

MASS SPECTROMETRIC ISOTOPE DILUTION ANALYSIS OF URANIUM AND PLUTONIUM PARTICIPATION IN THE INTERNATIONAL LABORATORY PROGRAM - IDA 80

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ABSTRACT

The present work describes the analytical procedures developed and the results obtained during the participation in the international intercomparison program IDA - 80 jointly organized by the Safeguard Project of the Gesellschaft für Kernforschungszentrum Karlsruhe, Germany, and the Central Bureau of Nuclear Measurements, Geel, Belgium. Elemental concentrations of uranium and plutonium were determined in different samples supplied by the organizers. Sample types included irradiated nuclear fuel solutions as well as synthetic solutions containing uranium and plutonium. The experimental procedures developed for the elemental values obtained are compared with the certified values and the values obtained by other participants. The result show that the relative standard deviations (RSD) and the accuracies obtained are, in general, less than 2% for both elements.

INTRODUCTION

Accurate determination of the isotopic composition and the contents of the fissionable elements uranium and plutonium is of fundamental importance from the point of the view of nuclear material safeguards. Nuclear material accountancy is based on the destructive measurements which provide values for the fissionable elements and isotopes in circulation. Destructive measurements are also used to calibrate non-destructive methods of assay. Both "declaration values" from nuclear plants and organizations and verification values obtained by the Safeguards Authorities are based on destructive measurements by laboratories [1]. Uncertainties in the overall determination are generated by plant measurements, sampling techniques and the analytical methods employed.

The analytical method that is universally employed for the accurate determination of the isotopic composition and the element content is the mass spectrometric isotope dilution (MSID) [2]. In order to determine the uncertainty of the analytical measurements of uranium and plutonium by MSID method in the routine operating conditions an

interlaboratory program called "Isotope Dilution Analysis - 80" (IDA -80) was organized jointly by "Safeguards Project of the Gesellschaft für Kernforschungszentrum Karlsruhe" (KFK), Germany, and Central Bureau of Nuclear Measurements, (CBNM), Geel, Belgium.

The objectives and the design of the program have been discussed in detail in [3] and [4]. The major aims of the program were:

- a) to determine in an uniform manner for each laboratory the reproducibility of its measurements;
- b) to permit each laboratory to determine its bias;
- c) to investigate the following sources of uncertainties in the measurements technique: behavior of the diluted active input, sample preparation, spiking procedure, effects of "ageing" on analytical procedure;
- d) to investigate possible improvements by the application of specific procedure like use of dried spike, "in situ" spiking procedure and use of common spike solution.

The measurement program is divided into two parts. The first part being concerned with the measurements on material containing fission products originating from a

reprocessing plant. Two main types of test solutions are distributed for this part:

- a . input solution A (undiluted)
- b . diluted input solution B .

The samples were prepared by the organizers from the original feed solution taking at the reprocessing plant "Wiederauffarbeitungsanlage", Karlsruhe, on february 13, 1980.

The sample preparation method has been described in the detail in [4].

Solution A is originating from the input of the WAK reprocessing plant and solution B was obtained from solution A by dilution with 6M HNO₃ in an exactly know factor of 82.78±0.02 in weight. Those solutions were distributed in the following manners:

- a) solution B unspiked, in the liquid form (BU) in a sealed glass ampoule;
- b) solution B unspiked, in 3 dried aliquots (BUI, BUII, BUIII) of exactly known quantities in sealed glass vials;
- c) solution B spiked, in the liquid form (BS) with mixed uranium - plutonium spike at the Central Bureau of Nuclear Measurements, Belgian, in a sealed glass ampoule, and
- d) solution A spiked, in dried aliquot (AS) at the reprocessing plant by "in situ" spiking technique using solid spike in sealed glass vials.

This parts is of particular interest for nuclear safeguards, as it guaranties results on undiluted input strictly valid for the time and place of sampling (i.e of an inspection).

For the second part of the program, a synthetic uranium-plutonium (R) sample of exactly known composition and free of fission products was received in the following manner:

- a) unspiked solution (RU), in a sealed glass ampoule, carried out with participant's own spike and with common spike supplied by CBNM, and
- b) liquid solution (RS) spiked by CBNM, in a sealed glass ampoule.

In this program twenty eight laboratories from fifteen countries and two international organizations participated . The Mass Spectrometry Laboratory of IPEN was the only laboratory from South America to participate in the program.

EXPERIMENTAL PROCEDURE

As the first step towards the participation, a laboratory for handling the irradiated solutions was installed [5].

The chemical preparation of the samples were carried out in three independent steps. Each step was carried out in a separated glove box. One of them was used exclusively for the preparation, dissolution and weighing of the sample .

The samples were then transferred to the second glove box for the redox procedure, chemical separation and

purification of the uranium and plutonium fractions. The third glove box was used for the mounting and dismounting of the filament assemblies, cleaning of the filament cartridges plates, bases, and posts as well as for the deposition of the samples in the filament .

The sample introduction unit of the mass spectrometer was modified for the introduction of the filament cartridges with the deposited samples.

Chemical Procedure. The chemical procedure employed in the present work involves the steps of the preparation of the mixed uranium and plutonium standard solution, redissolution of dried samples, addition of mixed uranium and plutonium tracer, redox procedure and chemical separation as showed in Fig.1. The details of the chemical separation is described in [5] and [6].

All the samples analysed were subjected to the same chemical and mass spectrometric scheme. Three sub samples were taken and eighth measurements were carried out for each one.

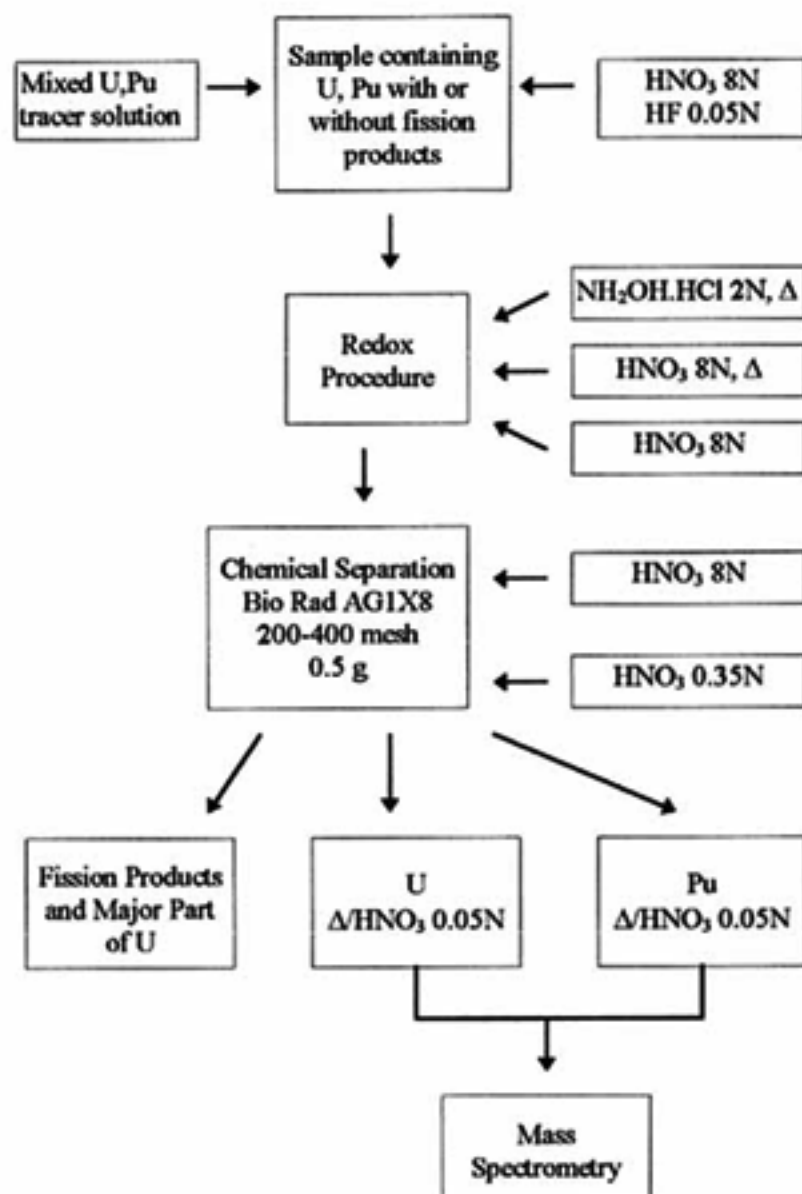


Figure 1. Chemical Procedure Scheme of Uranium and Plutonium Adopted.

Mass Spectrometric Procedure. The mass spectrometer employed for the isotopic analysis of U and Pu was the Varian Mat TH5 single focussing thermionic mass

spectrometer. The ions were detected by a system of Faraday Cup or secondary electron multiplier. The output from the detector was coupled to strip chart recorder and to an on line computer system (Spectrosystem SS 106). The main mass spectrometric analytical procedure consists of deposition of the sample, filament heating procedure, data recording and evaluation. The details can be found elsewhere [7-9].

RESULTS AND DISCUSSION

Calibration of the Laboratory Mixed Uranium and Plutonium Spike. The laboratory mixed spike was calibrated by isotope dilution technique using mixed uranium and plutonium standard solutions with 4.769×10^{18} atoms of $^{238}\text{U/g}$ solution and 2.452×10^{16} atoms of $^{239}\text{Pu/g}$ solution. The values obtained for ^{233}U and ^{242}Pu in the trace solutions were: $6.14 \pm 0.06 \times 10^{18}$ atoms of $^{233}\text{U/g}$ solution, $2.25 \pm 0.04 \times 10^{16}$ atoms of $^{242}\text{Pu/g}$ solution. This solution was used to spike the following samples: BU (liquid), BU (dried) and RU (liquid).

MSID Analysis of Uranium and Plutonium in Solution A and B. The first part of the programme involved the analysis of two types of test solutions, namely, the undiluted input solution A and the diluted input solution B. The solution B was received in three forms: BU (liquid), BU (dried) and BS (liquid). Elemental concentrations of U and Pu are presented in Table 1 as the mean value of measurements carried out for three subsamples. For each subsample eight measurements were performed.

TABLE 1. Concentration of U and Pu in B and A samples measured by MSID technique.

Sample type	U (mg/g sol.)	RSD (%)	Pu ($\mu\text{g/g sol.}$)	RSD (%)
BU(liq.)	2.095	0.43	7.198	0.12
BU(dried)	2.094	0.77	7.099	1.24
BS(liq.)	2.069	0.09	7.163	0.26
AS(dried)	171.5	1.72	594.7	0.27

MSID analysis of U and Pu in BU (liquid) samples. Elemental concentrations of U and Pu in the BU (liquid) solution were determined by MSID technique using laboratory's own spike. The average values obtained for the three spiking runs were 2.095 mg U/g sol. and 7.198 $\mu\text{g Pu/g sol.}$ The Relative Standard Deviation (RSD) for the laboratory mean were of the order of 0.43% for U and 0.12% for Pu.

MSID analysis of U and Pu in BU (dried) samples. Three dried BU samples were spiked with laboratory mixed spike and the U and Pu concentration were determined.

The average values obtained were 2.094 mg U/g sol. and 7.099 $\mu\text{g Pu/g sol.}$ The RSD of analyses being 0.77% and 1.24% respectively for U and Pu. A comparison of the average U and Pu values obtained for BU (liquid) and BU (dried) samples show that the values are in agreement to within $\pm 0.1\%$ for U and $\pm 1.4\%$ for Pu. The large uncertainty for Pu is due to the first spiking run for BU (dried) sample which yielded a value different from other spiking runs. Neglecting first spiking run, the average concentration recalculated for Pu was 7.150 $\mu\text{g Pu/g sol.}$ and the RSD yielded 0.09%.

MSID analysis of U and Pu in BS Solution. Three aliquots of the diluted solution B previously spiked by the organizers using mixed uranium plutonium spike were analysed. The mean values obtained were 2.069 mg U/g sol. and 7.163 $\mu\text{g Pu/g sol.}$, with RSD of 0.09% and 0.26%, respectively. The U and Pu values obtained for BS agree within $\pm 1.2\%$ for U and 0.5% for Pu with those obtained for BU (liquid) and BU (dried) samples. For safeguard material accountancy proposes it is useful to have three types of sampling for U and Pu measurement.

MSID analysis of U and Pu in Undiluted Dissolved Solution A Prespiked In situ by Central Bureau of Nuclear Measurements, (CBNM), Belgium. Three dried samples of undiluted solution A, with the same U/Pu ratio found at the reprocessing plant, were analysed. Those samples were spiked "in situ" by using a solid mixed tracers enriched in ^{235}U and ^{242}Pu nuclides. The results obtained are presented in the Table.1.

MSID Analysis of Uranium and Plutonium in Synthetic Sample Solution R. In this part of the programme a synthetic sample of uranium and plutonium devoid of fission products was analysed for the elemental concentration. The programme was intended to compare the measurement uncertainties in the samples without fission products. The solution R was analysed with laboratory's own spike (RU) as well as with the spike supplied by the organizers (RUS). A third set of samples are prespiked and supplied (RS). Elemental concentrations of U and Pu are presented as the mean value of three replicate analysis for each of the solutions showed in Table 2.

TABLE 2. Concentration of U and Pu in R samples measured by MSID technique.

Sample type	U (mg/g sol.)	RSD (%)	Pu (mg/g sol.)	RSD (%)
RU	1.726	0.20	7.972	0.20
RUS	1.707	0.20	7.936	0.40
RS	1.716	0.54	7.955	0.36

Analysis of RU using laboratory's own mixed spike. The average value obtained for this solution were 1.726 mg U/g sol. and 7.972 µg Pu/g sol., with RSD of 0.2% and 0.2%, respectively.

Isotope Dilution Analysis of RUS Solution Prespiked by C.B.N.M. The analysis is similar to the BS solution, where the solution was prespiked by the organizers and sent to the laboratories for analysis. The average value obtained for this solution are 1.707 mg U/g sol. and 7.936 µg Pu/g sol., with RSD of 0.2% and 0.4%, respectively.

MSID Analysis of RS Solution Spiked by Mixed Tracer Solution Supplied by the Organizers (C.B.N.M.). For this part of the program the participants were requested to use as isotope diluent a pre calibrated tracer solution supplied by the organizers. The average value obtained for this solution were 1.716 mg U/g sol. and 7.955 µg Pu/g sol., with RSD of 0.5% and 0.4%, respectively.

GENERAL DISCUSSION

As the aim of the program was to evaluate the interlaboratory deviations of the analytical measurements, the values obtained in the present study were compared with the certified values. For the sample solution A, B and R the elemental concentration values of uranium and plutonium were established and certified jointly by CBNM, Belgium and the National Bureau of Standards (NBS), Washington, USA and these values are given in Table 3.

TABLE 3. Concentration of U and Pu in A, B, and R Samples [10].

Sample	Element concentration U(mg/g solution)	Element concentration Pu(µg/g solution)
A	169.66±0.12 (3s)	597.3±1.8 (3s)
BU	2.0491±0.0019 (3s)	7.193±0.018 (3s)
RU	1.7154±0.0017 (3s)	7.982±0.019 (3s)

The elemental concentration values of U and Pu in A, B and R solutions, calculated based on the analytical results of the present investigation, are in agreement with the certified values with a maximum deviation of about ±2% for uranium and 0.4% for plutonium.

An evaluation of the accuracy of the analytical determination of uranium, plutonium by mass spectrometric isotope dilution method of our laboratory is attempted by comparing our results with the "BETWEEN - LABORATORY RSD" and INTERLABORATORY RSD [11]. These RSD's were calculated from the results submitted to the organizers by the 28 participating laboratories. The terms "BETWEEN LAB RSD",

INTERLAB RSD and RD are defined in the appendix. Table 4 and 5 show the comparison of the RSD's and RD.

TABLE 4. Comparison of the Accuracy of Uranium Determination.

	Uranium						
	BU Liq	BU Dried	BS Liq	AS Liq	RU Liq	RS Liq	RUS Liq
Between-Lab RSD (%)	0.69	1.00	0.54	0.46	0.58	0.34	0.36
Inter Lab Spread (%)	0.72	1.03	0.53	0.47	0.48	0.40	0.34
RD (%) Present Study	2.2	2.2	0.97	1.09	0.62	0.03	0.49

TABLE 5. Comparison of the Accuracy of Plutonium Determination

	Plutonium						
	BU Liq	BU Dried	BS Liq	AS Liq	RU Liq	RS Liq	RUS Liq
Between-Lab RSD (%)	0.80	2.54	0.73	0.49	1.22	0.29	0.28
Inter Lab Spread (%)	0.83	2.54	0.33	0.54	1.25	0.35	0.47
RD (%) Present Study	0.07	0.6	0.42	0.44	0.13	0.34	0.58

The BU samples show a higher positive bias compared to BS (liquid) sample which was prespiked. This difference may be attributed to a spike calibration error during first part of the program.

CONCLUSION

The participation in the interlaboratory programme on the "Mass Spectrometric isotope dilution analysis of U and Pu in the reprocessing input solution IDA 80" showed through the results the capability of our laboratory for U and Pu determinations in nuclear irradiated fuel samples

The good agreement of U and Pu concentration for BU (liq), BU (dried) and BS (liq) shows that there isn't any significant difference on using liquid or dried samples and different spiking procedure.

The element concentrations are within the uncertainty ranges of the agreed certified values for both uranium and plutonium.

Good results for the measurements on liquid samples are not in accordance with the hypothesis of possible "ageing" interferences.

Several evaluation results indicate the presence of measurement uncertainties due to mass-dependent errors sources such as isotope fractionation in the ion source.

APPENDIX

1. Relative standard deviation between lab. (RSD %)

$$BI_{lab}RSD(\%) = \frac{100}{C} \sqrt{\frac{1}{N-1} \sum_i (\bar{C}_i - \bar{C})^2 - \frac{1}{6N} \sum_i \sum_j (C_{ij} - \bar{C}_i)^2}$$

where:

- i = identification of the laboratory (1 to 28)
- j = measurement (1 to 3)
- N = number of participating laboratories (28)
- \bar{C}_i = mean concentration value of laboratory 'i'
- \bar{C} = grand mean concentration value of all laboratories
- C_{ij} = conc. value of 'j' measurement of laboratory 'i'

2. Interlaboratory spread (%)

$$InterLabSpread(\%) = \frac{100}{C} \sqrt{\frac{1}{N-1} \sum_i (\bar{C}_i - \bar{C})^2}$$

3. Relative deviation obtained in the present study (%)

$$RD(\%) = \frac{100}{C} (C_{cert} - \bar{C})$$

where:

- \bar{C} = laboratory mean concentration
- C_{cert} = certified concentration

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