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International Journal of Mass Spectrometry 270 (2008) 127–133

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Application of the isotope dilution technique for ^{93}Zr determination in an irradiated cladding material by multiple collector-inductively coupled plasma mass spectrometry

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Received 29 October 2007; received in revised form 4 December 2007; accepted 5 December 2007

Abstract

The determination of ^{93}Zr concentration, a long-lived radionuclide present in spent nuclear fuel and in the structural components of nuclear reactors, is a major issue for nuclear waste disposal purpose and to validate neutronic calculation codes. To measure ^{93}Zr concentration in irradiated cladding material with a high precision, an analytical method based on the use of multiple collector-inductively coupled plasma mass spectrometer (MC-ICPMS) combined to isotope dilution technique was developed. First a radiochemical separation of zirconium from a zircaloy sample (a zirconium alloy used as a cladding material for nuclear fuel elements), has allowed to obtain a very pure zirconium fraction with no potential isobaric interferences for mass spectrometric measurements. Then as the determination of all zirconium isotope ratios in the sample is necessary for the isotope dilution method, a MC-ICPMS procedure was developed to perform these precise measurements. Finally, the determination of ^{93}Zr concentration in the same sample was performed, after preparation and calibration of a ^{96}Zr spike solution. The uncertainties obtained on isotope ratios of zirconium by MC-ICPMS were in the order of 0.1%. The final uncertainty obtained on the ^{93}Zr concentration in the nuclear material used and after chemical purification was lower than 0.6%.

Keywords: MC-ICPMS; ^{93}Zr; Isotope dilution; Nuclear field

1. Introduction

Determination of high precision isotope composition of zirconium presents a large interest in terrestrial and extra-terrestrial materials [1,2]. In the nuclear field, determination of ^{93}Zr concentration with a high precision level is a major issue for waste management.

The zirconium isotope ^{93}Zr is a long-lived pure β particle emitting radionuclide, with a maximum energy of 56 keV and a half-life of 1.53×10^6 years [3]. It is produced mainly by nuclear fission of uranium 235 in nuclear fuels but also by neutron activation of zirconium used as cladding fuel element (because of the low neutrons absorption cross section of the isotope 92 of zirconium). A possibility to determine ^{93}Zr is the use of liquid scintillation counting, which can provide a precision of few percent or less, after separation from other pure β-particle and β–γ emitters [3]. Using this technique several preparation steps must be involved to separate ^{93}Zr from the main interfering radionuclides (^{55}Fe, ^{93}Mo, ^{93m}Nb, etc.). An other possibility is the direct determination of ^{93}Zr by inductively coupled plasma mass spectrometry (ICPMS) when ^{93}Zr is free from isobaric interferences and therefore no chemical separation is necessary [4,5]. Nevertheless, the relative uncertainty obtained with this technique is in the order of several percents. The best way to improve the accuracy of ^{93}Zr concentration is to use the isotope dilution (ID) technique combined to multiple collector-inductively coupled plasma mass spectrometer (MC-ICPMS). In this case it is necessary to remove all the possible isobaric interferences (Mo, Ru and Nb) by chemical separation. This method provides in this way an accuracy correlated to the one of the spike used and of the isotope ratio measurements, which is typically less than 1%. In addition, using the isotope dilution method,

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doi:10.1016/j.ijms.2007.12.005

the sources of uncertainties are well understood and controlled [6].

Zirconium isotope composition can be measured by thermal ionisation mass spectrometry (TIMS) but the low ionisation efficiency due to its high ionisation potential ($I_{Zr} = 6.84$ eV) makes it difficult to analyse [7]. In contrast to TIMS, MC-ICPMS offers better ionization as a result of the plasma ion source and high precision measurements associated with multi-collector detection system [2,8,9]. This high sensitivity and precision of the MC-ICPMS technique allows determination of zirconium isotope ratios with a precision better than 0.1%. Therefore ^{93}Zr determination by isotope dilution in irradiated samples could be performed at a precision in the order of some per-mil.

This paper presents the analytical procedure developed for the determination of ^{93}Zr concentration in nuclear materials using isotope dilution mass spectrometry with a ^{96}Zr spike. First, a detailed description of the MC-ICPMS procedure developed to obtain precise and accurate Zr isotope ratio measurements is presented and the results obtained on zirconium natural standard solutions are reported. The choice of a normalization ratio for mass bias corrections is then discussed and the results obtained are compared with previous data found in the literature. The procedure was then applied to the determination of non-natural zirconium isotope abundances in an irradiated sample. The long-term reproducibility of isotope ratio measurements performed on the Isoprobe MC-ICPMS was also evaluated.

Secondly, the preparation and calibration of the ^{96}Zr spike is presented and part of the discussion is dedicated to the step of equilibration between the spike and the sample in relation to the complex solution chemistry of zirconium. Finally, results and reproducibility obtained on the ^{93}Zr concentration determined by isotope dilution from a purified irradiated zircaloy sample are presented.

2. Experimental

2.1. Mass spectrometry analysis

All measurements were performed on a sector field MC-ICPMS Isoprobe from GV Instruments (Manchester, UK). This instrument consists of a standard ICP source, a rf-only hexapole collision cell for collisional focusing, a sector field and a multicollector system with 9 Faraday cups [10]. Liquid sample introduction is performed via a PFA micro-concentric nebulizer (0.1 ml/min) and a quartz cyclonic chamber. A Pt guard electrode, inserted between the torch and the load coil, allows to increase the sensitivity [11]. The modifications realized on the Isoprobe in order to handle radioactive materials have been previously described [12,13]. The operating conditions of the instrument are listed in Table 1. The ion beam intensity was optimized on a daily basis by adjusting the torch position, gas flows, ions focusing and sector field settings. The baseline was measured at half masses and corrected on line during each measurement. The sample analysis baseline was measured after cleaning the sample introduction system with a 0.5 M HNO_3 solution. The Zr data were acquired in static multicollection mode with Faraday cups. The collector setting is given in Table 2. Possible interferences from Ru and Mo have been evaluated by monitoring the 97 and 98 masses on the H5 and H7 detectors. The Faraday amplifier gain was calibrated daily prior to the analytical session. The fluctuations of the electric gains were lower than 20 ppm/day.

Table 1
Optimum operating parameters used for Zr isotope ratio measurements by MC-ICPMS (Isoprobe, GV Instruments)

rf power	1350 W
Plasma gas flow rate	13.5 l min^{-1}
Auxiliary gas flow rate	1 l min^{-1}
Nebulizer gas flow rate	0.8 l min^{-1}
Ar hexapole gas flow rate	1.4 ml min^{-1}
Sample uptake rate	0.1 ml min^{-1}
Nebulizer type	Meinhard
Spray chamber type	Cyclonic

2.2. Materials, solutions and sample chemical preparation

All Savillex™ PFA vials and Teflon© (PTFE) materials were cleaned with analytical grade concentrated nitric acid, hydrofluoric acid and Milli-Q (Millipore) water before used. Nitric and hydrofluoric acids (Ultrex, Bäcker) and Milli-Q water were used to obtain the diluted solutions and the blank solution used in the experiments. For the chemical separation of zirconium, all the acids used were of analytical grade. To prevent any natural contamination of the irradiated samples, Zr impurities content in all the materials and acids used was controlled by ICP-SFMS (Element 2, Thermo Fisher Scientific). All the concentrations determined were less than 10 ppt.

2.2.1. Zirconium standard solutions

No isotopic standard reference material is available for zirconium then two elemental Zr standard solutions were analysed in this study: a NIST SRM 3169 and an ICP (SPEX) standard solutions. All the experiments to optimize the analytical parameters were performed with a 300 ng/g zirconium solution. Both solutions have the same isotope composition, within the ana-

Table 2
Collector configuration used for determination of Zr isotope abundances by MC-ICPMS

Collector Faraday	L2	Ax	H1	H2	H3	H4	H5	H7
Mass	90	91	92	93	94	96	97	98
Sample Zr Ab%	Zr (51.4%)	Zr (9.2%)	Zr (19.1%)	Zr (0.3%)	Zr (17.3%)	Zr (2.7%)		
Interfering element			Mo	Nb	Mo	Mo, Ru	Mo	Mo, Ru

The estimated Zr isotope composition in the irradiated nuclear sample used in this study is indicated.

lytical uncertainties as supported by previous works [2,8]. The standard solution used to calibrate the ^{96}Zr spike was the NIST SRM 3169 with a certified concentration of 9.99 ± 0.04 mg/g. This standard solution contains nitric and hydrofluoric acids at an approximate volume fraction of 10% and 2%, respectively.

2.2.2. *Preparation of the enriched ^{96}Zr solution*

The zirconium spike solution was prepared by dissolution of ZrO_2 powder enriched at 86.4% in ^{96}Zr (Eurisotop). The ZrO_2 powder was dissolved in a 4 ml HF/2 ml HNO_3 mixture heated at 130 °C in PTFE bomb during 1 week. Once the dissolution of the powder completed, the solution was evaporated close to dryness and then diluted in the same media than the NIST solution (HNO_3 10%/HF 2%). The absence of Mo and Ru impurities was verified by ICPMS. The concentration of this spike solution was then determined by isotope dilution.

2.2.3. *Chemical purification of zirconium from an irradiated sample*

High precision zirconium isotope measurements by MC-ICPMS require the preparation of a sample free of isobaric interferents at the 90–96 masses (Mo, Ru, Nb). But as in the same sample the activity of ^{93}Zr has to be measured by liquid scintillation counting for an other objective (to obtain a precise and reliable half life value of this radionuclide), intensive decontamination steps were also carried out to eliminate all of the remaining β interferents (^{55}Fe, ^{93}Mo, ^{93m}Nb, etc.). These steps are briefly described in the following paragraphs and illustrated in Fig. 1.

A mineralization of about 120 mg of an irradiated zircaloy sheath was performed in HNO_3 and HF media. Since zirconium compounds in aqueous solution are characterized by their high degree of hydrolysis and absorption, and by their propensity to form various complex ions and polymer [14], relatively high acid concentrations (HNO_3 or HCl) were used throughout all the experimental steps to prevent the hydrolysis of Zr in solution.

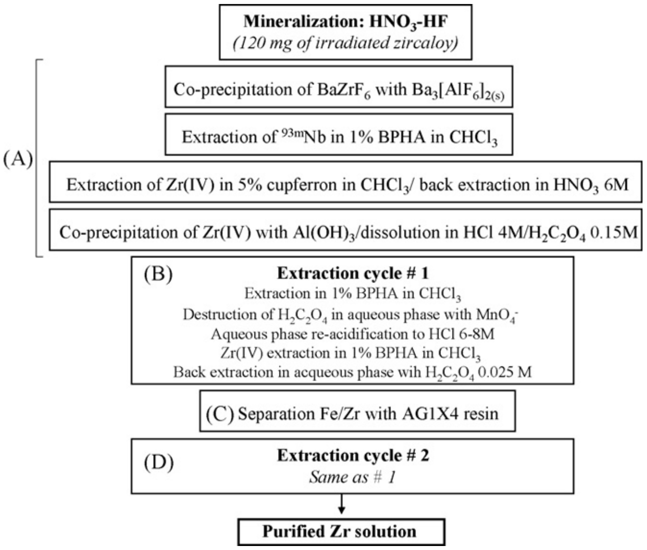

Fig. 1. Scheme of the different steps of the chemical purification of zirconium in the irradiated sample.

The first separation step is a combination of precipitation/dissolution, solvent extraction reactions followed by a co-precipitation/dissolution (step A in Fig. 1). Consequently, a zirconium solution in the form of the highly stable $Zr(C_2O_4)_2$ complex in $H_2C_2O_4$ 0.15 M and HCl 4 M was obtained.

Then, solvent extraction cycles (steps B and D in Fig. 1) were completed twice to remove specifically the ^{93m}Nb and ^{93}Mo interferents still present at trace level. Between these two solvent extraction cycles an additional purification step using an anionic exchange resin (step C in Fig. 1) was added to eliminate the isotope ^{55}Fe that can also interfere at low level in liquid scintillation counting.

Consequently, a first purified solution of ^{93}Zr (source no. 1: 50 ml of $Zr(C_2O_4)_2$ in 0.1 M $H_2C_2O_4$) was obtained following the radiochemical protocol previously described. The global recovery of the entire procedure is about 70%.

Another radiochemistry was applied to a 1 ml aliquot of the first source, consisting in three successive extraction cycles (same as cycle extraction # 1, step B in Fig. 1), and leading to a 25 ml solution of ^{93}Zr as $Zr(C_2O_4)_2$ in 0.025 M $H_2C_2O_4$ (source no. 2). The global recovery of these three cycles is about 75%. This radiochemistry is not necessary for MC-ICPMS measurements but essential for liquid scintillation counting to be sure that the sample is absolutely free of any β impurities. The results presented are obtained on this second source.

3. Results and discussion

3.1. *Precision and accuracy of mass spectrometric measurements*

A significant feature of plasma source mass spectrometry is the instrumental mass bias. The mass bias is the deviation of the measured isotope ratios from the “true” value and is related to the enhanced extraction and transmission of the heaviest ions [15]. This mass discrimination is around 3% amu^{-1} for Zr with the Isoprobe instrument used. To correct for this instrumental bias, an absolute and precise normalization value must be chosen. The mass discrimination for zirconium is corrected with a value of the ^{94}Zr/^{90}Zr ratio of 0.3378 ± 0.0002 [16]. The representativeness of this absolute isotope ratio has been extensively discussed in literature [16,17] and it is the reference value used for the determination of the atomic weight of zirconium [16]. The precision on this ratio appears satisfactory considering the final precision required in this work for the determination of ^{93}Zr concentration in irradiated samples. The zirconium isotope ratios obtained on natural solution were measured by MC-ICPMS. Instrumental mass fractionation was corrected with the “standard-sample bracketing” approach which involves the measurement of a standard between samples and using an exponential law fractionation [18]. During the analytical session (over 6 months) 33 analyses of natural zirconium solutions were performed. Each analysis was constituted of four blocks and each data block corresponded to the completion of 10 cycles of 10 s integration time each. The internal precision

Table 3
Summary of natural Zr isotope abundances found in the literature data and Zr isotope ratios obtained by MC-ICPMS in this study

Reference	Technique	Normalization ratio	$^{91}Zr/^{90}Zr$	$^{92}Zr/^{90}Zr$	$^{94}Zr/^{90}Zr$	$^{96}Zr/^{90}Zr$
IUPAC [22]			0.21808(104)	0.33333(166)	0.33780(547)	0.05442(175)
[20]	TIMS		0.22002(4)	0.33410(6)	0.33592(6)	0.05363(1)
[17]	TIMS	$^{94}Zr/^{90}Zr = 0.3381$	0.21799(5)	0.33338(6)		0.05439(7)
[19]	TIMS	$^{94}Zr/^{90}Zr = 0.3382$	0.21799(5)	0.33338(6)		0.05439(7)
[16]	TIMS		0.21814(22)	0.33324(13)	0.33779(21)	0.05440(9)
[9]	MC-ICPMS	$^{91}Zr/^{90}Zr = 0.21814$		0.33394(2)	0.33917(4)	0.05463(1)
[8]	MC-ICPMS	$^{91}Zr/^{90}Zr = 0.21814$		0.33394(2)	0.33916(5)	0.05463(1)
[2]	MC-ICPMS	$^{94}Zr/^{90}Zr = 0.3381$	0.21793(2)	0.33338(3)		0.05437(1)
This study ($n = 33$)	MC-ICPMS		0.21806(4)	0.33333(4)	0.33776(11)	0.05443(3)

The isotope ratios are externally normalized with a "standard-sample bracketing" approach using an exponential law fractionation. For IUPAC values are indicated the representative isotope composition [22].

obtained varied from 0.02% to 0.06%, the last value being found for the $^{96}Zr/^{90}Zr$ ratio. Table 3 shows the data obtained on natural Zr solutions and the reference values found in the literature. All of the data reported from literature were internally normalized by the ratio indicated in the table. Internal normalization is not possible in the case of zirconium isotope analysis of irradiated materials due to the absence of natural invariant ratio in the sample, therefore the reproducibility was evaluated externally by the standard bracketing approach.

External reproducibility was evaluated for these 33 measurements by applying a student coefficient ($\nu = 32$). The external reproducibility obtained was better than 0.1% for all the measured isotope ratios. It is obvious from Table 3 that isotope ratios values obtained with the analytical procedure developed are in very good agreement with the one of Minster and Ricard [17,19], but also with the "absolute" values of Nomura et al. [16] and are within the range of recent MC-ICPMS values obtained by Schönbächler [2]. Values obtained by Hirata [8,9] were acquired using a different internal normalization ratio. Despite the fact that it is not possible to compare the values at the range of uncertainty performed by the different laboratories, it is very interesting to underline the very good agreement of zirconium isotope ratios values at a range of uncertainty of 0.2%. Only the values on the ratios $^{91}Zr/^{90}Zr$, $^{94}Zr/^{90}Zr$ and $^{96}Zr/^{90}Zr$ determined by Shima [20] present differences with the others in the order of 1%. These differences could be explained (at least for one part) that different ion detectors were used [16].

The Zr isotope composition of the purified irradiated zircaloy sheath sample was then determined using the same "standard-sample bracketing" approach. The sample, conditioned initially in $H_2C_2O_4$ was evaporated and redissolved in 1 ml HNO_3 2%. The MC-ICPMS measurements of this sample were always performed between runs of Zr standards, which concentrations were adjusted to match within 20% of the sample's concentration values. As a result of the chemical separations performed from the irradiated sample, no isobaric interference correction for Mo and Ru was necessary. In Table 4 are presented the results obtained on the sample which was analysed nine times in four different days. Reproducibility of the data evaluated by the relative standard deviation ($k = 1$) is better than 0.1% for the four ratios $^{91}Zr/^{90}Zr$, $^{92}Zr/^{90}Zr$, $^{94}Zr/^{90}Zr$ and $^{96}Zr/^{90}Zr$ and is about 0.12% for the $^{93}Zr/^{90}Zr$ ratio (taking into account the uncertainty on the absolute $^{94}Zr/^{90}Zr$ isotope ratio used for normalization). The atomic weight of Zr in the sample was calculated to be $91.243 \pm 0.0022\ \mathrm{g\ mol^{-1}}$ ($k = 2$).

3.2. Calibration of the spike solution

After dissolution of the enriched ZrO_2 powder, a diluted solution of the ^{96}Zr spike was prepared. The Zr isotope composition of this solution was carefully measured and its concentration was then determined by reverse isotope dilution using the NIST SRM 3169 standard solution.

3.2.1. ^{96}Zr spike isotope composition

The Zr isotope ratios of this spike solution were determined by MC-ICPMS and instrumental mass fractionation was corrected with the "standard-sample bracketing" approach. To prevent any problems of memory effects, the sample introduction system was cleaned with 2% HNO_3–0.01% HF during 5

Table 4
Zirconium isotope ratios obtained on the purified zirconium irradiated sample by MC-ICPMS measurements

	Sample isotope ratios				
	$^{91}Zr/^{90}Zr$	$^{92}Zr/^{90}Zr$	$^{94}Zr/^{90}Zr$	$^{96}Zr/^{90}Zr$	$^{93}Zr/^{90}Zr$
1	0.17948	0.37150	0.33623	0.05302	0.00574
2	0.17945	0.37154	0.33634	0.05304	0.00573
3	0.17950	0.37162	0.33642	0.05306	0.00575
4	0.17945	0.37155	0.33630	0.05304	0.00575
5	0.17947	0.37157	0.33638	0.05307	0.00574
6	0.17947	0.37153	0.33629	0.05304	0.00574
7	0.17948	0.37155	0.33628	0.05304	0.00573
8	0.17953	0.37171	0.33656	0.05311	0.00575
9	0.17950	0.37160	0.33629	0.05305	0.00575
Mean	0.17948	0.37157	0.33634	0.05305	0.00574
S.D. ($k = 1$)	0.00003	0.00006	0.00010	0.00003	0.00001
R.S.D. (%)	0.01	0.02	0.03	0.05	0.12
Uncertainty (%)	0.03	0.03	0.04	0.06	0.12

The sample was analysed nine times during four different days. S.D. and R.S.D. (%) represent the absolute and relative external precision (1σ) obtained for the nine measurements. "Uncertainty (%)" represents the external precision taking into account uncertainty on the absolute $^{94}Zr/^{90}Zr$ isotope ratio used for normalization.

Table 5
Zirconium isotope ratios measured in the ^{96}Zr spike solution (Eurisotop) by MC-ICPMS

	Spike isotope ratios			
	^{91}Zr/^{90}Zr	^{92}Zr/^{90}Zr	^{94}Zr/^{90}Zr	^{96}Zr/^{90}Zr
1	0.36985	0.53216	0.79752	17.1104
2	0.36945	0.53196	0.79692	17.1088
3	0.36989	0.53195	0.79678	17.1088
4	0.37015	0.53273	0.79761	17.1262
Mean	0.36984	0.53220	0.79721	17.1136
S.D.	0.00029	0.00037	0.00042	0.0085
R.S.D. (%)	0.08	0.07	0.05	0.05
Uncertainty (%)	0.08	0.08	0.06	0.06

The sample was analysed four times during two different days. "Uncertainty (%)" represents the external precision taking into account uncertainty on the absolute ^{94}Zr/^{90}Zr isotope ratio used for normalization.

to 10 min. Washout of Zr usually required less than 5 min. The spike solution was analysed during two different analytical sessions and results are presented in Table 5. Reproducibility of the Zr isotope ratios evaluated by the relative standard deviation is better than 0.1% for all of the ratios (taking into account the uncertainty on the absolute ^{94}Zr/^{90}Zr isotope ratio used for normalization). The atomic weight of Zr in the spike was calculated to be 96.33 ± 0.13 g mol^{-1} ($k = 2$).

3.2.2. ^{96}Zr spike concentration

From the ^{96}Zr spike solution, two diluted solutions were prepared gravimetrically in the same nitric–hydrofluoric acid media. The concentrations of these two solutions were 12.83 ± 0.05 and 8.93 ± 0.04 µg g^{-1}, respectively. The equation for the determination of the spike zirconium concentration is the following equation (1):

$$[\mathrm{Zr}]_{\mathrm{Sp}} = [\mathrm{Zr}]_{\mathrm{NIST}} \frac{m_{\mathrm{NIST}}}{m_{\mathrm{Sp}}} \frac{M_{\mathrm{Sp}}}{M_{\mathrm{NIST}}} \frac{(96)_{\mathrm{NIST}}}{(96)_{\mathrm{Sp}}} \frac{(^{90}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{NIST}} - (^{90}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{Mix}}}{(^{90}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{Mix}} - (^{90}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{Sp}}} \tag{1}$$

where NIST is the SRM 3169 solution, mix the sample–spike mixture and Sp the spike; *m* and *M* are the respective masses and atomic weights of NIST SRM 3169 and spike and "(96)" is the atomic abundance of ^{96}Zr expressed in atoms. All the isotope ratios are expressed in atoms.

Several gravimetrically mixtures of spike and diluted SRM 3169 solutions were realized and (^{90}Zr/^{96}Zr)$_{\mathrm{Mix}}$ ratios were determined by MC-ICPMS with the analytical method previously described. These different experiments were performed to be sure that a perfect isotope equilibration between the NIST and the spike Zr solutions. The results obtained for the zirconium concentration in the spike with these six different mixtures (four with the diluted solution at 12.83 ± 0.05 µg g^{-1} and two with the 8.93 ± 0.04 µg g^{-1} solution) are presented in Table 6. The relative standard deviation on these six mixtures is better than 0.25% ($k = 1$). The final uncertainty on the zirconium spike concentration was evaluated by the combination of standard uncertainty of each parameter [21]. Uncertainties for the major components of the ID equation are indicated in Fig. 2. The value obtained for the Zr concentration in the spike is 12.78 ± 0.06 µg g^{-1} ($k = 2$). In Fig. 2, the relative contribution (in percents) of the main sources of uncertainty is shown for the spike zirconium concentration. The principal source of uncertainty is the one of the NIST reference solution used for calibration of this spike (about 80% of the total uncertainty budget).

Table 6
Zirconium concentration of the ^{96}Zr spike solution determined by MC-ICPMS measurements and isotope dilution

	Spike concentration, [Zr] (µg g^{-1})
1 (A)	12.784
2 (A)	12.781
3 (A)	12.817
4 (A)	12.803
1 (B)	12.741
2 (B)	12.746
Mean	12.779
S.D.	0.030
R.S.D. (%)	0.24

Six different sample–spike mixtures were realized using two different diluted NIST SRM 3169 zirconium solutions. The concentration of solution A was 12.83 ± 0.05 and 8.93 ± 0.04 µg g^{-1} for solution B.

3.3. Determination of ^{93}Zr concentration in irradiated samples using ID technique

The ^{93}Zr concentration in the purified zirconium fraction sample was determined by isotope dilution from the following equation (2):

$$[\mathrm{Zr}]_{\mathrm{S}} = [\mathrm{Zr}]_{\mathrm{Sp}} \frac{m_{\mathrm{Sp}}}{m_{\mathrm{S}}} \frac{M_{\mathrm{S}}}{M_{\mathrm{Sp}}} \frac{(96)_{\mathrm{Sp}}}{(96)_{\mathrm{S}}} \frac{(^{93}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{Mix}}}{(^{93}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{S}} - (^{93}\mathrm{Zr}/^{96}\mathrm{Zr})_{\mathrm{Mix}}} \tag{2}$$

where Mix, S and Sp stands, respectively, for mixture, sample and spike; *m* and *M* are the masses and atomic weights in

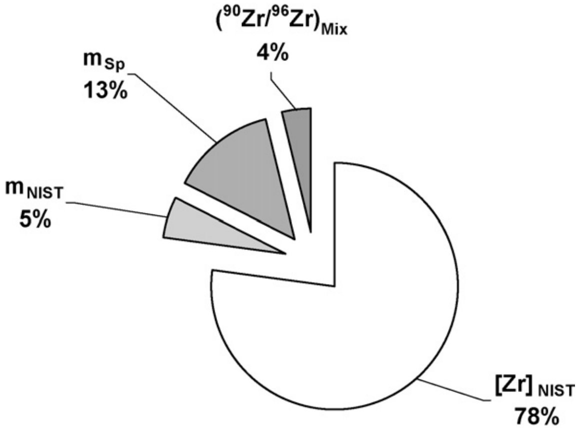

Fig. 2. Relative contribution (%) of the main uncertainty sources for the $[\mathrm{Zr}]_{\mathrm{Sp}}$ concentration determined by MC-ICPMS and isotope dilution.

Table 7
^{93}Zr concentration of the purified irradiated sample determined by MC-ICPMS and isotope dilution

	Sample concentration, [^{93}Zr] (μg g^{-1})
1	0.06297
2	0.06296
3	0.06314
4	0.06315
5	0.06333
6	0.06317
7	0.06313
Mean	0.06312
S.D.	0.00013
R.S.D. (%)	0.20

Seven different sample–spike mixtures were realized, the last one (7) being performed 5 months later to ensure that zirconium was well equilibrated both in the sample and spike solutions.

the sample and the spike, "(96)" is the atomic abundance of ^{96}Zr expressed in atoms. All the isotope ratios are expressed in atoms.

Seven mixtures of the spike and sample solutions were prepared by weight to determine the (^{93}Zr/^{96}Zr)$_M$ ratio in the sample by MC-ICPMS. Each solution was evaporated after mixing, and then redissolved in HNO_3 2% media. Six mixtures were prepared within a short period of time and the last one 5 months later, to make sure that zirconium was well equilibrated both in the sample and in the spike solutions. The seven mixtures results obtained for the sample zirconium concentration are presented in Table 7. The mixture realized 5 months later is designated as "7" in the table and do not show any deviation with respect to the others. The relative standard deviation obtained on the seven mixtures results is 0.2% ($k = 1$). The final uncertainty on the zirconium sample concentration was evaluated by the calculation of combined uncertainties of each contributing term [21]. Uncertainties of the major components of the ID equation are indicated in Fig. 3. The value found for the ^{93}Zr concentration in the sample was $0.0631 \pm 0.0004\ \mu\text{g g}^{-1}$ ($k = 2$). The relative uncertainty obtained for the concentration of ^{93}Zr in nuclear materials after chemical purification is about 0.6%. The relative contribution, expressed in percents, of the main uncertainty sources for the ^{93}Zr concentration in the sample is given in Fig. 3. The uncertainty of the spike concentration determined in the laboratory accounts for half of the total uncertainty, which is the major uncertainty contribution.

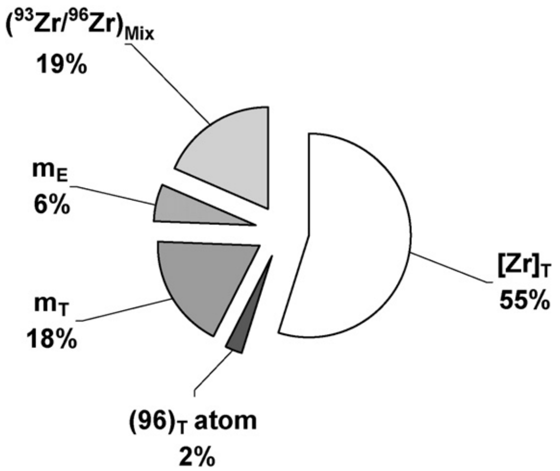

Fig. 3. Relative contribution (%) of the main uncertainty sources for the [^{93}Zr]$_S$ concentration determined by MC-ICPMS and isotope dilution.

4. Conclusion

This study presented the development of an MC-ICPMS procedure to perform high precision zirconium isotope abundance measurements in natural commercial solutions. A ^{96}Zr spike solution was prepared and calibrated in concentration by reverse isotope dilution using a NIST standard Zr solution. From an irradiated zircaloy sample, ^{93}Zr was first isolated from sample matrix and from other radionuclides by means of selective chemical separation methods using liquid–liquid extractions and ion exchange separation. The ^{96}Zr spike solution was then used to determine, by isotope dilution, the ^{93}Zr concentration in this sample. The mass spectrometric method developed offered the possibility to determine the concentration of ^{93}Zr in the irradiated sample with a combined uncertainty better than 0.6%.

Acknowledgments

The authors would like to thank Philippe Cassette (CEA/DRT/DETECS/LNHB) and Ivan Laszak (CEA/DEN/DPC/SECR/LANIE) for their advice and valuable discussions.

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