USE OF CONTROLLED-POTENTIAL COULOMETRY SYSTEM FOR PLUTONIUM ANALYSIS AT THE IAEA NUCLEAR MATERIAL LABORATORY

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ABSTRACT

Controlled Potential Coulometry (CPC) is routinely used by the International Atomic Energy Agency's Nuclear Material Laboratory (NML) to verify plutonium stock solutions that are either prepared from pure PuO_2 materials or gravimetrically by dissolution of plutonium metal, latter ones being used as source solutions to prepare U/Pu large-sized dried (LSD) spikes. However, CPC requires costly expensive maintenance, and is particularly sensitive to interferences from certain elements. Therefore, many laboratories use isotopic dilution analysis (IDA) mass spectrometry methods for Pu determination, and only a few laboratories still have the expertise, instrumentation and software capabilities to routinely use CPC method. With the aim of promoting the CPC as a primary analytical method for determination of plutonium amount, investigations were conducted with the IAEA Network Analytical Laboratories (NWAL) to extend the use of CPC for the analysis of Pu samples with lower Pu content and complex sample composition. Inter-comparison samples were prepared by the IAEA/NML and analysed by laboratories in France and the USA. The results confirmed that CPC can be applied to lower Pu amounts if adequate sample preparation protocol is applied, and for analysis of synthetic samples containing U and Pu at a low molar U/Pu ratio, while analysis of U/Pu containing inspection samples requires proper bias correction due to uranium and iron interferences.

INTRODUCTION

Coulometry is an analytical technique based on the measurement of a quantity of electricity Q involved in an electrochemical transformation (during either oxidation or reduction) and is governed by the Faraday's law. Controlled-potential coulometry is a method of choice for determining plutonium in solution and considered to be a "primary" method because its methodology is based on physical parameters which can be calibrated very accurately. It allows to attain high trueness with bias close or below 0.1% on low sample amounts, typically a few milligrams of matter [1]. Since 2019, IAEA's Office of Safeguards Analytical Services (SGAS) collaborates with two NWALs, CETAMA/LAMMAN laboratory (France) and SRNL laboratory (US) to promote the use of CPC and strengthen NML capabilities for analysis of safeguards inspection samples, aiming for CPC being used as alternative technique to IDA. A first CPC interlaboratory comparison exercise was organized in 2019 with SGAS-NML, CETAMA/LAMMAN and SRNL as participating laboratories, and specific tests were conducted in parallel at the SGAS-NML by applying CPC on U/Pu synthetic mixture and real inspections samples.

1.CPC INTERLABORATORY COMPARISON EXERCISE

Pu stock solution for interlaboratory comparison was prepared at SGAS-NML by dissolution of the certified reference material NBL CRM 126-A (Pu metal), with Pu concentration being adjusted to suit the routine analytical procedures of laboratories taking part in the exercise. The reference (make-up) value of the Pu stock solution was assigned by gravimetry and verified by IDA using two different Pu-242 spike materials, as well as by CPC. The assigned reference value of Pu amount content was (8.8510 +/- 0.0051) mg/g (k=2) whilst the average value of the verification results obtained by IDA and CPC was 8.84874 mg /g. At the time of aliquoting, the Pu mass fraction in the stock solution was corrected for evaporation, was found to be (8.8510 ± 0.0053) mg /g. Twenty-five (25) dried nitrate samples were prepared, by aliquoting Pu stock solution into penicillin vials each containing approximately 5 mg (for CETAMA/LAMMAN) and 17 mg Pu (SRNL). Samples were shipped to the CETAMA/LAMMAN and SRNL laboratories where the Pu content of each sample was analysed after being dissolved and transferred to coulometric cells. The relative differences between the results reported by

different laboratories in comparison to the reference value are presented in Figure 1. While the data reported by CETAMA/LAMMAN are generally higher than the reference value, the data reported by SRNL are lower in comparison to the reference value. SRNL noted significant difficulties in obtaining a homogeneous sample solution by dissolution of several dried nitrate samples before transfer to coulometry cells and CPC measurements [2]. SRNL performed the dissolution of the samples in accordance to International Standard ISO 12183. Picture 1 presents the sample solutions that exhibit visual difference between a successful dissolution, and a sample that exhibited dissolution difficulties. Analyses for the samples with dissolution issues exhibited a strong negative bias (up to approx. -0.95%), therefore only results for samples visually homogeneous are presented in Figure 1. Previously, SRNL had successfully dissolved dried Pu nitrate samples and analysed samples by CPC with an expanded uncertainty of 0.073% (relative). Dissolution issues were less prominent in the smaller 5 mg Pu samples analysed at the CETAMA/LAMMAN and analytical results presented in Figure 1 obtained for 5 mg Pu samples corresponds to results obtained using 2 mg Pu sub-aliquots. However, in order to reduce the potential bias related to quantitative mass transfer, an optimisation of the sample preparation protocol was needed to achieve an expanded measurement uncertainty of 0.2% even with small Pu amounts [3]. The experiences with sample preparation protocols used by SRNL and CETAMA/LAMMAN indicate that preparation of dried Pu nitrate samples as well as dissolution and quantitative transfer of the samples prior to CPC analysis, is not very straightforward.

2 ANALYSIS OF U-PU MIXED SAMPLES

IDA using thermal ionization mass spectrometry (TIMS) is the main method applied in SGAS-NML for analysis of milligram size Pu samples collected during IAEA in-field verification activities. CPC is used to validate stock solutions prepared from pure Pu reference materials (Pu metals NBL CRM126-A or CETAMA MP2) for preparation of large-size dried spikes (LSD) and Pu spike solutions. Investigations were conducted by the SGAS-NML to extend the application of CPC to the analysis of inspection samples as an alternative to IDA. In this study, tests were conducted using both U/Pu synthetic mixtures prepared at the SGAS-NML and actual inspection samples collected at Japanese R&D facilities. Several inspection samples were selected for analysis by CPC to demonstrate the applicability of CPC to the different types of inspection

samples - samples containing only Pu, or samples containing U and Pu with different U/Pu amount ratios. Precision of the CPC analysis was determined by estimating a bias by comparing CPC results with IDA results used as "expected" values. Additionally, the quality of the CPC results was also evaluated by evaluation of results obtained for pure Pu stock solutions.
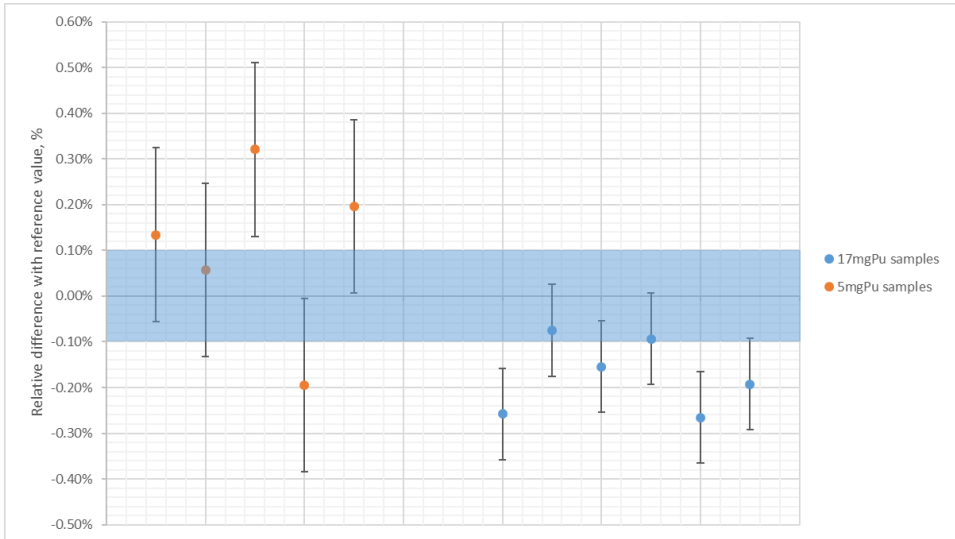

Figure 1. Relative difference between reference value and Pu concentration content results (and their combined uncertainties) obtained by NWAL laboratories

Picture 1. Example of successful dissolution (left) and sample that exhibited dissolution difficulties (right).

2.1 APPARATUS

Coulometric measurements were done using the apparatus developed and qualified by SRNL for the IAEA [4]. This system consists of a measurement cell installed in a glove box and an electronic measurement unit contained in a rack outside the glove box. The measurement cell is a 10 mL glass container filled with 0.5 M H_2SO_4 support electrolyte and fitted with an O-ring seal/lid suitable for its internal equipment: inlet tube for Ar inert gas supply, glass stirrer, Pt mesh working electrode, saturated calomel reference electrode (SCE), Pt wire counter electrode. The electronic measurement unit is composed of a potentiostat and an integrator combining electronic circuits and printed circuit boards upgraded with state-of-the-art components. This system is designed to measure the concentration of Pu samples in the 5 to 10 mg range with an accuracy of +/-0.1 % as a result of its improved current stability and internal calibration capabilities. The sample preparation, analytical procedure and calculation method applied were based on the international standard (ISO) for the controlled-potential coulometric assay of plutonium [5]. Iron impurities are known to interfere significantly during CPC measurements of Pu. However, the formal potentials of plutonium and Fe are sufficiently close in dilute sulphuric acid that they are electrolysed in approximately equal fractions during a standard CPC analysis. It is thus possible to correct CPC analyses of Pu in the presence of Fe by subtracting the amount of Fe electrolysed, as determined through a separate analytical technique. In the present study, an Agilent Cary 60 UV-VIS spectrophotometer was used (applying ASTM international standard for measuring iron content) to determine the Fe concentration in the studied samples and compensate for its interference during the CPC analyses of Pu [6].

2.2 ANALYSIS OF SYNTHETIC SAMPLES

Pure Pu source material (NBL CRM 126-A) and standard U material (U_3O_8 powder) were used as source materials, to prepare U and Pu stock solutions. From those solutions fifteen (15) coulometry samples containing about 4 mg Pu with a different U/Pu amount ratio were prepared. Coulometric blank measurements in H_2SO_4 medium were within expected range (observed fluctuations: 8 – 17 µg in Pu equivalent) and the formal potential (E°') of the Pu^{4+}/Pu^{3+} redox pair measured within expected range (between 491 and 495 mV/SCE at 25°C) discarding the

potential interference from uranium sulphate even for high U/Pu ratio. For U/Pu amount ratios up to 5, the CPC measurements were seen to be consistent with the expected value obtained by IDA (as shown in Figure 2), confirming that CPC performance is satisfactory. This was demonstrated also by the CETAMA/LAMMAN, analysing samples prepared from pure Pu reference materials with U/Pu amount ratios up to 10 [7].
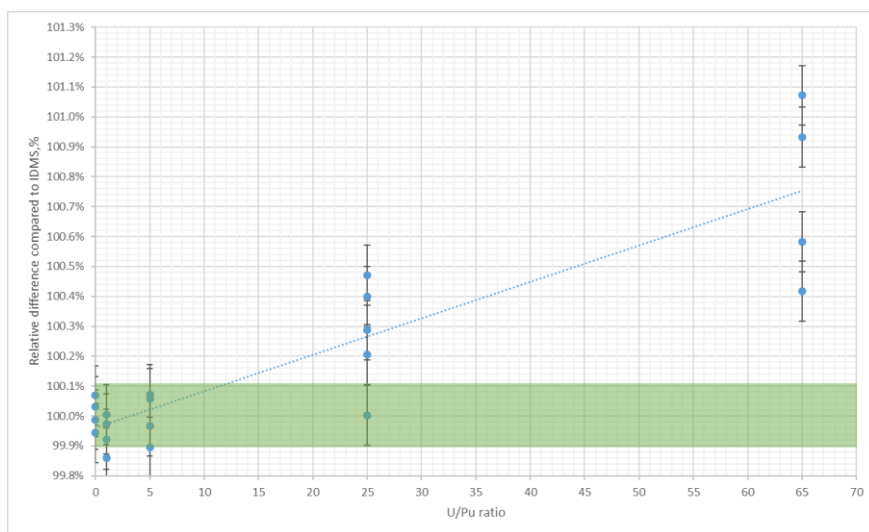

Figure 2. Relative difference between CPC results (blue dots) with "expected" values obtained by IDA (green band, expected value of 100% +/-expanded uncertainty of 0.1%). CPC results are not corrected for Fe interference.

A positive bias, possibly linked to the presence of an impurity interfering with coulometric measurements, was observed for samples with higher U/Pu amount ratios. This positive bias could be explained by the effect of sulphate complexation that reduces the difference between the Pu and U potentials (see Table 1) and therefore increase interference of uranium during the reduction step of Pu^{4+} to Pu^{3+}. The same experimental results are shown in Figure 3 after performing a correction for Fe content. It can be seen that the chosen technique resulted in an overcorrection of the analysis results even for low U/Pu ratio samples, showing a negative bias with quite scattered results.

Table 1. Comparison of redox potentials E° vs. S.CE. in various acids [8][9]

Acid media	Pu^{4+}/Pu^{3+} mV	U^{4+}/UO_2^{2+} mV
$[H_2SO_4]= 0.5$ M	490	420
$[HNO_3]= 1$ M	690	Not available
$[HCl]= 1M$	720	310±30
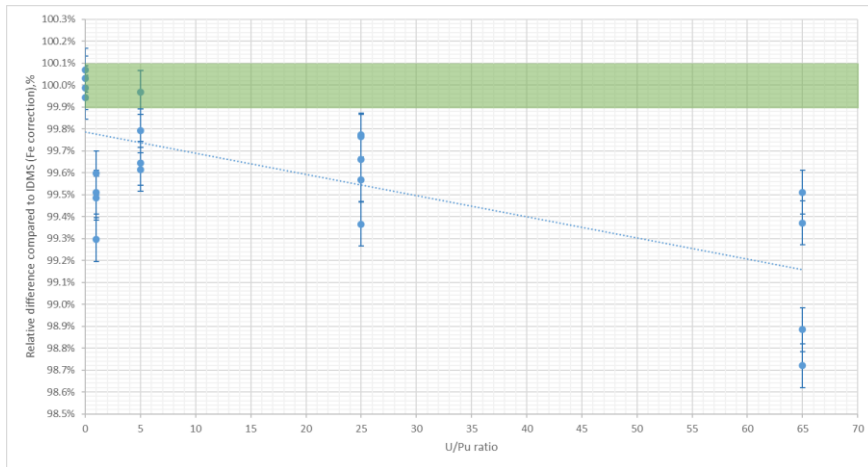
Figure 3. Relative difference of Pu amount found in U-Pu synthetic mixture obtained by CPC (blue dots, corrected for Fe interference) in comparison to "expected" value determined by IDA (green band), for samples with different U/Pu amount ratios.

The Fe content of each studied synthetic sample shown in Figure 4. indicates a correlation between iron content and the U/Pu amount ratio. Although the exact source of the bias remains unclear, a potential interference of uranium on the spectrophotometric measurement of Fe is suspected (peak tailing in 510 nm region). Such interference has already been reported in previous IAEA CPC studies for Pu samples containing 100 mg of uranium or more [10]. Negative bias observed for samples containing more than 100 mg U per aliquots that were corrected for interferences due to Fe (samples corresponding to U/Pu ratio 25 and 65 presented in Figure 3) could therefore be explained by an over-estimation of Fe content.
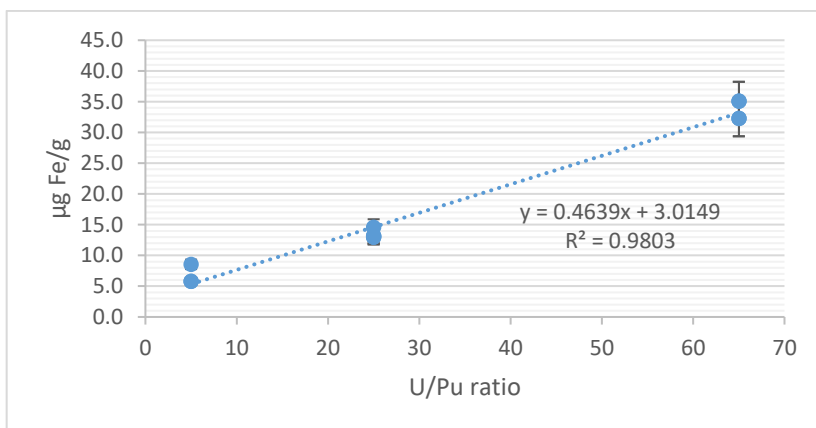
Figure 4. Iron content measured by spectrophotometry in synthetic mixtures in relation to the U/Pu amount ratio of each mixture. The precision of Fe measurements is based on ASTM E394-09 for [Fe] > 0.5 ppm)

2.3 ANALYSIS OF INSPECTION SAMPLES

Thirteen (13) inspection samples containing about 4 mg of Pu were sampled in-field in addition to sampling plan for inspection activities at Japanese R&D facilities. Although being purified through the PUREX process, these samples could potentially contain impurities issuing from the facility, and transuranic elements related to the process of irradiated spent fuel. In previous studies, the interference of such impurities with CPC analyses was evaluated by the controlled addition of Np, Am, Cr, Fe and U on samples containing Pu amount from 10 to 20 mg [8]. Considering the content of Am and Np in inspection samples tested in this study (as evaluated by gamma spectrometry measurements), Np (1wt%/Pu) and Am (3.6 wt%/Pu) were unlikely to be present in quantities significant enough to cause interference with CPC measurements. However, Fe amount was found to be approximately 7.5 wt%/Pu, therefore interferences due to Fe are likely to occur during the CPC measurements of Pu. Inspection samples were analysed by CPC using same protocol as used for synthetic samples: coulometric blank measurements were within expected range (observed fluctuations: 8 – 16 µg) and the formal potential (E°') measured was a bit lower than usual (between 470 and 497 mV/SCE). This lower formal potential has also been observed in previous experiments [5], [7], and could be attributed to slight effect from Fe (formal potential of $FeSO_4$ = 433 mV/SCE) and/or complexation effect of sulphate anions. Recovery for Pu for lowest U/Pu amount ratio sample (Pu=3.38mg, U=0.18mg, U/Pu=0.05) was 100% (no

Fe correction applied) but the relative difference between CPC measurements and the known IDA result was significant (+4.5%) for all other samples with higher U/Pu amount ratios. Furthermore, depending on the U/Pu amount ratio, the bias of the CPC results was seen to vary erratically between 0 and 9 %. The large bias between the CPC results and IDA results could be reduced by correcting the CPC results for Fe interferences. Nonetheless, even after Fe correction, the bias between CPC and IDA values exceeded the expected criteria with average relative difference of -0.9% even for samples with low U/Pu amount ratio.

CONCLUSIONS

The interlaboratory comparison exercise showed that it is possible to apply CPC method using subsample aliquots containing only 2 mg of Pu, prepared from pure Pu reference materials. However, for larger 15 mg-size Pu dried sample aliquots additional investigations are needed to address potential bias related to dissolution issues and sample heterogeneity. It was therefore suggested to launch a second CPC interlaboratory comparison exercise with CETAMA/LAMMAN and SRNL in 2021. It was agreed that SGAS-NML would propose the sample dissolution procedure and present how successfully it was applied in NML. The results obtained for the analysis of different U/Pu synthetic mixtures and inspection samples confirmed that the CPC method is particularly sensitive to the impurities present in the samples. As such, it was shown that CPC can be applied directly without Fe correction on pure U/Pu mixed samples with U/Pu amount ratios up to 5 but at higher U/Pu amount ratios, the interference of U and others elements becomes increasingly important. Studies on inspection samples confirmed that presence of interfering species in the samples prevents the direct use of CPC for Pu amount determination and that choice of nitric acid electrolyte media versus sulphuric acid electrolyte media might reduce interference due to the presence of uranium.

ACKNOWLEDGMENTS

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