	281	2827		509	464	373

IMPURITY ELEMENT - SILICON

COBALT USED - YES

R METAL				P METAL		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	35	34	29	21	17
	2	33	33	25	21	13
	3	32	32	102	19	177
PS-30	1	46	44	35	29	20
	2	42	41	49	27	36
	3	42	45	52	28	40
PS-22	1	43	42	40	27	24
	2	41	43	44	26	32
	3	44	41	42	30	30
PS-22-UD	1	48	44	37	30	21
	2	41	44	44	28	35
	3	48	53	41	39	31
H METAL				H-4		
DF	CRM	LDM	HDM	CRM	LDM	HDM
PS-6	1	306	244	304	191	180
	2	296	281	311	179	176
	3	308	236	368	174	176
PS-30	1	359	352	364	252	228
	2	358	369	341	219	220
	3	346	648	347	221	220
PS-22	1	325	273	332	233	221
	2	333	228	329	220	225
	3	321	165	353	225	225
PS-22-UD	1	341	368	310	261	227
	2	340	345	306	218	227
	3	366	340	296	229	229