ELSEVIER

International Journal of Mass Spectrometry 184 (1999) 109–118

International Journal of Mass Spectrometry

Calibration procedures for a multicollector mass spectrometer for cup efficiency, detector amplifier linearity, and isotope fractionation to evaluate the accuracy in the total evaporation method

K.L. Ramakumar[a], R. Fiedler[b,]*

[a]*Fuel Chemistry Division, Bhaba Atomic Research Centre, Mumbai-400085, India*
[b]*I.A.E.A./Safeguards Analytical Laboratory, A-2444 Seibersdorf, Austria*

Received 11 April 1997; accepted 23 November 1998

Abstract

The procedure used for the evaluation of the cup efficiency factors of a multicollector mass spectrometer is described and results are given that were obtained with three different isotopes (^{187}Re, ^{238}U, and ^{239}Pu). A check of the linearity of the detector amplifier system including the Faraday cup itself is described using the uranium reference material of IRMM (Institute for Reference Materials and Measurements) series 072. These reference materials allow the determination of the mass fractionation on the ^{235}U/^{238}U ratio to correct the ^{233}U/^{235}U ratio which is used to check the linearity of the whole system at different ion intensities. The correction factors determined through these procedures were applied to the results of isotope analyses obtained by total evaporation in order to evaluate the magnitude of residual biases. The mass spectrometer used for these tests is a 12 year old Finnigan MAT 261 with nine fixed Faraday collectors in a configuration allowing simultaneous measurement of all uranium and plutonium isotopes. (Int J Mass Spectrom 184 (1999) 109–118) © 1999 Elsevier Science B.V.

Keywords: TIMS; Cup efficiency factors; Multicollector measurements; Total evaporation

1. Introduction

The simultaneous collection of all isotopes involved in a measurement has many advantages, but requires a very accurate knowledge of a number of calibration parameters as mentioned below. Some of these factors can be determined relatively simply by the software delivered with the instrument. The user oriented software used for all described measurement methods has been developed initially in 1990 in a cooperation between IRMM (Institute for Reference Materials and Measurements), IAEA (International Atomic Energy Agency), and LANL (Los Alamos National Laboratory, NM) and was adapted and improved over the years at the Safeguards Analytical Laboratory (SAL) of the IAEA [1]. The following parameters are important for precise and accurate analyses: magnet calibration, gain calibration, cup efficiency factors, linearity check of amplifier, and systems calibration.

The measured atom ratio ($R^{i/j}_{(\mathrm{meas})}$) of isotopes of

---

* Corresponding author.

PII S1387-3806(98)14273-2

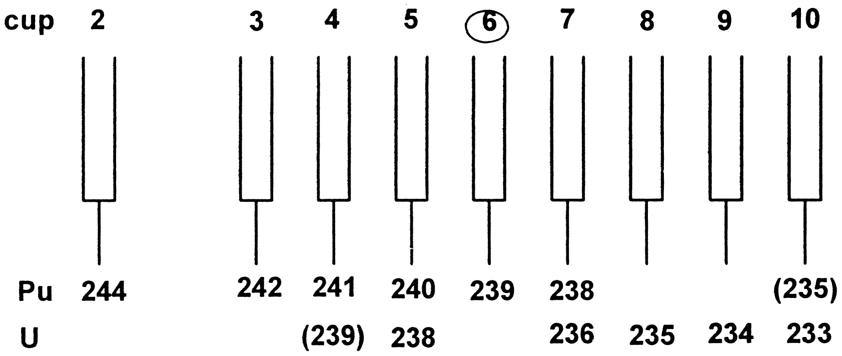

Fig. 1. Faraday cup configuration of the MAT 261.

masses *i* and *j* of an element needs to be corrected for several systematic effects to obtain accurate measurements. The expected atom ratio ($R^{i/j}_{\text{(corrected)}}$) is calculated as follows:

$$R^{i/j}_{\text{(corrected)}} = \frac{R_{\text{(measured)}}}{(\text{Gain})_{i/j} \times (\text{CF})_{i/j}} \times [1 + B \times (j - i)] \qquad (1)$$

where $(\text{Gain})_{i/j}$ is the relative gain ratio of the amplifier/analog to digital converter used for measuring the ion currents because of isotopes of masses i and j, $(\text{CF})_{i/j}$ is the relative cup efficiency ratio of Faraday collectors used for collecting ions of isotopes of masses i and j, and B is the isotopic fractionation factor per atomic mass unit and $(j - i)$ is the atomic mass difference between the isotopes being measured.

The software foresees three modes of data collection: peak jumping, multicollection, and total evaporation.

In our laboratory the total evaporation measurement method is selected for all routine and special samples. The instrument used for the tests and evaluation of all required factors was a 12 year old Finnigan MAT 261 mass spectrometer. This instrument is equipped with nine Faraday collectors in a fixed distance to cover the mass range from 233–244 (see Fig. 1). To date, 32 000 analyses were performed with this instrument; about 30 000 on Pu samples and the rest on uranium samples. Fig. 1 shows the configuration of the nine Faraday cups for U and Pu. Cup 6 was chosen as the reference cup for the magnet calibration.

2. Experiment

2.1. Magnet calibration

The magnet calibration is performed using the isotopes shown in Table 1. This calibration is done daily or at least every second day. Five or six isotopes from this table should be used when a wide mass range is to be covered. A frequent check of the masses 185–242 is required to ensure proper magnet setting for the analysis of U and Pu.

2.2. Gain calibration

When multicollector measurements are performed, a gain calibration should be done at least twice a

Table 1
Magnet calibration isotopes

	Mass	Element
1	23	Na
2	41	K
3	185	Re
4	187	Re
5	239	Pu
6	242	Pu

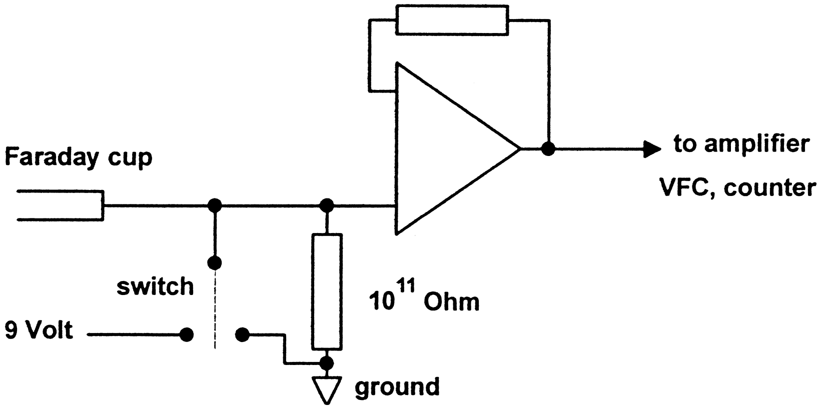

Fig. 2. Schematic of the electronic gain calibration.

week. This is done first by grounding the input of the preamplifier and then applying a very stable voltage of 9 V to this point (see Fig. 2). The ground potential and the 9 V signal are connected to all amplifiers, the gain per volt are calculated and stored in a table until the next calibration is done.

2.3. Cup efficiency calibration

The determination of the relative cup efficiency factors was carried out using $^{187}Re^+$, $^{238}U^+$, and $^{239}Pu^+$ ions. The software developed in SAL uses a peak jump sequence with symmetrical scanning between the reference cup (cup 6) and any other cup [2]. The scanning sequence for all cups involved is shown in Fig. 3.

The results of the measurements done with $^{187}Re^+$ ions with an ion intensity of about 5 × 10^{-12} A (500 mV) are tabulated in Table 2.

The cup efficiency calibration measurements were repeated with $^{238}U^+$ and $^{239}Pu^+$ ions. Here the ion intensity varied between 2 × 10^{-11} and 4 × 10^{-11} A (2–4 V signal). More than one measurement was done using the same filament loading. Time was spent to get a very stable ion beam. The summary of all measurements of the three different elements (average) is shown in Table 3. A graphical presentation of this table is given in Fig. 4. No significant mass dependence of the cup efficiency factors was observed.

Table 4 compares the cup efficiency factors measured in 1994 with the new data. This indicates

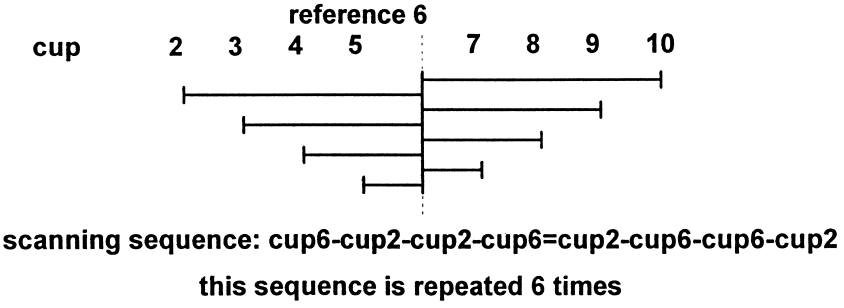

Fig. 3. Measurement scheme and sequence for the evaluation of the cup efficiency factors.

Table 2
Results of the cup efficiency calibration using ^{187}Re ions

Run #	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8	Cup 9	Cup 10
1	1.000 96	1.001 21	1.000 76	1.000 31	1	1.001 32	1.000 28	1.001 08	1.001 08
2	1.000 86	1.001 35	1.001 45	1.000 53	1	1.001 44	1.000 76	1.000 82	1.001 35
3	1.000 7	1.001 16	1.001 08	1.000 58	1	1.001 3	1.000 34	1.001 06	1.001 15
4	1.000 71	1.001 1	1.001 17	1.000 7	1	1.001 34	1.000 63	1.000 58	1.001 23
5	1.000 95	1.001 46	1.001 17	1.001 07	1	1.001 55	1.000 69	1.000 6	1.000 96
6	1.000 7	1.000 79	1.000 84	1.000 31	1	1.001 21	1.000 31	1.000 56	1.000 76
7	1.000 81	1.001 59	1.001 61	1.000 9	1	1.001 2	1.000 3	1.000 94	1.001 06
Avg.	1.000 81	1.001 23	1.001 15	1.000 63	1	1.001 34	1.000 47	1.000 81	1.001 08
Sd.	0.000 12	0.000 26	0.000 3	0.000 29	0	0.000 12	0.000 21	0.000 23	0.000 2

dramatically that a cup efficiency calibration needs to be performed at least once a year if accuracies of 0.1% or better are to be achieved. Fig. 5 shows the results of cup efficiency factor evaluations performed in 1994 and 1996.

It appears that the cup which is normally used to collect the most intense isotope (^{239}Pu) is significantly less efficient. The measurements were repeated using cup 4 as the reference cup in order to rule out unknown artefacts. Fig. 6 shows the result that efficiency factors are independent of which cup is used as the reference. The authors have no explanation for the difference of cup 4 analysed 1994 and 1996. The cup efficiency can be influenced by the geometric form of the cup, the inside layer and the area where the ion beam loses its charge.

2.4. Linearity check

The linear response of Faraday cup detectors 2, 5, 6, and 7 was checked by measuring the ^{233}U/^{235}U atom ratios of the IRMM 072 reference materials, with ratios ranging between 1 and 0.001 (see Table 5). As in the multidetection mode the ion beams corresponding to different isotopes are collected in separate Faraday cup detectors, it is essential to measure carefully the linear response factors of all detectors relative to the incident ion beam.

In the data collection protocol used for IRMM-72/1 and 72/5 standards, the same idle and integration times of 4 and 2 s were used for all three uranium isotopes (^{233}U, ^{235}U, and ^{238}U). For IRMM standards 72/8 and 72/11, in view of the low abundance of ^{233}U the idle and integration times were increased to 8 s for this isotope. The heating of the sample was controlled manually and the peak jump method was used for the measurement. Symmetric scanning was used while carrying out the peak jumping. The measurements were carried out at two ^{238}U^{+} ion intensities ($> =$ 1 V and $\sim$ 0.5 V) for IRMM standards 72/1 to 72/8. In the case of IRMM-72/11, measurements were carried out at 2.0 V signal intensity.

After measuring the atom ratios of ^{233}U/^{235}U ($R_{3/5}$), ^{233}U/^{238}U ($R_{3/8}$) and ^{235}U/^{238}U ($R_{5/8}$), the linearity response of the Faraday cup detector is calculated as follows:

Table 3
Summary of the average of the cup efficiency calibration using three different isotopes ^{187}Re, ^{238}U, and ^{239}Pu

Element	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8	Cup 9	Cup 10
Re	1.000 81	1.001 23	1.001 15	1.000 63	1	1.001 34	1.000 47	1.000 81	1.001 08
U	1.000 88	1.000 92	1.001 13	1.000 66	1	1.000 86	1.000 56	1.000 76	1.000 87
Pu	1.000 72	1.001 05	1.001 07	1.000 53	1	1.001 03	1.000 35	1.000 56	1.000 99
Avg.	1.000 8	1.001 07	1.001 12	1.000 61	1	1.001 08	1.000 46	1.000 71	1.000 98

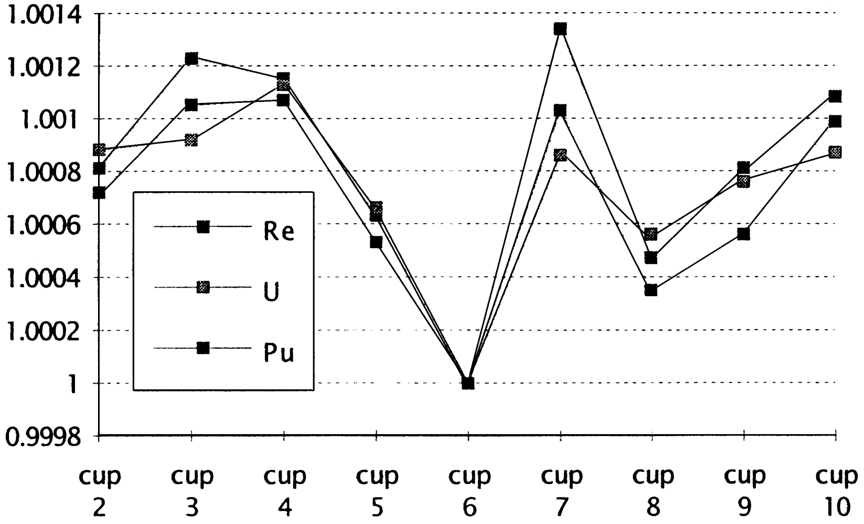

Fig. 4. Cup efficiency factors measured with Re$^+$, U$^+$, and Pu$^+$ ions.

$$K = \frac{R_c^{5/8}}{R_{5/8}} \tag{2}$$

where $R_{5/8}$ is the measured ^{235}U/^{238}U ratio and $R_c^{5/8}$ is the certified ^{235}U/^{238}U ratio

$$B = \frac{(K - 1)}{3} \tag{3}$$

This factor B is used to correct the measured ^{233}U/^{235}U atom ratio for isotopic fractionation:

$$R'_{3/5} = R_{3/5} \times (1 + 2 \times B) \tag{4}$$

The linearity factor of cup (x) is then given by:

$$\mathrm{LF}_{(x)} = \frac{R'_{3/5}}{R^c_{3/5}} \tag{5}$$

where $R_c^{5/8}$ is the certified ^{235}U/^{238}U ratio.

In the case of an ideal detector with perfectly linear response, the linear response factor is expected to be one for all the intensities of the incident beam and all

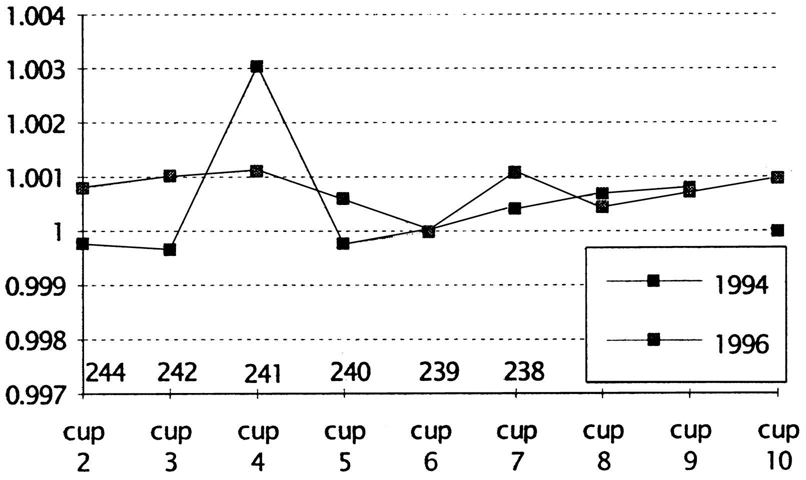

Fig. 5. Cup efficiency factors measured 1994 and 1996.

Table 4
Cup efficiency calibration data of 1994 and 1996

Year	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8	Cup 9	Cup 10
	244	242	241	240	239	238			
1994	0.999 76	0.999 66	1.003 03	0.999 76	1	1.000 41	1.000 69	1.000 81	0.999 98
1996	1.000 8	1.001 07	1.001 12	1.000 6	1	1.001 09	1.000 45	1.000 71	1.000 98
Diff (%)	0.104	0.141	−0.191	0.084	1	0.068	−0.024	−0.01	0.1

^{233}U/^{235}U isotope ratios. The results of the linearity factors obtained for the different cups are tabulated in Table 6. These values are the average of 2–4 replicate measurements.

The linearity factors are acceptably close to one for cups 5, 6 and 7. However, for cup 2, the response appeared to deviate significantly from linearity particularly at lower ^{233}U/^{235}U atom ratios of 0.01 and 0.001 (see Fig. 7). This observation requires further investigation to verify whether this may be an artefact because of higher uncertainties in the peak centering of the beam in the cup, especially for side cups and low beam intensities.

2.5. Systems calibration (mass fractionation test)

An important factor affecting the accuracy in isotopic ratio measurements by thermal ionisation mass spectrometry is the isotopic fractionation. It results from the thermal evaporation of the sample from the filament in the ion source during the mass spectrometric analysis. Even though the isotopic fractionation is mass dependent (Rayleigh's distillation law : rate of evaporation is proportional to $1/\sqrt{mass}$), it can be assumed to be linear with mass within the isotopic mass range of an element, particularly in case of heavier elements such as U and Pu. A number of parameters affect the isotopic fractionation behaviour. These include the sample amount, sample loading and analysis conditions such as temperature of analysis, data collection mode (peak jumping, multicollection, or total evaporation, etc.). Measurements should be carried out under identical and reproducible conditions to obtain reproducible isotopic fractionation.

The isotopic fractionation factor per atomic mass unit during the measurement of isotopes of masses *i* and *j* of an element is carried out as follows:

$$B = \frac{1}{(j/i)} \times \left(\frac{R^{i/j}_{(\text{true})}}{R^{i/j}_{(\text{obs})}} - 1 \right) \tag{6}$$

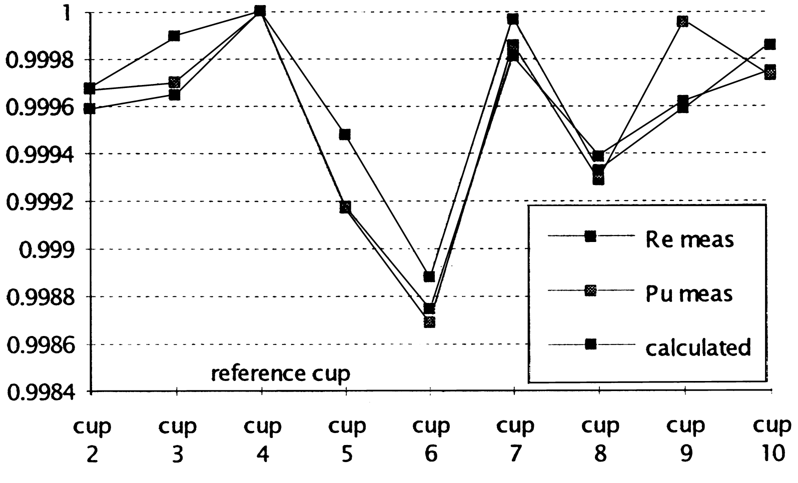

Fig. 6. Cup efficiency factors derived from measurements using cup 4 as the reference cup.

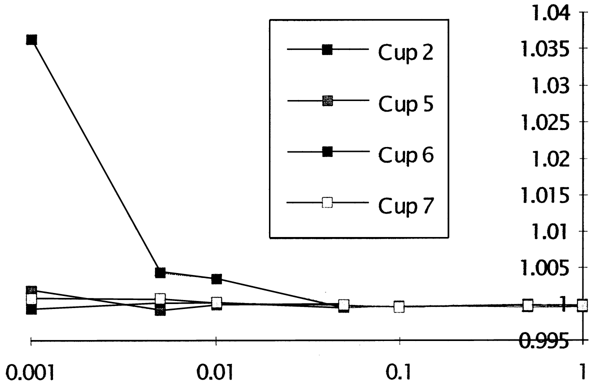

Fig. 7. Graphical presentation of the linearity factors for different cups.

where *B* is the isotopic fractionation factor per atomic mass unit, $R_{i/j}^{(\mathrm{obj})}$ is the measured atom ratio of isotopes *i* and *j*, and $R_{i/j}^{(\mathrm{true})}$ is the true or certified atom ratio.

Certified isotopic reference materials are analysed to determine the *B* Factor. Using this *B* Factor, the fractionation correction for any measured atom ratio ($R^{k/l}$) of the isotopes of masses *k* and *l* of the same element is effected as follows:

$$R_{(\mathrm{corrected})}^{k/l} = R_{(\mathrm{obs})}^{k/l} \times (1 + (l - k) \times B) \tag{7}$$

The standard reference material used for measuring the mass fractionation factors of U and Pu are tabulated in Tables 5 and 7.

The measurement protocol routinely used at SAL for all uranium measurements was used for data collection in total evaporation mode [3–5]. The relative cup efficiency factors determined in the present work were used in the calculations. Each IRMM standard was analysed four times and the *B* Factor calculated using ^{233}U/^{235}U atom ratio as given in Table 8. It is seen that the *B* Factor is negligibly small

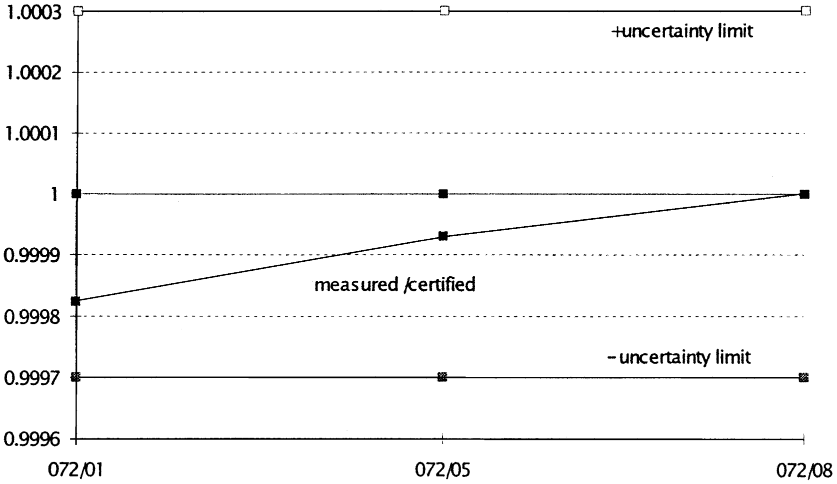

Fig. 8. Uranium 072 standards with ratios from 1.0−0.01 measured in total evaporation mode.

Table 5
Reference ratios for IRMM 072 used for linearity check

IRMM identification	$\text{Ratio}_{233/235}$	$\text{Ratio}_{233/238}$	$\text{Ratio}_{235/238}$
72/01	1.000 331	0.991 357	0.991 029
72/05	0.100 01	0.099 309	0.992 991
72/08	0.010 166	0.010 097	0.993 189
72/11	0.000 968	0.000 961	0.993 21

Table 6
Relative linearity factors for cups 2, 5, 6, 7

Signal (V)	Cup 2	Cup 5	Cup 6	Cup 7
1	0.999 737	0.999 907	0.999 575	0.999 65
0.5	0.999 921	0.999 861	0.999 529	0.999 744
0.1	0.999 721	0.999 69	0.999 739	0.999 556
0.05	0.999 681	0.999 9	0.999 481	0.999 875
0.01	1.003 513	0.999 991	1.000 181	1.000 242
0.005	1.004 36	0.999 195	1.000 215	1.000 773
0.001	1.036 615	1.001 965	0.999 419	1.000 833

Table 7
Certified ratios of the plutonium reference materials

IRMM No.	$R_{9/2}$	$R_{2/9}$
290/A1	1.025 14	0.975 477
290/F1	10.057 4	0.099 429
290/G1	0.101 358	9.866 602

meaning that there was no significant isotopic fractionation. Fig. 8 shows that the experimentally determined $^{233}U/^{235}U$ atom ratio in all the IRMM standards is within the accuracy limit.

Thus, with the total evaporation mode, it is possible to measure *U* isotopic ratios free of isotopic fractionation bias, provided that the cup efficiency correction factors are determined periodically.

The Pu measurement protocol was used for measuring the IRMM 290 series plutonium standards in total evaporation mode. As the ions of different Pu isotopes are collected in different Faraday cups (e.g. $^{239}Pu^{+}$ in cup 6, $^{240}Pu^{+}$ in cup 5, and $^{242}Pu^{+}$ in cup 3), the atom ratios are corrected for the relative gains and the relative cup efficiencies (CF) of the detectors. These factors are already included in the data evaluation module of the measurement protocol. Ion ratios of $^{242}Pu/^{239}Pu$ measured for the 290/A1 standard are almost free of bias as is seen from the negligibly small *B* Factors (Table 9). The two other standards 290/F1 and 290/G1 show differences which are greater than the uncertainty of the certified values. The measurements were repeated using different cups with $^{239}Pu^{+}$ in cup 8, $^{240}Pu^{+}$ in cup 7 (meas 1), and $^{242}Pu^{+}$ in cup 5 (meas 2) in order to confirm that the observation is not due to an uncontrolled error in the estimate of the relative cup efficiency factors. The two measurement sets of the IRMM 290 series are in good agreement (Fig. 9).

There is no explanation as to why the result of 290/A1 is within the specified limits while 290/F1 and 290/G1 yield too high $^{242}Pu/^{239}Pu$ ratios. This cannot be explained by mass fractionation, as the trend goes in the wrong direction. In addition, the measurements of IRMM 072 for uranium do not indicate any significant mass fractionation.

Table 8
Measured ratios $^{233}U/^{235}U$ and its bias factor per mass

	IRMM-72/1			IRMM-72/5			IRMM-72/8	
Run No.	$R_{3/5}$	*B* Factor	Run No.	$R_{3/5}$	*B* Factor	Run No.	$R_{3/5}$	*B* Factor
193	1.000 174	0.000 079	200	0.099 993	0.000 087	201	0.010 166	0.000 014
194	1.000 156	0.000 088	219	0.100 014	−0.000 021	202	0.010 168	−0.000 099
195	1.000 135	0.000 098	220	0.100 002	0.000 04	203	0.010 166	−0.000 031
196	1.000 157	0.000 087				204	0.010 165	0.000 025
Avg.	1.000 156	0.000 087		0.100 003	0.000 035		0.010 166	−0.000 024
SD	0.000 016			0.000 011			0.000 001	
RSD (%)	0.0016			0.011			0.011	
Ref.	1.000 331	±.03%		0.100 01	±.03%		0.010 166	±.03%

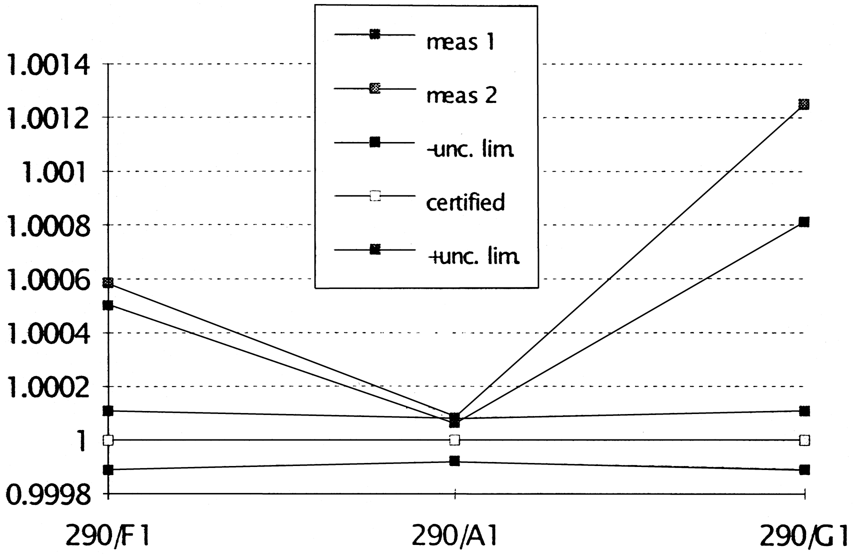

Fig. 9. IRMM 290/F1, A1, and G1 measured with two cup configurations.

3. Conclusion

This exercise has demonstrated that parameters such as cup efficiency factors, linearity response, and mass fractionation factors need to be checked frequently. The older a mass spectrometer becomes, the more important is the control of these parameters. The total evaporation method provides nearly mass fractionation free mass spectrometric analyses. Small variations in ratios can be analysed with a high repeatability, giving accuracies on routine samples that were not possible years ago. The results obtained

Table 9
Measured ratios ^{242}Pu/^{239}Pu and its bias factor per mass using cup 6 for ^{239}Pu (meas 1)

	290/F1		Run	290/A1		Run	290/G1	
Run No.	$R_{2/9}$	B Factor	No.	$R_{2/9}$	B Factor	No.	$R_{2/9}$	B Factor
150	0.099 484	−0.000 184	145	0.975 66	−0.000 063	158	9.875 17	−0.000 309
151	0.099 494	−0.000 218	146	0.975 505	−0.000 01	159	9.876 58	−0.000 356
152	0.099 489	−0.000 201	147	0.975 671	−0.000 066	160	9.877 08	−0.000 373
153	0.099 484	−0.000 184	148	0.975 637	−0.000 055	161	9.875 18	−0.000 309
154	0.999 481	−0.000 174	149	0.975 57	−0.000 032	175	9.874 05	−0.000 271
171	0.099 484	−0.000 184	167	0.975 511	−0.000 012	176	9.874 83	−0.000 297
172	0.099 475	−0.000 154	168	0.975 639	−0.000 055	178	9.875 68	−0.000 326
173	0.099 48	−0.000 171	169	0.975 51	−0.000 011	188	9.873 89	−0.000 266
174	0.099 474	−0.000 151	170	0.975 508	−0.000 011	189	9.871 92	−0.000 199
184	0.099 464	−0.000 117	181	0.975 428	0.000 017	190	9.873 86	−0.000 265
185	0.099 453	−0.000 08	182	0.975 394	0.000 028	191	9.872 46	−0.000 217
186	0.099 476	−0.000 158	183	0.975 4	0.000 026			
187	0.099 488	−0.000 174						
Avg.	0.099 479	−0.000 165		0.975 536	−0.000 02		9.874 61	−0.000 29
Sd.	0.000 1			0.000 11			0.001 58	
Rsd (%)	0.01			0.011			0.016	
Ref.	0.099 429			0.975 477			9.866 602	

with the IRMM 072 and 290/A1 indicate that with total evaporation, no mass fractionation correction is required.

Acknowledgements

The authors thank R. Perrin, D. Donohue, J. Parus, and S. Deron for useful discussions during the course of the experiments. Thanks are also due to H. Klose, A. Zoigner, H. Ziegler, and D. Klose for providing the U and Pu standards for the mass spectrometric measurements. Many thanks also are extended to G. Grabmueller, who shared his instrument with the authors for a period of 3 months.

References

[1] P. de Bievre, P. Hansen, K. Mayer, R. Fiedler, D. Rokop, R. Perrin, Int. J. Mass Spectrom. Ion Processes 145 (1995) 117.
[2] C.K. Bayne, D. Donohue, R. Fiedler, Int. J. Mass Spectrom. Ion Processes 134 (1994) 169.
[3] M. Romkowski, S. Franzini, L. Koch, Proceedings of the ESARDA Symposium, 12–14 May 1987, London.
[4] E.L. Callis, R.M. Abernathey, Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics, June 5–10 1988, San Francisco.
[5] R. Fiedler, D. Donohue, G. Grabmueller, A. Kurozawa, Int. J. Mass Spectrom. Ion Processes 132 (1994) 204.