Plutonium Coulometry at CETAMA; Recent Advancement and Performance Studies

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ABSTRACT

Safeguards activities are mainly based on nuclear material controls and rely *de facto* on validated analytical methods dedicated to actinides. The validation of analytical methods requires certified reference materials which are provided by different metrological laboratories throughout the world. In the case of plutonium (Pu), the CETAMA provides reference materials (CRM) in different forms such as pure Pu metal, pure Pu nitrate solution and, most recently, mixed U-Pu nitrate solution. The homogeneity and characterization value of these Pu CRMs are systematically verified by Controlled Potential Coulometry (CPC), the most accurate technique for the determination of Pu amount content in materials or solutions. This paper reviews the progress of Pu CPC at the CETAMA's metrological laboratory and the evaluation of its performance.
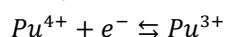
INTRODUCTION

Controlled Potential Coulometry (CPC) is a primary method for determining plutonium amount content in actinide materials [1-6]. The technique can attain a high level of accuracy and is often used to validate the Pu reference value in combination with ID-TIMS. As a reference material (RM) producer, the CETAMA (Analysis Method Establishment Committee) currently uses CPC to test the homogeneity, stability and characterization value of plutonium CRM solutions, namely the *EQRAIN Pu* and *EQRAIN (U+Pu)* series [7]. CPC's performance in terms of trueness and precision was recently assessed for the characterization of pure Pu nitrate solutions [8] and for mixed uranium (U) - Pu nitrate solutions with a 100:1 U:Pu ratio [9]. Expanded relative uncertainties were shown to lie below 0.14% (*k=2*) for 5 mg samples. This uncertainty is in full compliance with the IAEA's ITVs 2010 recommendations [10] and is also consistent with the level of uncertainty of the standards. Recently, the CETAMA participated in an interlaboratory comparison dedicated to Pu coulometry organized by the IAEA-NML Seibersdorf laboratory [11]. The standards provided for the comparison were supplied as dry Pu nitrate residues and, following an initial dissolution step (which underwent optimization during the tests), were analyzed according to the CETAMA's routine procedure. Concerning trueness, no bias was observed between the mean value of 5 replicates and reference value. The expanded relative uncertainty was evaluated to be 0.20% (*k=2*) for 2 mg samples. The results demonstrated that CPC can be considered a reference analytical method for the determination of the Pu mass fraction in samples of dry Pu nitrate residue.

APPLICATION OF COULOMETRY TO THE DETERMINATION OF PLUTONIUM AMOUNT CONTENT

Fundamentals of coulometry

Coulometry is an analytical method based on the measurement of a quantity of electricity (Q) involved in an electrochemical reaction, such as the single-electron reaction involving the Pu(IV)/Pu(III) redox pair: $$Pu^{4+} + e^- \leftrightarrows Pu^{3+}$$
Assuming a selective reaction (without other competitive electrochemical reactions), Faraday's Law applies and relates the quantity of electricity (Q) flowing during the reaction to the quantity of matter transformed in solution according to the relationship (Eq.1):

$$m_{Pu} = \frac{Q}{nF} M_{Pu} \qquad \text{Eq. 1}$$

where: *m: mass of the element to be measured (g); M: molar mass of the element (g/mol); n: number of electrons involved in the electrochemical transformation of the element; F: Faraday's constant [12]; Q: quantity of electricity accumulated for the quantitative transformation of the species under consideration (C).*

The CPC method is a so-called primary direct method of measurement because it is based only on physical standards (current and time) and does not require the use of chemical standards. Consequently, the method is very accurate when the measurement protocol is well controlled.

Controlled-Potential coulometry (CPC)

During CPC, the potential of the working electrode is kept constant in relation to a reference electrode by means of a potentiostat and a three-electrode set-up. The applied potential corresponds to a value at which the expected electrochemical transformation is predominant. The integration of the current i as a function of time makes it possible to measure the quantity of electricity Q and determine the mass of the studied element present in solution. As such, the technique is both simple to implement and accurate. These crucial advantages have made CPC an analytical method of choice for the metrological determination of Pu in aqueous acidic

Implementation of coulometry

CPC relies on a three-electrode set-up with separate compartments for the reference- and counter- electrodes. This separation is necessary as the products generated at the working electrode must not come into contact with the counter-electrode, as this could lead to a side-reaction and as the electrical balance could become biased. The potential applied to the working electrode drives the completion of the reaction.

The assay is thus divided into 2 steps, reduction and oxidation (shown in Figure 1): it is during this last step that the amount of charge used (Q) is measured.
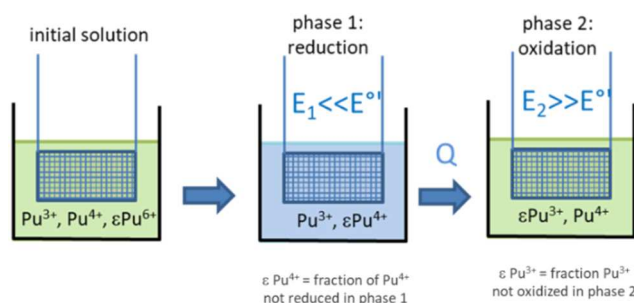

Figure 1 : Steps of the coulometric analysis of Pu.

Corrections

Unfortunately, the two steps of the coulometric procedure do not allow to achieve the desired analytical accuracy. As such, corrective factors must be introduced to take into account the electrochemical responses of the blank and residual currents as well as the incompleteness of the reaction. These corrections - which largely determine the accuracy of the coulometric method - are described hereafter.

The two components of the blank are respectively known [13,14] as the faradic (Q_f) and capacitive (Q_c) charges. These charges are considered sufficiently reproducible to the point where they can be measured in a blank measurement procedure in the presence of the electrolyte.

The blank correction, Q_b, corresponds to the capacitive term, Q_c, which results from the subtraction of the faradic term from the raw blank signal Q_1 (Eq. 2):

$$Q_b = Q_c = Q_1 - Q_f = Q_1 - i_{r1}t_1 \qquad \text{Eq. 2}$$

The correction for residual current is also applied to the raw signal of the analysis, Q_2, in order to obtain the net charge Q_s:

$$Q_s = Q_2 - Q_f = Q_2 - i_{r2}t_2 \qquad \text{Eq. 3}$$

The blank correction is finally applied to the net charge in order to obtain the effective charge, Q, which is used in Faraday's law:

$$Q = Q_s - Q_b = Q_2 - i_{r2}t_2 - (Q_1 - i_{r1}t_1) \qquad \text{Eq. 4}$$

In addition to these corrections, the accuracy of the measurements can be further improved by taking into account the fraction of Pu not reduced during the first stage of electrolysis and the fraction not oxidized during the second stage of electrolysis, symbolized by εPu^{4+} and εPu^{3+} in Figure 1.

This correction for the electrolysed fractions, noted f, makes it possible to quantify with accuracy the proportion of Pu electrolysed and is used as a corrective term for the expression of the final result [4, 15,16]. f , as a function of T and E°', and m_{Pu} are expressed as shown in Equation 5:

$$f = \frac{\exp(\frac{n \cdot F \cdot (E_2 - E^{\circ\prime})}{R \cdot T})}{1 + \exp(\frac{n \cdot F \cdot (E_2 - E^{\circ\prime})}{R \cdot T})} - \frac{\exp(\frac{n \cdot F \cdot (E_1 - E^{\circ\prime})}{R \cdot T})}{1 + \exp(\frac{n \cdot F \cdot (E_1 - E^{\circ\prime})}{R \cdot T})} \qquad m_{Pu} = \frac{Q}{nFf} M_{Pu} \qquad \text{Eq. 5}$$

where: *R: molar gas constant (= 8.314462618 J mol⁻¹ K⁻¹) [12]; T : solution temperature at the time of assay (K); E°' : formal potential; E₂: potential for oxidation step; E₁ : potential for reduction step.*

SAMPLES DESCRIPTION

Studies were performed on two types of reference materials, a mixed (U+Pu) nitrate aqueous solution from the CETAMA EQRAIN series and a Pu nitrate solid residue prepared by IAEA Seibersdorf for the purpose of an ILC on coulometry of Pu.

EQRAIN (U+Pu) solution
The mixed (Pu+U) solutions analyzed during the study were directly sampled from the standard solution *EQRAIN (U+Pu) 2* of Pu nitrate and uranyl nitrate supplied by the CETAMA's LAMMAN in HNO_3 (2.71 ± 0.14) mol L⁻¹. The Pu in the standard solutions used is traceable to the CETAMA's MP2 Pu metal CRM whilst the U is traceable to the CETAMA's MU 2 U metal CRM. The reference Pu amount content of the standard solution was determined to be (1.1192 ± 0.0013) g kg⁻¹ (k=2) on the date of fabrication (26/04/2017). The reference U content of the standard solution was determined to be (106.52 ± 0.13) g kg⁻¹ (k=2). The density of the reference solution is (1.26857 ± 0.00012) g mL⁻¹ at 20 °C (k=2). The amount content of Pu in the solution on the date of analysis was determined by taking into account the MP2 isotopy and the decay of the Pu isotope but it did not change significantly: the molar mass was determined to be (239.07453 ± 0.00002) g mol⁻¹ (k=2) on the date of analysis (26/03/2019).

IAEA Pu nitrate solid residue
The samples received from the IAEA were dry Pu nitrate extracts prepared in 10 mL glass vials. Each glass vial was sealed with a septum and an aluminum ring and contained a little more than 5 mg Pu under the form of a dry residue obtained from the evaporation of a known mass of Pu stock solution which was communicated to participants. No coating polymer was used to stabilize the dry extract as it was considered to be sufficiently adherent to the vial walls. The Pu used to prepare the vials is traceable to the NBL 126-A Pu metal CRM which molar mass at the date of analysis was calculated to be (239.11355 ± 0.00002) g mol⁻¹ on the 28/11/2018.
The reference Pu amount content of the standard solutions was determined to be (8.8510 ± 0.0053) g kg⁻¹ (k=2) on the date of fabrication (6/07/2018)

SAMPLE PRETREATMENT

Direct sampling and fuming to dryness (EQRAIN U+Pu solution)

As the mass fraction of Pu in the mixed (Pu+U) solutions is not particularly important (1.1 g kg^{-1}) no preliminary dilution of the EQRAIN standard solution was deemed necessary. The sample was thus used as received without dilution and weighed directly into the coulometric glass cells used for CPC analysis. All the weighing was performed with an analytical scale and corrected for air buoyancy in order to eliminate systematic errors.

Once the aliquots had been transferred and weighed, sulphuric acid (H_2SO_4) (1 mL, 3 mol L^{-1}) was added to the cells in order to stabilize the actinides as Pu(IV) disulphate and U(VI) sulphate crystals during the fuming procedure. A few drops of hydrogen peroxide (H_2O_2) (30% v/v) were further added to the solutions to reduce any Pu(VI) present to Pu(IV) [17,18]. The created solutions were left to homogenise and react overnight prior to fuming to dryness under a nitrogen sweep. Upon drying, any chloride, fluoride, and volatile organic compound impurities in the samples were eliminated. The presence of H_2SO_4 in the fumed solutions further prevented the formation of insoluble oxides by stabilising the Pu and U as soluble sulfate crystals.

Dry residue dissolution (IAEA Pu nitrate solids)

The first step of analysis was the dissolution of the Pu nitrate solid adhering to the walls of the vial by introducing a portion of 5 mol L^{-1} nitric acid solution into the vials and allowing it to react for a period of 24 hours. The created solution was then homogenised, and partially sampled (transferring only part of the solution to the electrolysis cell). Care was taken to measure the total mass of dissolving solution before sampling as well as that of each sample transferred to the coulometric cell. The validity of the tare communicated at shipment was confirmed after cleaning and drying the vial. Two samples were taken per vial, each corresponding to a Pu mass close to 2 mg. To evaluate the total quantity of Pu originally contained in each vial, it was necessary to determine the fraction of dissolution solution taken from the vial. The amount fraction of Pu could be calculated in g kg^{-1} of solution from the Pu mass and the weight of solution (net mass transmitted by the IAEA). The proportionality factor r, equivalent to the ratio of the mass of the total solution contained in the vial after dissolution to the mass of solution sampled, is expressed (using the masses corrected for air buoyancy) as shown in Equation 6:

$$r = \frac{m_{total\,solution}^{corrected}}{m_{sample}^{corrected}} \qquad \text{Eq. 6}$$

The final step of the sample preparation consisted in fuming the prepared solutions to dryness in the electrochemical cell in the manner as previously described for the EQRAIN (U+Pu) solutions.

COULOMETRIC ASSAYS

Protocol

The analysis of the Pu content of solutions followed the ISO 12183 standard [17] and was performed through a four-step procedure:

Step 1: Electrical calibration of the analog-to digital converter.

Step 2: Electrode pre-treatment. Prior to analysis, the Au working electrode was electrochemically cleaned through a pre-treatment procedure in HNO$_3$ (0.9 mol L-1) with two drops (approx. 100 µL) of sulfamic acid (1.5 mol L^{-1}). Sulfamic acid was added to the solution as a non-electrochemically active inhibitor for any nitrous acid [5, 17, 18].

Step 3: Blank measurement. In the same medium used for the pre-treatment procedure, a blank measurement was performed. During the blank measurement, a reductive potential $E_1 = E^{\circ\prime} - 230\,mV$ was applied to the working electrode, followed by an oxidative potential $E_2 = E^{\circ\prime} + 230\,mV$.

During the latter step, the duration of oxidation (t_1), residual current (i_{r1}), and raw quantity of electrical charge used (Q_1) were recorded [17].

Step 4: Coulometric analysis of Pu. The electrolyte used for the pre-treatment and blank measurements was transferred to the coulometric cell containing the dried sample to be analysed. The dried sample was dissolved in the solution through mild agitation. After this, the analysis procedure consisted in applying the same reducing potential E_1 followed by the same oxidising potential E_2 . During the oxidation step, the duration of oxidation (t_2), residual current (i_{r2}), and raw quantity of electrical charge used (Q_2) were measured.

Measurement of the formal Pu(IV)/Pu(III) redox potential
The measurement of the formal redox potential E°' is essential to evaluate the level of completion of both the reduction and oxidation reactions and to express the f factor corresponding to the electrolyzed fraction. It was determined from coulograms recordings such as those shown in Figure 2. The E°' value varies on whether the solution corresponds to a pure Pu sample or to a mixed U-Pu sample because it is sensitive to Pu-sulphate complexation. Indeed, the U in the mixed sample is 100 times more concentrated than Pu and the solid residue of uranyl sulfate brings into solution a significant amount of sulphate in the analytical medium after dissolution. E°' value equals (677 ± 5) mV/SCE for pure Pu nitrate medium and (595 ± 5) mV/SCE in mixed U-Pu medium. The shift in potential is of about 70 mV and has to be taken into account to modify in consequence the applied potentials, E₁ and E₂, and to express *f* accurately [9].
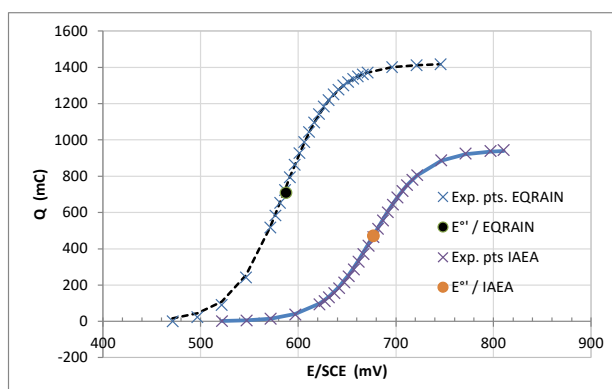

Figure 2 : Coulograms of pure Pu (solid line) and mixed U-Pu solution (dotted line) in HNO₃ (0.9 mol L⁻¹). The inflexion point of each curve (corresponding to the solution's $E^{0\prime}_{Pu(IV)/Pu(III)}$) has been marked.

Results
Table 1 shows the detail of the results of the CPC analyses for both experiments. The final value for the Pu mass fraction was taken as the arithmetic mean value of the 5 or 4 selected results. The repeatability of measurement was also estimated from the standard deviation of replicates.

Experiment	[Pu] (g/Kg)	Experiment	[Pu] (g/Kg)
CC01-0007-2	8.86292	YD56	1.1219
CC01-0008-1	8.85608	YD57	1.117
CC01-0008-2	8.87942	YD58	1.1188
CC01-0009-1	8.83376	YD59	1.1199
CC01-0009-2	8.86838		
Mean value	**8.86011**	Mean value	**1.1194**
st. dev.	0.01703	st. dev.	0.0021
rel. st. dev.	0.19%	rel. st. dev.	0.18%

Table 1 : Results for the experimental determination of Pu mass fraction for AIEA and EQRAIN U+Pu 2 solutions.Calculation of the Pu mass fraction mean value in g kg⁻¹.

UNCERTAINTY EVALUATION

Mathematical expression of the Pu mass fraction

In the case of the EQRAIN solution, the mathematical model of the Pu mass fraction is:

$$\%_w Pu = \frac{(Q_2 - Q_1 - i_{r2}t_2 + i_{r1}t_1)}{nFf} \frac{M_{Pu}}{m_{sol.}^{EQRAIN}} \qquad \text{Eq. 7}$$

In the case of the IAEA samples, the mathematical model of the Pu mass fraction becomes:

$$\%_w Pu = \frac{(Q_2 - Q_1 - i_{r2}t_2 + i_{r1}t_1)}{nFf} \frac{M_{Pu}}{m_{sol.}^{AIEA}} \frac{m_{sol.}^{vial}}{m_{sample}} \qquad \text{Eq. 8}$$

where $m_{sol.}^{AIEA}$ is the mass of solution which was dried by IAEA before shipment and communicated prior to analysis. The ratio $\frac{m_{sol.}^{vial}}{m_{sample}}$ represents the *r* factor.

Monte Carlo Method approach

The uncertainty of measurement results was calculated through the Monte Carlo Method based on the propagation of probability distribution function [19].

This method is pertinent when the measurand mathematical model is complicated (nonlinear expressions) and when the uncertainties of the input are not of the same order of magnitude.

Therefore, it was deemed an appropriate method for the estimation of the uncertainties for *f* and Pu mass fraction *%ₓPu*. The method, based on the sampling of a great number of input quantities (N) at random and according to their probability distribution (N ≈ 10^6) (the calculations were performed using the JMP®14.0 SAS institute Inc. software), allows to plot the probability distribution function of *f* or *%ₓPu*. From the probability function plotted, the parameters expectation and variance of distribution can be estimated.

With MCM simulations, the coverage interval (*CI*) of the distribution comes directly from the probability density function of the measurement result. If the probability density functions from the MCM simulations are symmetrical and not significantly different from a Gaussian shape, it is possible to express the standard uncertainty terms by dividing the *CI* from MCM by 4.

Input parameters and their distribution

As regards the mathematical expressions, the Pu mass fraction is a function of 14 or 16 parameters, which numerical value, standard uncertainty and distribution are needed as input data for the MCM calculation code.

Given as an example, Table 3 gathers the parameters information for the determinations of the Pu mass fraction of an IAEA and an EQRAIN samples.

| input variables | IAEA characterization | | | input variables | EQRAIN characterization | | |
	value	andard uncertaint	assumed distribution		value	standard uncertainty	assumed distribution
Q_1 (mC)	9.9	0.5	normal	Q_1 (mC)	7.6	0.5	normal
i_{r1} (µA)	0.82	0.7	normal	i_{r1} (µA)	1	0.7	normal
t_1 (s)	351	$1/\sqrt{3}$	uniform	t_1 (s)	287	$1/\sqrt{3}$	uniform
Q_2 (mC)	957.5	0.5	normal	Q_2 (mC)	1443.2	0.5	normal
i_{r2} (µA)	1.3	0.8	normal	i_{r2} (µA)	4.7	0.8	normal
t_2 (s)	702	$1/\sqrt{3}$	uniform	t_2 (s)	933	$1/\sqrt{3}$	uniform
M_{Pu} (g/mol)	239.11355	0.00001	normal	M_{Pu} (g/mol)	239.07453	0.00001	normal
F (C/mol)	96485.33212	none		F (C/mol)	96485.33212	none	
R (J mol⁻¹K⁻¹)	8.314462618	none		R (J mol⁻¹K⁻¹)	8.314462618	none	
T (K)	298.5	$1/\sqrt{3}$	uniform	T (K)	296	$1/\sqrt{3}$	uniform
E° (mV/SCE)	676.9	2	normal	E° (mV/SCE)	591.4	2	normal
E_1 (mV/SCE)	445	0.4	normal	E_1 (mV/SCE)	371.9	0.4	normal
E_2 (mV/SCE)	904.8	0.4	normal	E_2 (mV/SCE)	831.4	0.4	normal
$m_{AIEA\ sample}$ (g)	0.57451	0.000057	uniform	$m_{EQRAN\ sample}$ (g)	3.1624	0.0006	uniform
m_{sample} (g)	3.48084	0.00058	uniform				
$m_{sol.\ vial}$ (g)	7.54475	0.00058	uniform				

Table 2 : Input parameters for the mathematical model of Pu mass fraction..

<u>Distribution probability function of Pu mass fraction and uncertainty determination</u>

The distribution profile of the Pu mass fraction is calculated by the JMP software with the input parameters shown in Table 3. For results concerning IAEA samples, the probability density function is plotted in Figure 3 with its quartiles shown in the box plot beside the graph. It can be seen that the Pu mass fraction appears to be symmetrical and of a Gaussian shape. The coverage interval *CI* can then be calculated by the difference of quantiles corresponding to 2.5% and 97.5% confidence level.
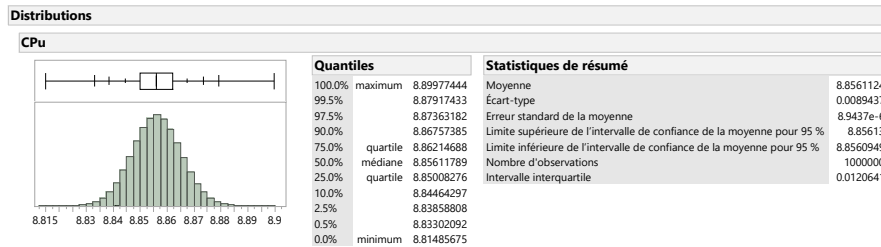
Figure 3 : Probability density function, quartiles, and statystical analysis for the $\%_w Pu$ as determined using the Monte Carlo Method for uncertainty determination (exp. CC01-0008-1).

Half of the coverage interval is equal to $0.01752\ \mathrm{g\ kg^{-1}}$ and is equivalent to the expanded uncertainty (assuming a normal distribution, which is approximately the case of this distribution).

The expanded uncertainty, *U*, can thus be estimated:

$$U_{IAEA}(\%_w Pu) = \frac{CI}{2} = 0.01752\ g\ kg^{-1} \quad (k=2)$$

For the EQRAIN sample characterization, the coverage interval was also deduced from the MCM calculated distribution and equaled $0.0015\ \mathrm{g\ kg^{-1}}$ and was used to estimate the expanded uncertainty:

$$U_{EQRAIN}(\%_w Pu) = 0.0015\ g\ kg^{-1} \quad (k=2)$$

FINAL EXPRESSION OF RESULTS AND COMPARISON TO THE REFERENCE VALUE

<u>Plot of results</u>

The plot in Figure 7 shows the individual IAEA experimental results, the mean value with its tolerance interval, and the reference value with associated uncertainty. CIs overlap, showing graphically that the values are not significantly different. The CI bars of the individual measurements also cover the CI of the experimental value, which confirms the absence of outliers.
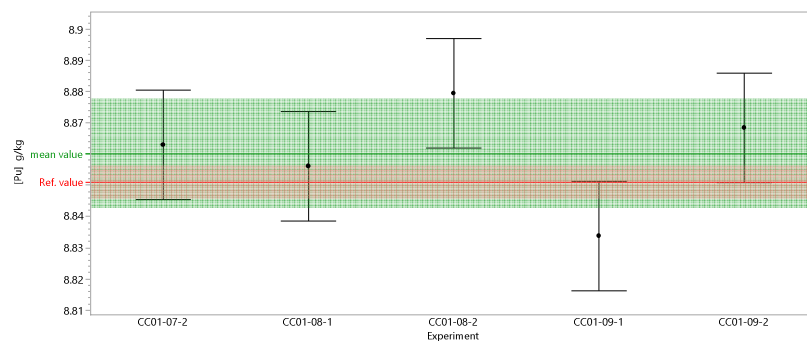

Figure 4 : Plot of the individual results and of the mean value (green solid line) for the determination of the Pu mass fraction in IAEA samples. The CIs of the reference value as well as that of the results (bands) and the reference value (red solid line) are also plotted.

The results for EQRAIN solution characterization are also plotted in Figure 8 with same information and the graph shows that the bias between the mean value and the reference value is non-significant as the CIs overlap.
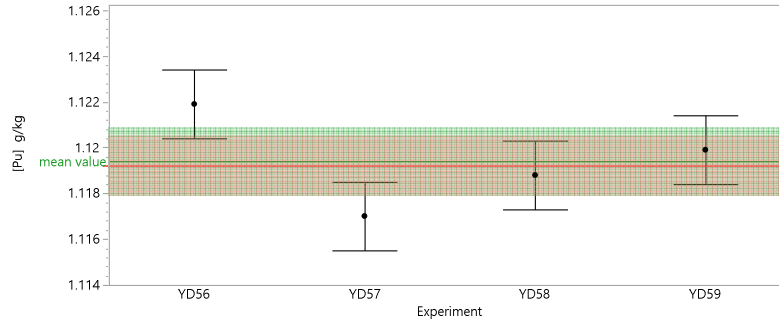

Figure 5 : Plot of the individual results and of the mean value (green solid line) for the determination of the Pu mass fraction in EQRAIN samples. The coverage intervals of the reference value as well as that of the results (bands) and the reference value (red solid line) are also plotted.

Expression of final results

The expression of the final result is based on the arithmetic mean value of the 4 or 5 results as well as on the estimation of uncertainty performed by applying the Monte Carlo Method to our analytical procedure.

For IAEA sample characterization, the method used corresponds to an analytical procedure comprising the dissolution of the solid sample as well as the Pu assay by CPC: the final result is:

$$\%_w^{IAEA} Pu = (8.860 \pm 0.018) \ g/kg$$
expanded relative uncertainty = 0.20% (*k=2*)

For the EQRAIN (U+Pu) sample characterization, the method used is the LAMMAN routine procedure with no preliminary dilution of the sample: the final result is:

$$\%_w^{EQRAIN} Pu = (1.1194 \pm 0.0008) \ g/kg$$
expanded relative uncertainty = 0.07% (*k=2*)

Comparison to reference value and method performance analysis

For IEA sample characterization, the bias on Pu mass fraction value was found to be positive and equal to 0.10%.

bThe estimation of the standard uncertainty in conditions of repeatability was calculated by the MCM approach and equaled 0.0088 g kg^{-1} and was used to estimate the trueness of the method.

The significance of the method's bias was then analyzed through the normalized deviation term, E_n , as shown hereafter (where *[Pu]$_{ref}$* = 8.8510 g kg^{-1}, u_{ref} = 0.0027 g kg^{-1}, and u_{exp} = 0.0088 g kg^{-1}). If E_n is lower than 2 in absolute value, the bias is considered non-significant.

$$E_n = \frac{\%_w Pu_{mean} - \%_w Pu_{ref}}{\sqrt{u_{exp}^2 + u_{ref}^2}}$$

In our case, this calculation gives:

$$|E_n| = \frac{|8.8601 - 8.8510|}{\sqrt{0.0088^2 + 0.0027^2}} = 1.0 < 2$$

As such, no bias is observed for the result corresponding to the mean of 5 replicates. The CPC method can thus be considered a true method for the determination of the Pu mass fraction measured from the dissolution of Pu nitrate solid residue. The relative uncertainty of the measurement in conditions of sampling representative of 2 mg of Pu was evaluated to be equal to 0.20% at *k=2*.

For EQRAIN (U+Pu) sample characterization, the bias on Pu mass fraction determination based on 4 replicates was found to be equal to +0.02%:

The estimation of the standard uncertainty in conditions of repeatability was calculated by the MCM approach and was found to be 0.00075 g kg^{-1} and was used to estimate the trueness of the method.

The normalized deviation term where $[Pu]_{ref}$ = 1.1192 g kg^{-1}, u_{ref} = 0.0007 g kg^{-1}, and u_{exp} = 0.00075 g kg^{-1}) was calculated and found to be lower than 2 in absolute value which means that the bias can be considered as non-significant.

$$|E_n| = \frac{|1.1194 - 1.1192|}{\sqrt{0.00075^2 + 0.0007^2}} = +0.20 < 2$$

Therefore, no bias is observed for the result corresponding to the mean of 4 replicates. The CPC method can thus be considered a true method for the determination of the Pu mass fraction in the presence of U in a ratio of U:Pu of 100:1. The relative uncertainty of the measurement in conditions of a sampling representative of 4 mg of Pu was evaluated to be equal to 0.069% at $k=1$ and comparable to the uncertainty of the method applied to pure nitrate solutions [8].

CONCLUSION

This work reports the latest advancements in the application of Controlled-Potential Coulometry (CPC) to Pu-containing samples at the CETAMA's metrological laboratory (LAMMAN). It focuses on the assessment of CPC's performance for the determination of Pu mass fraction in the presence of large amount of U and on the participation in an interlaboratory comparison (ILC) on Pu coulometry organized by IAEA.

The former case consisted in characterizing the CETAMA's EQRAIN U+Pu 2 reference material (traceable to MP2 and MU2 CRMs) and in evaluating the trueness and precision of the method in presence of a large excess of U, corresponding to a ratio U:Pu of 100:1. Results showed that the performance of the routine method is maintained as long as the Pu(IV)/Pu(III) formal potential, sensitive to sulfate brought along with U, is determined systematically. The bias of the method was not significant and the expanded relative uncertainty (k=2) was evaluated to be equal to 0.13% for a 4 mg-Pu sample.

The latter case concerned the IAEA's ILC whose reference material corresponded to a dried nitrate Pu solution. It enabled the LAMMAN to assess the performance of CPC for the characterization of Pu nitrate solid samples from a reference material traceable to NBL CRM 26-A with which we have less experience. No significant bias was observed and the expanded measurement uncertainty was determined to be 0.20% relative: it was higher than that which is usually obtained (0.10% relative) due to the additional dissolution step required which introduced supplementary source of error compared to our routine protocol adapted to Pu metal or Pu nitrate in solution. It is also important to note that the measurements performed in this study were carried out on sub-optimal quantities of Pu (2 mg rather than 5 mg), this would also have affected the quality of the analyses performed. In spite of these difficulties, results demonstrated that CPC remains a highly accurate method for the determination of Pu amount content in solid Pu nitrate samples.

ACKNOWLEDGEMENTS

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