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Precise Os isotope ratio and Re–Os isotope dilution measurements down to the picogram level using multicollector inductively coupled plasma mass spectrometry

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Abstract

This article describes analytical procedures to measure Os isotopic composition and to determine isotope dilution Re and Os concentrations accurately, precisely, and rapidly on a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS). For Os measurements, a custom made apparatus to allow efficient direct OsO₄ distillation into the plasma source is described. Static multi-Faraday cup measurements on 50 ng commercially available Os standard yield 2σ external reproducibilities of 0.016% for ¹⁸⁷Os/¹⁸⁸Os and 0.017% for ¹⁸⁶Os/¹⁸⁸Os ratios (*n* = 5). The mean values are indistinguishable within analytical uncertainty from those determined by negative thermal ionization mass spectrometry (N-TIMS). Further, amounts of 25–250 pg of spiked and unspiked analytes of the same Os standard have been determined by ion counting, which reproduced the ¹⁸⁷Os/¹⁸⁸Os ratio of the Faraday cup measurements within analytical uncertainty. Thereby, the in-run precision increases from 1.2% (25 pg, 2σ) to 0.14% (200 pg) with an overall external reproducibility of 0.32%. Measuring procedures for Re include Ir doping of the analytes for in-run mass fractionation correction, whereby Ir ion beams are detected on Faraday collectors and Re ion beams are simultaneously measured on ion counting electron multiplier collectors. The potential of the method was tested using Re spike calibration and Re-blank measurements, which showed that 0.2 pg Re can be accurately measured to a precision better than 1%, whereas larger samples (>10 pg) allow precisions that are significantly better than any other analytical uncertainty such as weighing errors. Thus, the feasibility of high precision Re–Os analyses at the pg level with multicollector ICP-MS is demonstrated. (Int J Mass Spectrom 197 (2000) 85–94) © 2000 Elsevier Science B.V.

Keywords: Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS); Re–Os; Isotope measurements

1. Introduction

Precise measurements of ¹⁸⁷Os/¹⁸⁸Os combined with accurate Re/Os ratios are of growing importance in studies relating to investigations of different geochemical mantle reservoirs, the evolution of earth's

core, mantle and continental crust, and the formation of economically interesting ore deposits in addition to Re/Os dating (see [1]). Thereby, the ability to measure ¹⁸⁷Os/¹⁸⁸Os isotope ratios of Os amounts as small as 10–100 pg to a precision with analytical uncertainties better than 1% (2σ) is often required for adequate geological interpretations.

Methods used for measuring Os isotope ratios for geological applications are resonance ion mass spec-

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trometry (RIMS; [2]), secondary ion mass spectrometry (SIMS; [3]), single collector inductively coupled plasma mass spectrometry (ICP-MS; [4]) and, most successful with regard to precision and accuracy, negative thermal ionization mass spectrometry (N-TIMS [5,6]). In the latter method, osmium is measured as the OsO_3^- ion, whereby considerable ionization efficiency (i.e. the ratio of OsO_3^- ions generated per Os atoms present in the analyte) of more than 1% can be achieved [5,6]. Os N-TIMS measurements are among the most difficult and time consuming thermal isotope ratio mass spectrometric methods. Samples must be very pure to achieve good ionization efficiencies and the electron supplier added [typically $\text{Ba}(\text{NO}_3)_2$ or $\text{Ba}(\text{OH})_2$] can produce a large charge build up in the source area that interferes with the focusing of the OsO_3^- ion beams (cf. [7]). Isotope analysis of rhenium by N-TIMS as ReO_4^- can yield ionization efficiencies up to 25% [6] and provides ample signal intensities for accurate Re concentration determinations by isotope dilution at the picogram level. However, in this technique an often cited problem is Re blank contribution from the diversely used filament materials (i.e. Pt, Ta, and Ni) and its near environment (source area). The variety of proposed solutions to this problem (e.g. [7–10]) is a reflection of its complexity. Further, Re only has two isotopes (^{185}Re and ^{187}Re) so that no in-run fractionation correction is possible in N-TIMS isotope dilution runs. A good fractionation correction for spiked $^{185}\text{Re}/^{187}\text{Re}$ ratios is important because the natural $^{185}\text{Re}/^{187}\text{Re}$ ratio is 0.598, close to unity, and therefore error magnifications in calculating concentrations from isotope dilution runs are inherently large. In N-TIMS, the fractionation correction for Re measurements of natural samples are based on fractionation determined from measurements of Re standard solutions, under the assumption that conditions such as evaporation under vacuum, filament temperatures, and ionization efficiencies are the same for natural samples and Re standards.

Multicollector inductively coupled plasma magnet sector mass spectrometry (MC-ICP-MS) has great potential for Re–Os isotope determinations because of the high ionization efficiency (as Os^+ and Re^+) of the

plasma and the simultaneous detection of all Os isotope beams. Problems are the low efficiency of most nebulizer systems and, for Os, the serious memory build up of nebulizers and spray chambers. Further, in ICP-MS the overall efficiency (i.e. the ratio of ions arriving at the collectors per atoms in the analyte) is limited by the generally $\sim 1\%$ transmission efficiency of the cones interface. Different uptake methods for Os analytes into the Ar plasma, such as solution nebulization, osmium tetroxide vaporization by leading the Ar sample gas through an oxidizing solution containing Os, and electrothermal vaporization from a graphite surface, have been investigated by Gregoire [11] and Hassler *et al.* [12]. The best overall efficiency reported from these experiments is 2×10^{-5} , obtained by OsO_4 evaporation. However, as the OsO_4 was released from the solution over a long period (30–40 min) the Os signals obtained were small and did not allow precise determinations of isotope ratios on very small samples.

To overcome the problem of inefficient and slow release of OsO_4 from sample solutions, we have studied its evaporation from small volumes of several oxidizing reagents. Efficient and rapid evaporation of OsO_4 allows Os isotope measurements lasting only 10 min, equal to N-TIMS analyses in internal precision and reproducibility for sample quantities down to ~ 100 pg. Further, we have investigated blank, memory, and mass fractionation in multicollector ICP-MS Re measurements introducing the Re analyte via a conventional nebulizer.

The Nu Instruments multicollector ICP mass spectrometer (Nu Instruments, Wrexham, North Wales, UK) used in these experiments is a double-focusing instrument in which an electrostatic analyzer is placed before the magnet in U configuration (Nier-Johnson geometry) to focus ion beams with up to 20 eV energy dispersion inherited from the plasma. Accelerating voltage is applied to the cones. Twelve Faraday collectors and three electron multipliers, operated in ion counting mode, form a fixed array. Two electrostatic lenses positioned between the magnet and the collector plane act as a zoom assembly, enabling the divergence of ion beams of different masses to be

Table 1
Os standard measurements

No.	Os (ng)	$^{186}\text{Os}/^{188}\text{Os}$	± 2 SE (absolute)	$^{187}\text{Os}/^{188}\text{Os}$	± 2 SE (absolute)
Faraday measurements, static mode					
1	50	0.119837	0.000076	0.106947	0.000079
2	50	0.119820	0.000038	0.106915	0.000055
3	50	0.119813	0.000028	0.106970	0.000024
4	50	0.119834	0.000014	0.106932	0.000019
5	50	0.119834	0.000016	0.106933	0.000024
Average	5 runs	0.119828	0.000020^a	0.106939	0.000018^a
N-TIMS^b	9 runs	0.119830	0.000005^a	0.106948	0.000018^a
		$^{190}\text{Os}/^{188}\text{Os}$	± 2 SE (absolute)	$^{187}\text{Os}/^{188}\text{Os}$	± 2 SE (absolute)
Triple ion counter, double jump					
I	0.250			0.10700	0.00018
II ^c	0.025	14.489	0.021	0.10720	0.00128
III	0.250			0.10694	0.00016
IV ^c	0.100	11.028	0.007	0.10674	0.00081
V	0.200			0.10699	0.00015
VI ^c	0.100	6.588	0.002	0.10661	0.00049
VII	0.200			0.10679	0.00017
VIII ^c	0.080	5.496	0.001	0.10686	0.00042
IX	0.200			0.10697	0.00022
Average of unspiked runs only				0.10694	0.00017^a
Average of all runs				0.10690	0.00034^a

^a Two standard deviation (absolute) of the population.

^b Data from Copenhagen; 30 ng runs of the same JM Os standard (R. Frei, personal communication, June 1999).

^c Spiked standard runs.

varied, so that multicollector measurements are possible for the full mass range of the elements.

2. Preparation of Os and Re analytes

2.1. Unspiked and spiked Os standard solutions

Approximately 100 μL of a 512.631 ppb Os standard solution [diluted from the 1000 ppm Johnson & Matthey (Karlsruhe, Germany) Os ICP standard solution] were transferred into teflon beakers and mixed with 3 ml of 8 N HBr to form stable OsBr_6^{2-} complexes. After drying down on a hot plate at 75 $^\circ\text{C}$, the residues were ready for ICP mass spectrometric analyses (for results see Table 1). Spiked Os standard solutions were prepared using the technique for digestion and homogenization of spiked natural rock samples. Os isotope determinations in geochemistry increasingly requires accurate determinations of Re/Os ratios as

well as $^{187}\text{Os}/^{188}\text{Os}$ ratios. Because of the very inhomogeneous distribution of the platinoids in most rocks, aliquoting is inappropriate. Therefore, the measurement of the $^{187}\text{Os}/^{188}\text{Os}$ ratio and the determination of the Os concentration by isotope dilution (using the $^{190}\text{Os}/^{188}\text{Os}$ ratio) have to be combined in a single procedure. Full isotope equilibration between Os standard and Os spike solutions must be achieved; this is commonly done by ensuring complete oxidation of all Os to OsO_4 while heating in an oven at 240 $^\circ\text{C}$ for 48 h in a closed Carius tube [13]. Amounts between 50 and 500 μL of an 0.4985 ppb Os standard solution (also diluted from the 1000 ppm Johnson & Matthey Os ICP standard solution), suitable quantities of enriched ^{190}Os tracer (0.9493 ppb total Os with $^{190}\text{Os}/^{188}\text{Os} = 302.906$), and 8 mL of inverse aqua regia were weighed into Carius tubes that were then sealed. During weighing and welding the Carius tubes were cooled down to -25 $^\circ\text{C}$ to avoid any evaporative loss of Os.

Table 2
Calibration measurements of Re spikes

Concentration runs ^a	Spike (g)	¹⁸⁵ Re/ ¹⁸⁷ Re	Spike (pg/g)	IC-run	¹⁸⁵ Re/ ¹⁸⁷ Re	±2σ ^b (absolute)
Spike for crustal samples						
Re crust/A	1.979	2.9050	1415	Re crust/1	28.805	0.016
Re crust/B	1.971	4.8210	1415	Re crust/2	28.806	0.026
Re crust/C	1.973	4.7430	1415	Re crust/3	28.760	0.022
Re crust/D	2.950	6.3740	1414	Re crust/4	28.805	0.049
Re crust/E	1.327	2.1980	1412	Re crust/5	28.808	0.037
Average			1414.2 ± 2.8^c		28.797	0.041^c
Spike for blank measurements						
Re100/A	2.073	0.7834	105.5	Re100/1	28.601	0.044
Re100/B	1.062	0.6887	105.5	Re100/2	28.560	0.044
Re100/C	2.022	0.9345	105.2	Re100/3	28.616	0.026
Re100/D	0.532	0.6470	106.8	Re100/4	28.705	0.032
Re100/E	1.022	0.7669	105.9	Re100/5	28.675	0.026
Average			105 ± 1.3^c		28.631	0.116^c

^a Diluted Re ICP standards were used to calibrate the spike concentrations.

^b 2σ (absolute) standard error of analyses.

^c 2σ (absolute) standard deviation of the population.

After heating for 48 h and cracking the Carius tubes, osmium was directly distilled into HBr using the technique described by Nägler and Frei [14]. After taking to dryness, samples were directly ready for ICP mass spectrometry. No further purification of Os was required before analysis (results reported in Table 1).

2.2. Spike calibration and reagent blank solutions for Re

In contrast to Os, homogenization of natural sample Re or Re standard solutions with Re spike solu-

tions is easily achieved. For spike calibration measurements (Table 2), the prepared Re spike solutions were added to dilutions of commercial Re ICP standard solutions (Johnson & Matthey, 1000 ppm Re). For the blank measurements reported, 5–10 g of the reagents (see Table 3) were weighed into teflon beakers and spiked with approximately 100 μl of ¹⁸⁵Re tracer solution (105.8 ppt Re, ¹⁸⁵Re/¹⁸⁷Re = 28.631; see Table 2). All samples were dried down on a hot plate at approximately 75 °C. The residues were taken up in 150 μl H₂O (Millipore, Bedford, MA), after which 20 μl of a 100 ppb Ir standard solution (in

Table 3
Re blank determinations by isotope dilution of reagents used during chemical separation

Reagent	Sample weight (g)	¹⁸⁵ Re/ ¹⁸⁷ Re (measured)	2 SE (absolute)	Total Re (pg)	Blank (pg/g)
14N HNO ₃ , 2×IR distilled	6.929	11.34	0.32	1.01	0.146
14N HNO ₃ , quartz distilled	7.032	17.17	0.72	0.387	0.055
14N HNO ₃ , quartz distilled	4.591	20.75	0.24	0.212	0.046
30% HCl, Merck ^a suprapur	5.787	8.15	0.12	1.588	0.274
6N HCl, quartz distilled	6.151	17.35	0.09	0.446	0.073
H ₂ O, Millipore	9.298	20.74	0.16	0.214	0.023
Ethanol, Merck pro analysis	7.042	19.31	0.11	0.267	0.038
Isoamylol, Merck zur Synthese	6.330	17.38	0.19	0.417	0.066
Isoamylol, Merck pro analysis	6.150	18.23	0.16	0.417	0.068

IR distilled = subboiling distillation under infrared lamps; quartz distilled = subboiling distillation in a quartz glass distillation apparatus.

^a Merck, Dietikon, Schweiz.

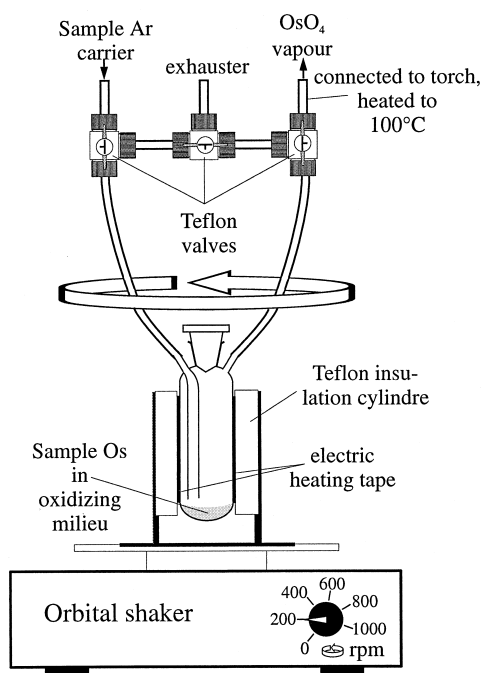


Fig. 1. Sketch of the OsO_4 evaporation line (not to scale).

1 N HCl) was added. After homogenization by ultrasonic agitation, the mixtures were ready for ICP mass spectrometric analyses.

3. Mass spectrometry

3.1. Introduction of Os as OsO_4 into the sample Ar stream

Fig. 1 shows a sketch of the Os evaporation apparatus, which is directly connected to the torch of the multicollector ICP-MS. The sample (with Os normally existing in the form of an OsBr_6^{2-} complex) is taken up in 150 μL concentrated (i.e. 18 N) sulfuric acid (GFS-chemicals, Powell, OH, originally doubly distilled) and transferred into the evaporation vessel with a pipette. Oxidation of Os and thus the formation and evaporation of OsO_4 is enhanced by adding an oxidant. OsO_4 is then taken up by the Ar sample carrier gas (flow rate of ~ 0.8 l/min) and carried through a 1/4 in. teflon tube into the torch, where

OsO_4 is dissociated and osmium is mainly ionized as Os^+ . Heating the evaporation vessel with a heating tape to 120 $^\circ\text{C}$ and shaking the vessel at ~ 200 rpm on an orbital shaker further increases the evaporation rate of OsO_4 , releasing at least 80% of the total sample Os in 9–18 min (depending on the total amount of Os). Shaking the evaporation vessel during heating not only enhances OsO_4 evaporation by enlarging the effective liquid surface, but also continuously homogenizes the sample reagent mixture, preventing the formation of a Os depleted surface layer. The three valves allow short circuiting of the carrier gas and purging of the distillation vessel, making it possible to replace vessels without switching off the plasma.

3.2. Oxidation reagents and overall ionization efficiency

Sample evaporation was tested with HNO_3 and H_2SO_4 of diverse molarities and with the addition of various types of oxidants with the aim of obtaining optimal evaporation rates and stable signal plateaus. We found that evaporation of OsO_4 using 8–14 N HNO_3 was not very efficient with any of the oxidants CrO_3 , H_2O_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$ (cf. [15]). In addition, a major drawback of nitric acid as a sample-carrying reagent for our purpose is its low constant boiling temperature of 120 $^\circ\text{C}$ (concentrated HNO_3), resulting in a HNO_3 vapor containing the sample OsO_4 during measurements, which condenses and dries in the evaporation line, building up a huge sample memory. Further, none of the above oxidants was efficient at the evaporation temperature of 120 $^\circ\text{C}$ over the time period needed for an analysis. Concentrated sulfuric acid, on the other hand, has a boiling point of 330 $^\circ\text{C}$, resulting in a nearly dry OsO_4 vapor. This not only has the advantage of minimal deposition of Os on the inner surface walls of the evaporation line, it also minimizes energy fluctuations of the plasma and results in stable Os isotope signals. The most convenient and efficient oxidant found for use with sulfuric acid is Nochromix (Godax Laboratories, Inc., Takoma Park, MD), a white crystalline oxidizer, normally dissolved in concentrated sulfuric acid to clean laboratory glassware. The addition of a few crystals of

Nochromix into the concentrated H_2SO_4 containing the sample Os yields fast and highly efficient oxidation to OsO_4 over the whole time span needed for an analysis (10–20 min). The chemical formulation of Nochromix is a registered trade secret, but it only contains substances rated as “slightly hazardous.” Blank experiments showed that Nochromix is absolutely Os-free and does not need purification before use.

A 15 min run of a 50 ng Os standard yielded an average intensity for the sum of all osmium isotope beam currents of 2.3×10^{-11} A ($= 1.44 \times 10^8$ cps), equivalent to an overall efficiency of 0.82×10^{-3} . A 12 min run on a chromite split (unpublished data) containing 22 ng total Os yielded an average ion current of all beams of 1.3×10^{-11} A ($= 0.81 \times 10^8$ cps), corresponding to an overall efficiency of 0.84×10^{-3} . Other runs on chromite separates showed efficiencies within the same range. Similarly, a 200 pg Os standard solution run produced an average current of all isotope beams of 8×10^{-14} A ($= 5 \times 10^5$ cps) for as long as 17 min, equal to an ionization efficiency of 0.80×10^{-3} . These remarkably consistent values show that overall efficiency for osmium using this evaporation technique is independent of total Os sample mass.

3.3. Memory effects

Memory results primarily from incomplete Os evaporation of the analyte solution and is removed by using a new, clean evaporation vessel for each sample. The teflon (PTFE-polytetrafluorethylen) tubing leading to the torch is heated to approximately 100 °C, hindering OsO_4 condensation on and diffusion into the tubing walls, thus minimizing the build up of sample memory in the evaporation line. The Os memory following vessel change after a sample run is less than 0.05%, which is much smaller than that observed when Os is taken up in a solution and nebulized into the plasma via a spray chamber. In addition, between two sample runs, the Os memory in the line can be liberated by evaporating 12 N H_2SO_4 plus an oxidant from a clean evaporation vessel (only used for this purpose) for 5–10 min. We assume that

the vapor wets the surface of the heated tubing, releasing the captured OsO_4 . The effectiveness of this cleaning procedure was tested following runs of Os standard solutions with total Os amounts of 50 ng, yielding ion currents of up to 3×10^{-11} A on ^{192}Os (abundance 41% of total common Os) during the analysis. Following vessel change after the run, the signal current of mass 192 was 1.5×10^{-14} A at the beginning of the cleaning procedure and decreased after 5 min to ~ 300 cps ($\cong 5 \times 10^{-17}$ A) detected on an ion counter. This is normally an insignificant memory contribution, even if the following sample contains two orders of magnitude less Os.

3.4. Uptake of Re analytes

Re analytes were nebulized using a microconcentric nebulizer (MCN 100, CETAC Technologies, Omaha, NE) in direct aspiration mode with a water-cooled Cinnabar cyclonic spray chamber (Glass Expansion, Camberwell, Victoria, Australia) at temperatures between 5 and 10 °C. After each run, the nebulizer and spray chamber were cleaned by taking up 0.5 N HCl for 2 min followed by H_2O for 1 min. Even if Re signals were $>100\,000$ cps during runs (i.e. >100 pg total Re), they decreased to well below 30 cps by this cleaning procedure.

3.5. Os measurement procedures

Samples larger than 10 ng yield ^{187}Os ion currents of $>5 \times 10^{-14}$ A and measurements can be carried out using Faraday collectors in the static mode. Apart from measuring all Os isotopes, the 12 Faraday collector array of the Nu Instruments ICP-MS allows simultaneous monitoring of isotopes of other elements that might interfere with Os isotope masses. Monitored isotopes are ^{182}W ($^{186}\text{W} \rightarrow ^{186}\text{Os}$), ^{185}Re ($^{187}\text{Re} \rightarrow ^{187}\text{Os}$), and ^{194}Pt ($^{190}\text{Pt} \rightarrow ^{190}\text{Os}$ and $^{192}\text{Pt} \rightarrow ^{192}\text{Os}$). ^{182}W and ^{194}Pt were not detected, but occasionally very small signals of ^{185}Re were detected during measurements of natural rock samples. Because of their occasional nature, these Re occurrences are considered to be sample rather than blank Re, indicating that the spiked Re composition of the

sample must be used for the interference correction of ^{187}Re on ^{187}Os . The accuracy of the Re interference correction can easily be tested by plotting the recorded ^{185}Re intensity against the corrected $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition for all data blocks. The value of mass fractionation determined using the stable $^{192}\text{Os}/^{188}\text{Os}$ ratio (= 3.082614 [16]) remained constant during the measurements. Therefore, although OsO_4 evaporation is likely to entail a Rayleigh distillation effect similar to that encountered in TIMS ([17]), this can be considered negligible compared to the large mass fractionation of the ICP-MS interface. The latter is adequately described by an exponential fractionation law. For an isotope abundance ratio R of isotopes with masses m_1 and m_2

$$R_{\text{measured}} = R_{\text{true}}(m_1/m_2)^F \quad (1)$$

where F is the exponential fractionation factor. The spike used is enriched in the ^{190}Os isotope. For the fractionation correction of sample spike mixtures the procedure of Krogh and Hurley [18] and Hofmann [19] was used on-line. This involves finding the true $^{192}\text{Os}/^{188}\text{Os}$ ratio of the mixture by intersection of a fractionation line with a mixing line in $^{190}\text{Os}/^{188}\text{Os}$ versus $^{192}\text{Os}/^{188}\text{Os}$ space. After this, F can be calculated:

$$F = \frac{\ln[(^{192}\text{Os}/^{188}\text{Os})_{\text{measured}}/(^{192}\text{Os}/^{188}\text{Os})_{\text{true}}]}{\ln(192/188)} \quad (2)$$

However, whereas fractionation in three isotope (e.g. $^{190}\text{Os}/^{188}\text{Os}$ versus $^{192}\text{Os}/^{188}\text{Os}$) space is described by a straight line for a linear fractionation law, this is not the case if an exponential law is used. The easiest way to solve this problem is by iteration. The fractionation factor found by the first (“linear”) approximation is used to define the slope S that a line between the (approximately) true ratios and the measured ones would have:

$$S = \frac{(^{190}\text{Os}/^{188}\text{Os})_{\text{measured}}[1 - (188/190)^F]}{(^{192}\text{Os}/^{188}\text{Os})_{\text{measured}}[1 - (188/192)^F]} \quad (3)$$

The intersection is then newly defined and a new fractionation factor, closer to the true one, is calculated.

For samples containing less than 1 ng Os, all masses are measured using ion counters. The three ion counting collector slits available in the Nu Instruments mass spectrometer (labeled IC_0 , IC_1 , and IC_2) are equidistant and in the mass range of Os the dispersion is best adjusted to two mass units between adjacent ones. This allows ion counting runs in sequences of two cycles: One of ^{192}Os , ^{190}Os , and ^{188}Os and the second of ^{189}Os , ^{187}Os , and ^{185}Re . Data from the first cycle are used to determine the fractionation factor and the $^{190}\text{Os}/^{188}\text{Os}$ ratio for the Os concentration as described above. Using the result, the fractionated $^{189}\text{Os}/^{188}\text{Os}$ ratio of the spike-sample mixture is then calculated. Multiplication with the measured $^{187}\text{Os}/^{189}\text{Os}$ ratio from the second cycle gives the “measured” $^{187}\text{Os}/^{188}\text{Os}$ ratio. Appropriate Re, fractionation, and spike corrections are then made on this ratio.

For this procedure the use of ad hoc gain corrections derived from bracketing standard runs is not appropriate, because of the combined spike-fractionation correction. A gain calibration of the ion counters relative to each other is required. This is done using the masses ^{188}Os , ^{190}Os , and ^{192}Os of an Os standard. The fact that the mass fractionation during the calibration run is not known is not a problem because the two gain factors are determined using the same (assumed) fractionation factor. This is illustrated by a simple three-isotope example with masses m_0 , m_1 , and m_2 collected in slits IC_0 , IC_1 , and IC_2 , respectively. C_1 and C_2 are the apparent gain factors for IC_1 and IC_2 relative to IC_0 . R_1 and R_2 are true N_{m_1}/N_{m_0} and N_{m_2}/N_{m_0} abundance ratios; M_1 and M_2 are the measured values. R_1 has a constant value, and R_2 is variable. B is a sample run aimed at determining R_{2B} . A is a run of a Os standard in which C_1 and C_2 are determined from the known isotope ratios R_1 and R_{2A} , using as assumed fractionation factor F_A [see Eqs. (1) and (2)]:

$$C_1 = \frac{M_{1A}}{R_1(m_1/m_0)^{F_A}} \quad (4)$$

and

$$C_2 = \frac{M_{2A}}{R_{2A}(m_2/m_0)^{F_A}}$$

The apparent fractionation factor in run *B* is determined from the known value of R_1 , using the apparent value for C_1 :

$$F_B = \frac{\ln(M_{1B}/R_1 C_1)}{\ln(m_1/m_0)} \quad (5)$$

Then the fractionation corrected value of R_{2B} is determined:

$$R_{2B} = \frac{M_{2B}}{C_2(m_2/m_0)^{F_B}} \quad (6)$$

Substituting C_2 from Eq. (4) and rearranging yields:

$$\frac{M_{2B}}{R_{2B}} = \frac{M_{2A}}{R_{2A}} (m_2/m_0)^{(F_B - F_A)} \quad (7)$$

Further, from Eqs. (4) and (5) follows:

$$F_B - F_A = \frac{\ln(M_{1B}/M_{1A})}{\ln(m_1/m_0)} \quad (8)$$

Eqs. (7) and (8) thus show that the end result is independent of the value of the assumed fractionation factor F_A . This argument holds equally for more complicated situations involving spike-sample mixtures. The use of apparent gain factors obtained with an assumed fractionation factor similar to its normal value (≈ 2) is advantageous in practice, as it allows in-run monitoring of ion counting measurements in the same way as for Faraday cup runs. The apparent gain factors are stable over at least several days. Our results further show that electron multiplier nonlinearity is not a problem for Os with the ETP electron multipliers used (ETP, Eermington, NSW, Australia).

For Os sample sizes between ~ 1 and 10 ng, a measuring procedure is used in which ^{188}Os , ^{189}Os , ^{190}Os , and ^{192}Os are detected on Faraday collectors, whereas ion counting collectors are used for ^{187}Os and for monitoring ^{185}Re . For such runs gain calibrations

of ion counters relative to Faraday collectors are made using measurements of Os standard solutions.

3.6. Re measurement procedure

The isotope dispersion for Re determinations is set so that ^{185}Re and ^{187}Re beams enter the ion counting collectors IC_0 and IC_1 , respectively, and ^{191}Ir and ^{193}Ir are measured in Faraday collectors. ^{192}Os is monitored in a Faraday cup to assess possible mass interference of ^{187}Os on ^{187}Re . No Os was detected, neither in measurements of Re standard solutions nor in those of spiked natural samples, demonstrating the effectiveness of the chemical separation of Re and Os.

Re analyses were carried out in the time-resolved mode provided by the software of Nu instruments. Thereby, the baselines for all collectors are defined by the signals detected on Re masses during a 1 min take up of pure Millipore H_2O . This is followed by sample take up and data collection during 5 min. The advantages of measuring Re in the time resolved mode are that even the smallest amounts of Re memory in the source are subtracted from the ion currents of the following sample, and that no sample solution is lost during baseline measurements at the beginning of each new data block. Although the overall efficiency of the nebulizer, spray chamber, and ICP-MS interface is $\sim 2 \times 10^{-4}$, the rapid sample take up nevertheless allows accurate analysis of subpicogram quantities of Re.

4. Results and discussion

4.1. Os measurement results

Results of Os standard solution runs are presented in Table 1. The mean $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ ratios of our Os standard solution, determined on 50 ng samples by Faraday cup measurements, are $0.106939 \pm 0.016\%$ (2σ standard deviation) and $0.119828 \pm 0.017\%$, respectively. These values are indistinguishable within analytical uncertainties from those determined on the same Os standard solution by

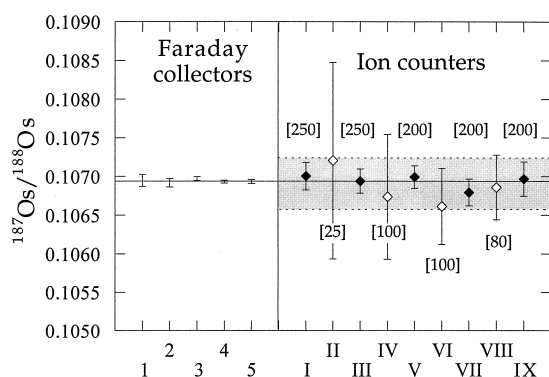


Fig. 2. Os standard Faraday (no symbol) as well as spiked (open diamonds) and unspiked (filled diamonds) ion counting runs. Numbers in brackets give total amount of Os in pg. Amounts down to 25 pg give accurate isotopic compositions, with the precision being correlated to the amount of Os measured.

N-TIMS at the Geologisk Institut in Copenhagen based on nine runs of 30 ng size ($^{187}\text{Os}/^{188}\text{Os} = 0.106948 \pm 0.017\%$, $^{186}\text{Os}/^{188}\text{Os} = 0.119830 \pm 0.004\%$; R. Frei, personal communication, June 1999). Furthermore, our ion counting measurements of this Os standard solution, with amounts ranging from 25–250 pg, produced within analytical uncertainty the same average $^{187}\text{Os}/^{188}\text{Os}$ value (i.e. $0.10690 \pm 0.32\%$). Thereby, (over-) spiked Os standard solutions agree well with the values determined on unspiked standard solutions (Table 1, Fig. 2). Whereas analytical uncertainties of the best available N-TIMS analyses at levels below 100 pg are still somewhat better ([20] report $^{187}\text{Os}/^{188}\text{Os}$ determinations by N-TIMS of 10 to ~ 35 pg total Os with analytical uncertainties of approximately 0.3% (2σ)). The present results nevertheless demonstrate the broad applicability of direct Os evaporation multicollector ICP mass spectrometry to geological problems requiring picogram level Os isotope analysis.

4.2. Re measurement results

Calibration results of 2 Re spike solutions with different concentrations are given in Table 2. The slightly lower isotopic composition of the less concentrated Re spike solution [105.8 pg/g; $^{185}\text{Re}/$

$^{187}\text{Re} = 28.631 \pm 0.127$, 2 SD (standard deviation) of population] relative to the more concentrated one (1414 pg/g; $^{185}\text{Re}/^{187}\text{Re} = 28.797 \pm 0.040$) can easily be explained by small blank contributions of the diluting reagents. The 105.8 ppt Re spike solution has been used for blank determinations of chemicals used during Re separation (Table 3). Results demonstrate that Re amounts as low as 0.2 pg can still be determined to a precision better than 1%. This renders the multicollector ICP-MS method described far superior to any known N-TIMS techniques for Re isotope dilution measurements.

5. Conclusion

The results demonstrate the high potential of magnet sector multicollector ICP-MS measurements for Os *IC-ID* and Re *ID* work down to very low concentration levels. The Os results equal N-TIMS measurements in analytical precision down to total amounts of approximately 100 pg, whereby the lower overall efficiency relative to N-TIMS is compensated for by the shorter duration of runs and the simultaneous detection of the isotope beams in a set of three ion counting collectors. For Re the absence of a filament blank and the in-run fractionation correction via Ir doping constitute a further major advantage over N-TIMS techniques.

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