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LAWRENCE LIVERMORE LABORATORY

University of California/Livermore, California

**ERROR ANALYSIS OF THE METHOD FOR THE DETERMINATION OF
PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY**

J. E. Harrar

J. W. Magana

J. C. Walden

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ERROR ANALYSIS OF THE METHOD FOR THE DETERMINATION OF PLUTONIUM BY CONTROLLED-POTENTIAL COULOMETRY

ABSTRACT

The sources and magnitudes of the systematic and random errors associated with this method are outlined. Calibration of the coulometric instrument by both chemical and electrical means is analyzed and the results obtained by the two techniques are compared statistically.

INTRODUCTION

Fission cross section measurements for a number of isotopes of uranium and plutonium are presently being made at LLL using the 100-MeV electron linear accelerator as a pulsed source for neutrons.¹ For these measurements, accurate chemical analyses of the purified isotope solutions are required. The determination of the plutonium concentration in one of these solutions by controlled-potential coulometry has prompted a careful examination of the errors associated with this technique.

Much of the data and the evaluation developed here is similar to that described in UCID-16553,² an analysis of the coulometric uranium method. However, the approach is somewhat different, because in the plutonium work, it was not known a priori whether the electrical and chemical calibration values were in rigorous agreement. Moreover, the isotopic composition of the plutonium metal used as the chemical standard was not known with great certainty and was different from that of the unknown sample.

Thus an integral part of the analysis here was an attempt to determine whether the chemical and electrical calibration values were significantly different.

METHOD FOR THE DETERMINATION OF PLUTONIUM

The method used for the coulometric determination of plutonium is the now standard one in which Pu(IV) is reduced to Pu(III) in 0.5 M H_2SO_4 at a platinum electrode at +0.31 V vs SCE, and then oxidized and measured at +0.67 V.³ Other details regarding how the quantity of plutonium is computed and the operation of the instrumentation can be found in Ref. 2.

ELECTRICAL CALIBRATION

The procedure used was the same as that described in Ref. 2. The instrument used to measure the readout voltages was a TYCO Model 404 digital voltmeter* and the voltage drop across the standard resistor was measured with a Rubicon Model 2700 potentiometer. The digital voltmeter has a specified accuracy of $0.02\% \pm 1$ digit on the range used; in this case, the 10-V range. The accuracy of the potentiometer is quoted as 0.5 mV and it has a resolution of 0.1 mV out of the measured 1.3 V. The characteristics of the other components used in the calibration are given in Ref. 2.

Table 1 summarizes estimates of the worst-case errors for the electrical calibration. The total error is given here for the value of Q_e in terms of coulombs per volt. To convert this to g Pu/volt, Q_e would be multiplied by the mean atomic weight of the determined plutonium and divided by the value of the Faraday constant, 96,484.6 C/mol.

Table 1. Worst-case systematic errors in the measurement of the coulometric electrical calibration value, Q_e . Coulometry system, Serial No. 2.

Quantity	Approximate value	Estimated error	Estimated relative error (%)
Voltage on std resistor	1.35 V	0.5 mV	0.05
Integrator readout voltage difference	11 V	3 mV	0.03
Elapsed time	1000 s	--	0.05
Value of std resistor	155 Ω	---	0.005
Sum of errors, $\Delta_e =$			0.14%

The most recent value and previous values obtained for the calibration of this instrument (Serial No. 2) are listed in Table 2. It was shown in Ref. 2 that there was no discernable drift in the calibration value for a similar instrument (Serial No. 1). Although there is not as much data here as for the Serial No. 1 instrument, there does not appear to be a drift here either. The relative standard deviation of a single calibration value, s_{Q_e} [see Eq. (3), Ref. 2] is 0.030%, and for the most recent set of data, $n = 4$.

* Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

Table 2. Electrical calibration values of controlled-potential coulometry system, Serial No. 2 (27- Ω range, mean of oxidation and reduction values).

Date of calibration	Mean value, $\bar{Q}_e$ (C/V)
May, 1967	0.36862
April, 1969	0.36849
April, 1972	0.36869

CHEMICAL CALIBRATION

High-purity plutonium metal, with the characteristics given in Table 3, was used for chemical calibration.

Table 3. Analysis of plutonium metal standard (α -metal, RR-504-5).

Isotopic composition		Impurity concentrations			
Isotope	wt%	Element	ppm	Element	ppm
^{239}Pu	93.33	Si	10	Cr	<10
^{240}Pu	5.82	Al	15	C	63
^{241}Pu	0.85	U	<100	Ca	<10
		Fe	60	Mg	100
		Ni	20		
<u>Pu assay</u>					
99.97%					

From the isotopic analyses, the mean atomic weight was calculated to be 239.08 g/mol, with an estimated uncertainty of about 0.1 g/mol.

Approximately 500 mg of this material was weighed to the nearest 0.01 mg on a Mettler Model H20T balance. This sample was dissolved in 6 M HCl, then the solution was fumed with H_2SO_4 and diluted to volume in a 50-cm³, Class A volumetric flask. One-cm³ aliquots of this solution were taken for coulometric analysis using a Bio-Rad 1-cm³ micropipet.

For comparison with the electrical calibration value, the chemical calibration value, Q_c , is computed in coulombs per volt using the formula:

$$Q_c = \frac{\left(\frac{\text{wt of Pu taken}}{239.08 \text{ g/mol}}\right) (\text{Pu purity})(\text{value of Faraday constant})(\text{pipet volume})}{(\text{net integrator readout, V})(\text{flask volume})} \quad (1)$$

Table 4 summarizes estimates of the worst-case errors associated with the measurement of the chemical calibration value.

Table 4. Worst-case systematic errors in the measurement of the coulometric chemical calibration value, Q_c . Coulometry system, Serial No. 2.

Quantity	Approximate value	Estimated error	Estimated relative error, (%)
Wt of Pu metal taken	0.5 g	0.26 mg	0.05
Pu metal purity	99.97%	0.01%	0.01
Flask volume	50 cm ³	0.05 cm ³	0.10
Pipet volume	1 cm ³	0.001 cm ³	0.10
Net integrator readout	11.5 V	3 mV	0.03
Mean at. wt. of Pu	239.1 g/mol	0.1 g/mol	0.04
Value of Faraday constant	96,500 C/mol	0.3 C/mol	0.0003
Sum of errors = Δ_c =			0.33%

Two samples of the high-purity plutonium metal were assayed to obtain values of the chemical calibration. As is customary, the voltage-divider factor was set to the value calculated for plutonium based on Q_e .^{*} The background charge was 0.022 mg Pu, and this was subtracted from the total readout to obtain the weight of Pu found. The results are shown in Table 5.

Table 5. Chemical calibration of coulometry system for plutonium.

0.50885 g Pu		0.52365 g Pu	
Pu found (mg)	Q_{c1} (C/V)	Pu found (mg)	Q_{c2} (C/V)
10.175	0.36831	10.478	0.36809
10.180	0.36815	10.458	0.36879
	$\overline{Q}_{c1} = 0.36823$	10.466	0.36850
		10.474	0.36822
	$\overline{Q}_c = 0.36834$		$\overline{Q}_{c2} = 0.36840$
			$s_{\overline{Q}_{c2}} = 0.00031$

The value of $\overline{Q}_c$ was calculated by summing all six of the individual determinations of Q_c ; the relative standard deviation of Q_{c2} is 0.084%, which is a normal value for coulometry at this level. The value of $s_{\overline{Q}_{c2}}$ will be used for comparing $\overline{Q}_c$ with $\overline{Q}_e$. Since two samples of metal were analyzed here, there were two independent determinations of Q_c , and the value of n to be associated with $\overline{Q}_c$ is two.

^{*}The value used was 0.9127.

COMPARISON OF $\overline{Q}_e$ WITH $\overline{Q}_c$

Since the mean value of the electrical calibration, $\overline{Q}_e = 0.36869$ C/V, differs somewhat (0.095%) from the mean value of the chemical calibration, $\overline{Q}_c = 0.36834$ C/V, it is of interest to know whether this difference could occur by chance or is the result of a systematic bias in one of the techniques. This can be learned by constructing a student's t-statistic.

The common population standard deviation can be found from:

$$\begin{aligned}
 s &= \frac{\left((n_e - 1)(s_{Q_e})^2 + (n_c - 1)(s_{Q_c})^2 \right)^{1/2}}{n_e + n_c - 2} \\
 &= \left[\frac{(3)(0.00011)^2 + (1)(0.00031)^2}{4} \right]^{1/2} \\
 &= 0.00018 \text{ C/V} .
 \end{aligned} \tag{2}$$

The value of the test statistic is:

$$\begin{aligned}
 t &= \frac{\overline{Q}_e - \overline{Q}_c}{s \left(\frac{1}{n_e} + \frac{1}{n_c} \right)^{1/2}} \\
 &= \frac{0.36869 - 0.36834}{0.00018 \left(\frac{1}{4} + \frac{1}{2} \right)^{1/2}} \\
 &= 2.3 .
 \end{aligned} \tag{3}$$

For a two-tailed test at the 95% confidence level ($\alpha = 0.05$) and 4 degrees of freedom ($n_e + n_c - 2$), the value of $t_\alpha = 2.78$. Our computed value of t is smaller than this; thus there is a 95% probability that the two calibration values are not truly different and that the observed discrepancy is merely the result of chance. Therefore, the two values, $\overline{Q}_e$ and $\overline{Q}_c$, are pooled to obtain a better estimate of the instrument calibration.

Part of the observed difference between the electrical and chemical calibrations may be due to the nonlinearity of the voltage divider, since two different settings were used. However, the specification for this component is 0.01%, and this is not sufficient to account for the difference.

POOLING THE TWO CALIBRATION VALUES

The pooled value for the instrument calibration for plutonium, $\overline{Q}$, could be obtained from a weighted mean of $\overline{Q}_e$ and $\overline{Q}_c$, weighted in proportion to their variances. However, because their variances do not differ greatly and because the value of $\overline{Q}_c$,

although less precise, tends to cancel chemical and technique errors, the values of $\overline{Q}_c$ and $\overline{Q}_e$ will be pooled with equal weights. Therefore, our best estimate of the calibration value is

$$\begin{aligned}\overline{Q} &= \frac{\overline{Q}_c + \overline{Q}_e}{2} = \frac{0.36834 + 0.36869}{2} \\ &= 0.36852 \text{ C/V} .\end{aligned}\tag{4}$$

The worst-case error in $\overline{Q}$ would therefore be equal to the mean of the individual errors in Q_e and Q_c , taken from Tables 1 and 4, together with the voltage-divider error. Thus

$$\begin{aligned}\Delta_{\overline{Q}} &= \frac{\Delta_e + \Delta_c + 0.01}{2} \\ &= \frac{0.14 + 0.33 + 0.01}{2} = 0.24\% .\end{aligned}\tag{5}$$

The relative standard deviation of $\overline{Q}$ can be calculated from the individual variances of $\overline{Q}_e$ and $\overline{Q}_c$ as was done in Ref. 2. The formula is

$$\begin{aligned}s_{\overline{Q}} &= \frac{1}{2} \left[\frac{(s_{Q_e})^2}{n_e} + \frac{(s_{Q_c})^2}{n_c} \right]^{1/2} \\ &= \frac{1}{2} \left[\frac{(0.030)^2}{4} + \frac{(0.084)^2}{2} \right]^{1/2} \\ &= 0.031\% .\end{aligned}\tag{6}$$

This value is to be combined with the systematic error, $\Delta_{\overline{Q}}$, from Eq. (5) to obtain a worst-case total error in Q and with the standard deviation of the measurements of the plutonium in the unknown solution to obtain the standard deviation of the estimates of concentration.

MEASUREMENT OF PLUTONIUM IN UNKNOWN SOLUTION

The sample analyzed was a solution of isotopically 99.978% pure plutonium-239 at a concentration of about 6 mg Pu/cm³. This solution was analyzed directly without dilution by taking 1-cm³ aliquots for the coulometric determination. As was done for the chemical calibration runs, the integrator readout was corrected for a blank equivalent to 0.022 mg Pu.

Replicates were run on the sample over a period of several months, during which time its concentration changed. The most recent set of measurements, the dispersion of which is typical, is the following:

$$\begin{array}{r}
 5.650 \\
 5.651 \\
 5.652 \\
 \hline
 \text{Mean} = 5.651 \text{ mg Pu/cm}^3
 \end{array}$$

$$s_m = 0.024\%$$

$$n_m = 3.$$

The relative standard deviation of the mean value of the plutonium concentration, $s_{\bar{P}_u}$, can be found by combining the standard deviation of the coulometric measurements, s_m , with that for $\bar{Q}$.

$$\begin{aligned}
 s_{\bar{P}_u} &= \left[\frac{(s_m)^2}{n_m} + (s_{\bar{Q}})^2 \right]^{1/2} \\
 &= \left[\frac{(0.024)^2}{3} + (0.031)^2 \right]^{1/2} \\
 &= 0.034\% .
 \end{aligned} \tag{7}$$

Table 6 summarizes estimates of the worst-case errors in the plutonium concentration value.

Table 6. Worst-case systematic errors in the coulometric determination of plutonium in the unknown solution.

Quantity	Approximate value	Estimated error	Estimated relative error (%)
Volume of sample taken	1 cm ³	0.001 cm ³	0.10
Net integrator readout	6 V	3 mV	0.05
$\bar{Q}$, calibration factor	0.37 C/V	--	0.27 ^a
Mean at. wt. of Pu	239.0 g/mol	0.01 g/mol	0.005
Value of Faraday constant	96,500 C/mol	0.3 C/mol	0.0003
Sum of errors, Δ_{Pu}			0.43%

^aSum of systematic and random errors.

SUMMARY AND CONCLUSIONS

The mean value for the most recent three determinations and its 95% confidence limits are

$$\overline{\text{Pu}} = 5.651 \text{ mg Pu/cm}^3 \pm 0.15\% . \quad (8)$$

The confidence limits are computed from $\overline{\text{Pu}} \pm t_a s_{\overline{\text{Pu}}}$, taking $t_a = 4.3$ from the t-distribution table for $n_m = 3$. The confidence limits reflect the effects of random errors on the measured value of the plutonium concentration. Earlier sets of analyses on this same solution have very nearly identical statistics.

The worst-case, or maximum expected, systematic error, which results from factors in Table 6, is 0.43%. The worst-case systematic error computed here for the concentration of plutonium is to be regarded as the worst possible error; that is, it is virtually certain that the true error does not exceed this value. If this error is intolerable, a new, smaller error limit could be formulated, but it would have a lower probability attached to it. Note that all the errors were assumed to be of the same sign, an unlikely but not impossible event. If any of the true errors are of different sign, they will tend to cancel and reduce the overall error.

In the chemical calibration and determination of plutonium in the sample, the dominant systematic errors result from volume measurements. This points out the value of using the weighed-solution techniques. Use of the chemical and the electrical calibration values together also is apparently worthwhile, provided they agree fairly closely. Time is the principal measurement that could be refined in the determination of the electrical calibration value; this could be accomplished by the use of a gated, crystal-controlled counter/timer. The chemical calibration results could be improved by using National Bureau of Standards plutonium metal as the standard substance.

Combination of the electrical and chemical calibration values to obtain an estimate for use in the plutonium measurement decreases the random error in $\overline{Q}$, compared to that obtained by using the chemical calibration value alone. This is shown by Eq. (6). This procedure also lends intuitive confidence to the results.

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