SPECTROCHEMICAL ANALYSIS OF METALLIC IMPURITIES
IN PLUTONIUM DIOXIDE

C. S. Homi

Process Control Laboratories
Operations Technical Support
Operations Division

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C. S. Homi

Process Control Laboratories
Atlantic Richfield Hanford Company
Richland, Washington 99352

ABSTRACT

The development history of the Atlantic Richfield Hanford Company spectrochemical method for impurity analysis of reactor grade plutonium dioxide is discussed. Topics included are: (1) carrier type and amount; (2) electrode design; (3) sample arcing and arcing environment; and (4) standards and analytical curves.

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INTRODUCTION

The Atlantic Richfield Hanford Company is under contract to supply plutonium for mixed oxide (Pu-U oxide) reactor fuel. The mixed oxide fuel will be used for the Fast Flux Test Facility (FFTF), a fast breeder test reactor. An analytical quality assurance program (1,2,3) was set up by the Atomic Energy Commission, Division of Reactor Development and Technology (RDT) to increase measurement reliability. The measurement of trace metallic impurities in plutonium is part of this program.

This report summarizes the development history of the spectrochemical method used at ARHCO for the impurity analysis of plutonium dioxide. Emphasis was placed on the analytical system rather than detection limits. Low detection limits are useless if reliable determinations can't be made at concentrations above these limits.

The RDT recommended method for determining trace metallic impurities in plutonium by emission spectroscopy is the carrier distillation technique using three different carriers, gallium oxide, silver chloride and sodium fluoride. Gallium oxide and an eleven-to-one (weight) mixture (4) of silver chloride-lithium fluoride were used for the methods discussed in this report. During the course of investigation, a procedure was developed which complied with the quality assurance program (1,2,3) that is, the measurement of trace metallic impurities fell within the required precision of plus 100 percent, minus 50 percent (1) over the specified concentration range. (Table I) Precision is based on blind standard performance for all specified elements.

Although the procedure(5) qualified under the stringent RDT(1,2,3) program, method investigation continued. A new improved procedure(6) was developed and precision tests were made on an internal control standard. The results are shown in Table II.

Seven elements in addition to those required by FFTF were included in this work. They are As, Ba, Bi, Ga, Nb, P and Zr. A list of all elements studied is in Table II.

Final measurements were made with both a photographic spectrograph and a direct reading spectrometer.

DISCUSSION

Methods based on the carrier distillation technique originally described by Scribner and Mullins(7) have been and are widely used for the spectrochemical analysis of trace metallic impurities in plutonium

TABLE I

IMPURITY LIMITS FOR PLUTONIUM DIOXIDE

RDT Standard Specifications

<u>Impurity</u>	<u>Limits in ppm by Weight of PuO₂ Max.</u>
Al	250
Be	20
B	10
Cd	20
Ca	500
Cr	200
Co	20
Fe	350
Li	10
Mg	100
Ni	300
K	200
Na	300
V	200
Ta	400
W	100
Sum of Cu, Zn, Si, Ti	800
Sum of Ag, Mn, Mo, Pb, Sn	200

Range for individual elements is $1/4$ to 2 times the specification limits. Range for element group is $1/8$ of individual element to specification limit. For example, range for Al would be 62 to 500 ppm.

TABLE II

PRECISION FOR IMPROVED METHOD

Standard Deviation of Single Measurement
for Control Standard

<u>Impurity</u>	<u>Concentration in Standard, ppm</u>	<u>Percent Deviation</u>
Ag	160	21
Al	200	13
As	200	3
B	20	13
Ba	80	26
Be	20	27
Bi	20	13
Ca	200	22
Cd	20	23
Co	20	14
Cr	200	21
Cu	20	37
Fe	250	20
Ga	80	37
K	160	14
Li	20	16
Mg	80	14
Mn	40	10
Mo	90	18
Na	160	20
Nb	160	17
Ni	250	18
P	200	15
Pb	20	11
Si	180	5
Sn	40	16
Ta	160	19
Ti	40	20
V	80	15
W	160	20
Zn	40	25
Zr	160	18

and uranium. In the carrier method the sample (PuO_2 or U_3O_8) is mixed with a compound (carrier) such as Ga_2O_3 and the mixture is loaded into a graphite electrode. When the electrode is arced the Ga_2O_3 is vaporized and co-distills impurity elements up into the arc plasma where their spectra is produced. The more refractory PuO_2 or U_3O_8 remains behind in the electrode crater. The need for separating the impurities from either plutonium or uranium is due to their complex spectra which can produce intolerable interferences. Chloride and fluoride carrier compounds not only co-distill impurity elements but react with some of the more refractory trace impurities forming volatile halide compounds. These halide compounds and in particular, AgCl , have proven to be the most versatile for use as carriers.

Chemically separating the impurity elements from plutonium has been done using solvent extraction and ion exchange techniques.^(8,9,10) Difficulty in dissolving plutonium dioxide, the use of corrosive acids such as HCl and HF plus lengthy sample preparation time can pose serious problems. An extraction method⁽¹¹⁾ is used at ARHCO for the analysis of Sm , Eu , Gd , and Sm (FFTF requirement) by X-ray emission because they do not respond to the carrier distillation method.

The experimental section is divided into four general headings: (1) carrier type and amount; (2) electrode design; (3) sample arcing and arcing environment; and (4) standards and analytical curves. Each of the preceding will be discussed separately even though they were not changed independently during the course of the investigation. A chronological discussion of the experimental work would tend to be confusing because it is almost always necessary to change more than one parameter at a time. For example, changes in electrode design require changes in arcing conditions, carrier amount and instrument parameters.

Specially prepared PuO_2 standards which contained all elements of interest at two concentration levels were used for most of the experimental work. Moving plate studies were made at each of the two concentrations and the line intensities for each element were hand drawn for reference, that is, for each time interval (10 seconds) the line was reproduced on a drawing. Line behavior for all elements at the two concentration levels were then reduced to one drawing. This technique proved invaluable for interpreting moving plate studies. A typical drawing for an element analysis line would look like the following:

Burn profile studies with the direct reading instrument were not made because only one element could be studied at a time. Also, self-reversal and line broadening effects would be difficult to detect. When a particular technique looked good on the moving plate study, tests were made on the direct reading spectrometer. The direct reader (Applied Research Laboratories Quantometer) is equipped with individual element timers so a start and stop time can be selected for each element. These times would be selected from the moving plate drawings. The criteria for timer selection were: (1) time interval in which the most intense spectra occurred, and (2) time interval which showed the maximum difference between the two concentrations when line broadening occurred. Sometimes this meant an intense portion of the time spectra would be omitted. For example, if the spectral intensities were the same for both concentrations during a particular time and if an appreciable amount of broadening occurred, that time was not used. All final times were selected after tests were made on the quantometer. Final time selection criterion for quantometer application was maximum intensity difference between two concentrations with minimal loss in sensitivity. Usually no change occurred in final timer selection.

EXPERIMENTAL

CARRIER TYPE AND AMOUNT

Several compounds and mixtures used for carriers have included: Ga_2O_3 ⁽⁷⁾ $\text{AgCl}:\text{LiF}$,⁽⁴⁾ AgCl ,⁽¹²⁾ $\text{AgCl}:\text{BaF}_2$,⁽¹³⁾ $\text{AgCl}:\text{PbF}_2$,⁽¹⁴⁾ NaF ,^(15,16) and $\text{AgCl}:\text{SrF}_2$.⁽¹⁷⁾ Emphasis was placed on studying Ga_2O_3 and the $\text{AgCl}:\text{LiF}$ mixture (11:1 weight ratio)⁽⁴⁾ because their behavior has been well documented^(4,7,12,18) and they were recommended carriers for use in the FFTF quality assurance program. Preliminary tests proved the $\text{AgCl}:\text{LiF}$ (11:1 mixture) to be superior over AgCl .

The existing laboratory procedure⁽¹⁹⁾ did not provide satisfactory analyses of Nb, Ta, W, and Zr. A high priority was placed on the analysis of refractory elements because FFTF specifications include Ta and W. Los Alamos Scientific Laboratory⁽¹²⁾ has reported detection limits of 40 ppm for Ta using 15 percent AgCl and 20 ppm for W using 40 percent AgCl . A carrier study was made with $\text{AgCl}:\text{LiF}$ at 8.2, 20, 30, and 40 percent. The investigation included other parameter changes such as arcing environment. The four refractory elements responded best using 30 percent $\text{AgCl}:\text{LiF}$. Most of the other elements responded best using 8.2 percent $\text{AgCl}:\text{LiF}$. Similar tests were run with Ga_2O_3 for the analysis of the remainder elements, and 4.2 percent was chosen. These three carrier mixtures were used in the original FFTF procedure.⁽⁵⁾ Development continued because of problems encountered with gas chamber etching (see section on sample arcing and arcing environment), using three carrier mixtures for each sample and limited analysis range for several elements.

Due to changes made in other parameters, the level of AgCl:LiF in the sample was restudied. Tests at the 20 percent level showed better results could be obtained for elements originally analyzed at the 8.2 percent level without compromising the four refractory elements. The two AgCl:LiF methods were combined into one at the 20 percent level. The Ga_2O_3 level was also restudied due to other parameter changes. It was hoped that some of the semi-refractories could also be analyzed in Ga_2O_3 as a back up to the AgCl:LiF carrier. Los Alamos⁽¹²⁾ reports using 4 percent Ga_2O_3 for the analysis of Al, Ca, Mg, and Si in ceramic grade plutonium dioxide. Their method could not easily be confirmed because they use pure oxygen for the arc atmosphere and an arc current of 18 amperes, conditions that cannot be achieved with our equipment. An increase in the Ga_2O_3 concentration made matters worse. The addition of graphite⁽¹²⁾ did improve the response of the four elements, but it also increased the plutonium spectra. Burt⁽²⁰⁾ uses 2 percent Ga_2O_3 in mixed oxide pellets, but employs NaF for the analysis of Ca and Al. Tests were made at reduced Ga_2O_3 concentrations of 1.2, 2.5, and 3 percent. The 2.5 percent level proved to behave the best for the analysis of Ag, Li, and P; however Al, Ca, Mg and Si did not respond. It should be pointed out tests with reduced levels of Ga_2O_3 were made earlier. Subsequent changes in other parameters contributed to the different behavior of Ga_2O_3 at the 2.5 percent level.

A problem was encountered in obtaining fine grain AgCl:LiF carrier. The carrier had been purchased from Spex Industries, Metuchen, New Jersey, and until January 1973, the particle size was acceptable (approximately 100 mesh). The carrier purchased after January 1973 was not acceptable because the particle size was too large (approximately 20 mesh).

Grinding the carrier in an agate mortar and pestle with liquid nitrogen did not reduce the particle size. Due to Spex Industries' problem in preparing usable carrier, a decision was made to prepare it ourselves. An American Society for Testing Materials (ASTM) method procedure⁽²¹⁾ for the preparation of 200 mesh AgCl was used and fine grain AgCl was prepared in the laboratory. The final mixed carrier (AgCl:LiF) was prepared by blending the two compounds in an agate mortar and pestle. The carrier is no longer prepared in the laboratory because another vendor, Zeebac Incorporated,⁽²²⁾ has been able to provide acceptable mixed carrier.

ELECTRODE SHAPE

The carrier electrode^(7,18) is designed for the fractional distillation of impurities from the sample charge. The deep crater prevents the arc plasma from coming in contact with the sample charge and the heavy walls prevent rapid electrode burn off. The Scribner-Mullin⁽⁷⁾ pedestal and the undercut electrodes⁽¹⁸⁾ (Figure 1) serve to concentrate the heat energy in the sample charge portion of the electrode. The use of either of these electrodes requires provision for venting the sample during

the early stages of arcing, otherwise the sample has the annoying tendency to blow up into the arc plasma. A vent hole is made in each sample charge by a special venting tool. (Figure 1) The vent hole in the sample charge permits the quiet release of gases from the sample and underlying graphite during the early stages of arcing. The amount of pressure applied to the sample charge with the venting tool is difficult to reproduce. Experience has shown a marked increase in plutonium background with increased venting tool pressure.

Dow Chemical, Rocky Flats, has departed from using the classical carrier electrode in their sodium fluoride procedure.⁽²³⁾ They use a Harvey type ASTM S-12 (100-L) for their sample electrode. (Figure 1) The problem of providing an expansion area for the sample charge is solved by pressing the sample into a pellet before it is placed in the electrode. The Rocky Flats pellet procedure, per se, was not investigated because problems could be foreseen in reproducing pellet pressures, cross contamination of samples in the press, and lengthy sample preparation time. However, their use of 100-L electrodes and the elimination of the venting tool was expanded upon. Since venting is necessary, contraction of the sample charge to allow venting from the sides was investigated.

When fuel grade PuO_2 is calcined at 950°C , a noticeable reduction in volume occurs. This reduction in volume can serve as an expansion area for the sample charge but heating the sample to 950°C is not feasible because AgCl melts at 455°C . Sucrose was introduced into the sample and removed by heat (425°C) after the sample had been loaded into an electrode, (100-L). The addition and removal of sucrose provided an expansion area for the sample charge, but analytical reproducibility was very poor. The absence of sucrose produced extremely intense plutonium spectra.

Another organic compound, 8-hydroxyquinoline, was tried and good reproducibility resulted. Other compounds were not tried because they were not readily available in the laboratory.

Even though the addition of 8-hydroxyquinoline to the sample solved the problem of venting, plutonium spectra continued to appear during the early stages of arcing. Reducing the sample charge (50 mg normally used) in the electrode and changing the arcing conditions did not help. Another electrode was tried and the plutonium spectra was almost virtually eliminated. The electrode (Ultra-Carbon 331007) is the same design as the 100-L, except the crater is .032 inch longer.

SAMPLE ARCING AND ARCING ENVIRONMENT

The original reason for using an argon-oxygen arcing atmosphere at ARHCO was the elimination of cyanogen band interference for rare earth analysis. Possible cyanogen band⁽¹²⁾ interference has been reported by Los Alamos.

SCRIBNER-MULLIN

NLCO

TAMPING AND VENTING TOOL
FOR SCRIBNER-MULLIN AND
NLCO ELECTRODES

100-L

331007

TAMPING TOOL FOR
331007 ELECTRODES

FIGURE 1 ELECTRODES AND TAMPING TOOLS

Additional benefits are the ability to further control the electrode temperature and to obtain a stable arc. The evolution of arc chambers is shown in Figure 2. The chimney apparatus and enclosed chamber use the same electrode base holder.⁽²⁴⁾ The chimney design did eliminate most of the cyanogen bands, but arcing stability was poor. Stable arcing conditions and a virtual elimination of cyanogen bands were obtained with the enclosed chamber. However, the useful life of this chamber was very short due to condensation of AgCl:LiF carrier on the walls and the subsequent etching due to the fluoride. Replacement costs were high because the chamber had to be fabricated out of quartz to allow passage of ultra-violet light. Several pyrex cylinders were designed with a hole in the side, but none proved satisfactory due to large increases in cyanogen band spectra. A commercial base and chamber, an enclosed Stallwood Jet,⁽²⁵⁾ was tested next. The Stallwood Jet produced the most stable arc, reduced the cyanogen spectra more than the enclosed chamber and suppressed line broadening. The chamber base contains a water jacket which was not used because of the difficulty in getting it plumbed in a glove box. No ill effects have been noted on the chamber base after several months usage. Although quartz chambers are provided with the Stallwood Jet, pyrex chambers work just as well. The sample electrode cannot protrude more than $3/8$ inch above the chamber base due to the light path cut out in the chamber. (Figure 2) This places the bottom edge of the 331007 electrode undercut approximately $1/16$ inch above the electrode base holder. As a result, the entire sample crater section is above the electrode base. The Scribner-Mullins or National Lead Company electrode cannot be used because their sample crater section is $5/8$ inch long which would put $1/4$ inch of the sample crater below the electrode base holder. Heat conduction to the base would prevent obtaining the desired temperature in the sample charge.

A mixture of oxygen and argon was used for all chamber atmospheres. The flow rate was held constant at 12 Standard Cubic Feet per Hour (SCFH). The oxygen-argon ratio for each chamber type was increased for maximum trace element response just below the point where plutonium started to appear in the spectrum. The AgCl:LiF carrier proved to be very sensitive to the amount of oxygen present. The 30 percent AgCl:LiF method⁽⁵⁾ uses a 1.5 to 30 oxygen to argon ratio. If the oxygen is increased to 2.0, an intolerable amount of plutonium spectra appears. The 20 percent AgCl:LiF method was originally set up at the 1.5 to 30 ratio, but a leak in the oxygen supply system while shooting standards, produced better results. The mixture was studied at lower oxygen-argon ratios after the leak was repaired and a ratio of 0.5 to 30 was chosen. Final gas ratio for the 2.5 percent Ga_2O_3 method is argon 20 and oxygen 3.

Arc current was held constant at 13.5 amps throughout all studies because better temperature control could be obtained by changing the oxygen-argon ratio.

FIGURE 2

STANDARDS AND ANALYTICAL CURVES

Two sets of calibration blends were used to calculate the final analytical curves. The primary calibration blends were prepared at Los Alamos Scientific Laboratory (LASL) for use in the FTTF analytical program.⁽¹⁾ The other blends were prepared at ARHCO to supplement the LASL blends and includes several elements not required by the FTTF analytical program. Recommended values for both sets are shown in Tables III and IV.

The LASL calibration blends are made up from a single mixture and diluted down to the final series. As a result, blends 4 and 5 contain 5825 and 11605 μg total metal impurities per gram PuO_2 . A total of 5302 μg per gram PuO_2 is reached in the highest ARHCO blend because the final series were prepared by cross blending four mixtures (Table IV). The behavior of two elements (Mo, W) in LASL blends 4 and 5 indicate total impurities suppresses their evolution from the sample electrode. Inter-element enhancement and suppression was observed in the ARHCO blends. In most cases one or two points for each element would be significantly higher or lower than the curve for the other concentrations. All data points for Ca were inconsistent in the ARHCO blends and were not used to generate the curve.

Atlantic Richfield Hanford Company blend data was normalized to fit LASL blend data by adding a constant blank value to the ARHCO values. In most cases, the blank value addition could be attributed to real blank in the ARHCO PuO_2 , however part of the curve shift could also be due to PuO_2 matrix differences. A blank value of 10 ppm was added to the LASL blend values for Si and a value of 15 ppm added to the ARHCO blends.

Figures 3 through 20 show all data points used for calibration and the approximate analytical curve for each element. Blank value additions are indicated on the figures. Final analytical curves were calculated by regression analysis. All of the curves except Al and Ta were either first or second order regressions. The criterion to determine the order of regression was comparing the standard deviation about the points (duplicate shots) to the standard deviation about the line for the different orders. Second or third orders were selected only if they showed marked improvement over first order and the deviation about the line was not lower than the deviation about the points.

CONCLUSION

The Stallwood Jet and eliminating the pointed venting tool contribute the most to the success of the method. Refinements to the method will continually be sought, however no major changes in the basic technique are anticipated.

TABLE III
LASL CALIBRATION BLENDS

<u>Element</u>	Blend Recommended Values				
	$\mu\text{g (M)}/\text{gPuO}_2$				
	1	2	3	4	5
Al	50	100	250	500	1,000
B	2	4	10	20	40
Be	2	4	10	20	40
Ca	40	65	140	265	515
Cd	2	4	10	20	40
Co	1	2	5	10	20
Cr	25	50	125	250	500
Fe	70	120	270	520	1,020
K	20	40	100	200	400
Li	1	2	5	10	20
Mg	10	20	50	100	200
Na	50	100	250	500	1,000
Ni	50	100	250	500	1,000
Ta	40	80	200	400	800
W	10	20	50	100	200
V	50	100	250	500	1,000
Cu	20	40	100	200	400
Si	40	80	200	400	800
Ti	20	40	100	200	400
Zn	20	40	100	200	400
Ag	10	20	50	100	200
Mn	15	25	55	105	205
Mo	10	20	50	100	200
Pb	10	20	50	100	200
Sn	15	25	55	105	205
Dy	10	20	50	100	200
Eu	10	20	50	100	200
Gd	10	20	50	100	200
Sm	10	20	50	100	200

TABLE IV

ARHCO CALIBRATION BLENDS (40 SERIES)

Element	Blend Recommended Values $\mu\text{g (M)}/\text{g PuO}_2$								
	1	2	3	4	5	6	7	8	9
Sm	800	400	8	200	80	40	16		
Eu	800	400	8	200	80	40	16		
Gd	800	400	8	200	80	40	16		
Dy	800	400	8	200	80	40	16		
Pb	100	50	1	25	10	5	2		
Sn	200	100	2	50	20	10	4		
Si	800	400	8	200	80	40	16		
Mo	400	200	4	100	40	20	8		
Be	100	50	1	25	10	5	2		
Co	100	50	1	25	10	5	2		
Ag		8	200	80	400	40		800	16
Li		1	25	10	50	5		100	2
As		10	250	100	500	50		1,000	20
P		10	250	100	500	50		1,000	20
Zn		2	50	20	100	10		200	4
Na		8	200	80	400	40		800	16
K		8	200	80	400	40		800	16
Cu		1	25	10	50	5		100	2
B		1	25	10	50	5		100	2
Cd		1	25	10	50	5		100	2
Bi		1	25	10	50	5		100	2
Fe	20	10	50	250	100	500	1,000		
Ni	20	10	50	250	100	500	1,000		
Cr	20	10	50	250	100	500	1,000		
Mn	4	2	10	50	20	100	200		
Ca	20	10	50	250	100	500	1,000		
Mg	8	4	20	100	40	200	400		
Ga	8	4	20	100	20	200	400		
W		200	400	80	8	40		16	800
Zr		200	400	80	8	40		16	800
Ta		200	400	80	8	40		16	800
Nb		200	400	80	8	40		16	800
Ti		50	100	20	2	10		4	200
Al		250	500	100	10	50		20	1,000
V		100	200	40	4	20		8	400
Ba		100	200	40	4	20		8	400

FIGURE 3. 20% AgCl:LiF METHOD

FIGURE 4. 20% AgCl:LiF METHOD

FIGURE 5. 20% AgCl:LiF METHOD

FIGURE 6. 20% AgCl:LiF METHOD

FIGURE 7. 20% AgCl:LiF METHOD

FIGURE 8. 20% AgCl: LiF METHOD

FIGURE 9. 20% AgCl:LiF METHOD

FIGURE 10. 20% AgCl : LiF METHOD

FIGURE 11. 20% AgCl:LiF METHOD

FIGURE 12. 20% AgCl:LiF METHOD

FIGURE 13. 20% AgCl:LiF METHOD

FIGURE 14. 20% AgCl:LiF METHOD

FIGURE 15. 20% AgCl:LiF METHOD

FIGURE 16. 20% AgCl: LiF METHOD

FIGURE 17. 20% AgCl:LiF METHOD

FIGURE 18. 20% AgCl:LiF METHOD

FIGURE 19. 2.5% Ga₂O₃ METHOD.

FIGURE 20. 2.5% Ga₂O₃ METHOD

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APPENDIX

CONDENSED GMI-02A PROCEDURE⁶REAGENTS AND SUPPLIES

1. AgCl:LiF carrier (11:1 mixture), special order from Zeebac Inc., 141 4th Avenue, Berea, Ohio, 44017, Catalog No. 8004.
2. Ga₂O₃ carrier, Spectrographically pure.
3. Eight-Hydroxyquinoline, reagent grade. Each bottle checked for impurities.
4. Wig-L-Bug vials, 1.0 inch x 0.5 inch with 3/8 inch plastic ball.
5. Electrodes, anode, Ultra Carbon 331007, (1989).
6. Electrodes, cathode, Ultra-Carbon 110407 (1509-1).

EQUIPMENT

1. Two muffle furnaces, 950° capacity, lined with one-fourth inch transite or quartz.
2. Two 500 mg torsion balances (Federal Pacific Electric Company).
3. One 50 mg torsion balance (Roller-Smith).
4. Spex Industries spark box model 9010 with stainless steel case.
5. Wig-L-Bug amalgamator adapted to hold 1.0 inch vials (Crescent Dental Manufacturing Company).
6. Applied Research Laboratories Quantometer, which includes a two-meter model 9500 spectrometer, model 5700 source unit and model 46000-E readout console with special integration timers.

PART A

1. Weigh 192 mg sample, 48 mg AgCl:LiF carrier and 10 mg 8-hydroxyquinoline into 1.0 inch Wig-L-Bug vial containing three-eighths inch plastic ball and wiggle for one minute.

2. Load 50 mg of each sample (from Step 1) into 331007 electordes. Load two electrodes per sample. Gently tap each electrode to settle charge and pack the sample with the plastic tamping tool.
3. Transfer electrodes to transite seating block and place in pre-heated furnace (200° C). Hold at 200° C for 20 minutes and increase temperature to 350° C. Remove electrodes.
4. Source unit setting: 350 μ h, 62 μ f, 12 ohms, 230 volts (14 amps). Console settings (Quantometer):

<u>Pre-Burn Timers</u>	<u>Total Burn Timers</u>
(sec)	(sec)
0 Zn, Cd, B, Si, Na, Sn, Ga	20 B
5 Fe, Ni, Ta, Mn, Mo, Ti, Co, Al, Nb	30 Sn
10 V, Cu, Zr, W, Cr, Be	40 Zn, Cd, Ga
40 Ba	60 Si
	90 Fe, Ni, Mn, Mo, Cu, Co, Al, W
	100 V, Ba, Ta, Na, Ti, Zr, Cr, Nb, Be

5. Place Stallwood Jet in lower arc box jaws and adjust gas supply to 30 S.C.F.H. for argon and 0.5 S.C.F.H. for oxygen. Adjust arc box gas flow to 12 S.C.F.H. Arc samples in Stallwood Jet Chamber.
6. Standard curves are prepared by plotting signal versus concentration on 2-cycle log-log paper.

PART B

1. Weigh 234 mg sample, 5.0 mg Ga₂O₃ carrier and 10 mg 8-hydroxyquinoline into 1.0 inch Wig-L-Bug vial containing three-eighths inch plastic ball and wiggle for one minute.
2. Follow steps 2 and 3 Part A.
3. Source Unit settings: 360 μ h, 62 μ f, 12 ohms, 230 volts (14 amps). Console settings (Quantometer)

Pre-Burn Timers

(sec)

0 Ag, As, Bi, Li,
K, Ca

5 Pb

10 P, Mg

Total Burn Timers

(sec)

40 Pb

50 Bi

70 Ag, As, P, Li

4. Place Stallwood Jet in lower arc box jaws and adjust external gas supply to 20 S.C.F.H. for argon and 3.0 S.C.F.H. for oxygen. Adjust arc box gas flow to 12 S.C.F.H.. Arc sample in Stallwood Jet chamber.
5. Standard curves are prepared by plotting signal versus concentration on 2-cycle log-log paper.

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