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# Precise isotope analysis of natural and enriched osmium samples using different ICP-MS instruments[☆]

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## Abstract

The application of inductively coupled plasma sector field mass spectrometers (ICP-SFMS), inductively coupled plasma quadrupole mass spectrometers with hexapole collision cell (HEX-ICP-MS) and multiple collector ICP-MS (MC-ICP-MS) for the determination of isotopic composition of highly enriched $^{187}$Os and osmium samples is described. Good agreement of isotopic abundance was found in the three applied methods. A precision (2RSD) of 0.21–0.001, 0.83–0.09 and 5.5–0.083% for osmium isotope ratios, depending on isotope abundance in an interlaboratory metallic osmium sample, was observed in MC-ICP-MS, ICP-SFMS and HEX-ICP-MS measurements, respectively. A $(NH_4)_2OsCl_6$ (specpure Johnson Matthey Chemicals, JMC) sample was also analyzed by the MC-ICP-MS. The measured osmium isotope composition of the metallic osmium and JMC sample corresponds to natural osmium known in literature, with $^{187}$Os abundance of 2.3 at.%. $^{187}$Os abundance in three highly enriched samples of not identified, but assumed to be from special geological Precambrian formation of Russian origin varied between 98.934 and 99.53%. In addition, the $^{186}$Os/$^{192}$Os, $^{188}$Os/$^{192}$Os, $^{189}$Os/$^{192}$Os and $^{190}$Os/$^{192}$Os isotope ratios in all three enriched samples were close to the natural isotopic composition. This may indicate radioactive decay of $^{187}$Re to $^{187}$Os in rhenium-rich osmium samples in which the original osmium with a low initial concentration was of natural isotopic composition. (Int J Mass Spectrom 218 (2002) 245–253)

*Keywords:* Inductively coupled plasma mass spectrometry; Isotope ratio measurement; Osmium

## 1. Introduction

Sensitive and precise measurements of osmium isotopic composition are important in the Re/Os dating method [1] used for the age determination of minerals and meteorites [1–3] and for investigating the evolutionary chronology of the earth, the solar system and the galaxy [2]. As a result of the radioactive β-decay of the long-lived $^{187}$Re isotope ($T_{1/2} = 4.23 \times 10^{10}$ years) stable $^{187}$Os is formed. Nier [4] performed an isotopic analysis of osmium using $OsO_4$ in 1937. The first evidence of highly enriched $^{187}$Os (∼99.5%) in molybdenite minerals was found in 1954 by Hintenberger et al. [5]. Highly enriched $^{187}$Os can be prepared from Precambrian Re-rich ores with a low initial osmium concentration. In this case the main

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portion of $^{187}$Os is formed due to the radioactive decay of $^{187}$Re. On the other hand, highly enriched $^{187}$Os can be obtained by electromagnetic separation from osmium isotopic mixture [6].

The major difficulty in osmium isotopic analysis is the very low abundance of this element in nature and isobaric interference by $^{187}$Re at mass 187, $^{184}$W and $^{186}$W at masses 184 and 186 and $^{190}$Pt and $^{192}$Pt at masses 190 and 192. A high mass resolution ($m/\Delta m > 100{,}000$) is necessary to resolve these isobaric interferences [6]. The abundance of Os in the earth's crust is less than $10^{-10}$ g/g [6], but a concentration in the range $10^{-8}$ to $10^{-6}$ g/g can be found in certain mantle-derived rocks and extraterrestrial material [7–9]. Accelerator mass spectrometry (AMS) [3,10] and resonance ionization mass spectrometry (RIMS) [11,12] have been proposed due to their high selectivity and high sensitivity for isotopic measurements of subnanogram quantities of Os with a precision of 3–10% depending on isotope abundance. Secondary ion mass spectrometry (SIMS) [2,6,13] and glow discharge mass spectrometry (GDMS) [6] were applied for Os isotope ratio measurements after chemical separation of Re. The high ionization potential of Os (8.7 eV) precludes isotopic analysis by thermal ionization mass spectrometry (TIMS) using positively charged metallic ions. Negative TIMS (N-TIMS) [14,15] was developed for monitoring the $OsO_3^-$ ions. However, AMS, RIMS and N-TIMS are among the most difficult and time-consuming analytical methods.

If the isotopic control of samples representing chemically extracted Os of high-purity (without significant Re contamination) is required, the solid-state mass spectrometric methods (SIMS, GDMS, secondary neutral mass spectrometry (SNMS)) are preferable, because they provide a precision of 0.01–0.02% and good accuracy [6]. In addition, they do not require any chemical sample preparation, thus overcoming the most problems connected with analyte losses and contamination of one sample by another. Inductively coupled plasma mass spectrometry (ICP-MS) [6,16–18] has been recently applied for Os isotope ratio measurements due to its excellent suitability for accurate and precise isotopic analysis and relatively low cost. The application of MC-ICP-MS allows precision to be improved to 0.016% (RSD) for $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os isotope ratios [19–22]. The main problems of ICP-MS are connected with chemical separation, possible losses of volatile Os during sample preparation and memory effects. A few efforts have been made to avoid these problems by developing special sample decomposition devices and introduction of Os into ICP via the gas phase [4,18,21–23].

Recently, rare and expensive, highly enriched $^{187}$Os metal was offered on the international market. Its origin was not identified, but assumed to be from special geological Precambrian formation of Russian origin [6]. The aim of this work was to determine the osmium isotopic composition of these metallic samples and to trace their origin. In addition, two natural osmium samples were also analyzed to make interlaboratory comparison between various instruments. The natural samples were analyzed 3 weeks before the highly enriched $^{187}$Os samples. Also the enriched samples were not available at that time in GSI, therefore cross-contamination and memory effects may be excluded. The isotopic ratios of the minor isotopes in the highly enriched $^{187}$Os samples were close to those given for natural Os in [24], indicating the enrichment method used was β-decay of $^{187}$Re. The work has been performed in two laboratories, using advanced ICP-MS instrumentation. The isotopic analysis of the natural samples also served interlaboratory comparison purposes.

## 2. Experimental

### 2.1. ICP-MS instrumentation

Three types of mass spectrometers equipped with an ICP ion source were used in this work, (1) and (2) are located at Research Centre Juelich and (3) at Geological Survey of Israel.

(1) A double-focusing ICP-SFMS (ELEMENT, Finnigan MAT, Bremen, Germany). The ICP torch was shielded with a grounded platinum

electrode (GuardElectrode$^{TM}$, Finnigan MAT), which is switched on (ground potential) or off (floating potential) electronically. For solution introduction a MicroMist microconcentric nebulizer with a minicyclonic spray chamber (both from Glass Expansion, Australia) was used.

(2) A quadrupole-based HEX-ICP-MS (Platform ICP, Micromass Ltd., Manchester, UK) consisting of an ion source with a shielded torch and quadrupole mass analyzer and an ion transfer system based on a hexapole collision cell. Helium was introduced into the hexapole cell as a buffer gas. Gas input into the hexapole was controlled by built-in mass flow controllers. A Meinhard nebulizer (J.E. Meinhard Associates, Inc., USA) with a Scott double-pass quartz spray chamber cooled to 4 °C was applied for solution introduction.

(3) Comparative measurements of the osmium isotopic ratios were performed with a double-focusing sector field MC-ICP-MS (Nu Instruments, UK) of Nier–Johnson geometry. The unique feature of this mass spectrometer is the use of a fixed multiple-collector array, including 12 Faraday cups and 3 ion counting detectors. The ion beams are targeted to the chosen collectors by the use of a variable dispersion ion-optical lens arrangement. Further details were described elsewhere [25]. The sample solutions were introduced into the plasma via the Meinhard or ultrasonic nebulizer. Instrumental operating conditions were as given in Table 1.

### 2.2. Samples and reagents

Pure osmium samples of unknown origin with highly enriched $^{187}$Os were subjected to isotopic analysis. Specpure $(NH_4)_2OsCl_6$ (JMC) with assumed natural isotopic composition of the stable Os isotopes was used for testing the quality assurance of the isotopic measurement. Interlaboratory comparison of osmium isotope ratio measurements were made using natural metallic osmium presumably also of JMC origin. Suprapure nitric acid and hydrochloric acid

Table 1
Optimized operating conditions used HEX-ICP-MS and ICP-SFMS for different sample introduction systems

| ICP-MS type | HEX-ICP-MS | ICP-SFMS | MC-ICP-MS | |
|---|---|---|---|---|
| Nebulizer type | Meinhard | Micromist | Meinhard | Ultrasonic |
| Spray chamber | Cooled Scott type | Minicyclonic | Peltier cooled | |
| RF power (W) | 1300 | 1150 | 1300 | 1300 |
| Cooling gas flow rate (L min$^{-1}$) | 13.5 | 14 | 13 | 13 |
| Auxiliary gas flow rate (L min$^{-1}$) (optimized daily) | 1.4 | 1.4 | 0.86 | 0.92 |
| Nebulizer gas flow rate (L min$^{-1}$) (optimized daily) | 0.86 | 1.32 | 0.82 | 0.90 |
| Solution uptake rate (mL min$^{-1}$) | 0.9 | 0.24 | 0.4 | 1.5 |
| Collision gas (He) flow rate (mL min$^{-1}$) | 10 | | | |
| Ion extraction lens (V) | 600 | 2000 | Optimized for maximum intensity | |
| Hexapole exit lens (V) | 600 | | | |
| Hexapole bias potential (V) | 0 | | | |
| Ion energy lens (V) | 2.0 | | | |
| Multiplier voltage (V) | 470 | | | |
| Mass analyzer pressure | | $2 \times 10^{-8}$ mbar | $<2 \times 10^{-9}$ mbar | |
| Mass resolution ($m/\Delta m$) | 300 | 300 | Approximately 300 | |
| Dwell time (s) | 0.2 | | | |
| Analysis time (min) | 5 | 5 | | |
| Number of runs | 6 | 6 | 2 | 2 |
| Number of blocks in one run | 1 | 5 | 5 | 5 |
| Total analysis time (min) | 30 | 150 | 30 | 30 |

Table 2
Digestion parameters

| Method | Power (W) | Temperature (°C) | Pressure (psi) | Warming-up time (min) | Digestion time (min) | Power percentage after 15 min heating |
|---|---|---|---|---|---|---|
| 1 | 600 | 80 | 13 | 15 | 20 | 15 |
| 2 | 600 | 150 | 90 | 15 | 20 | 70 |

(all from Merck, Darmstadt, Germany) were used for sample digestion. Nitric acid was further purified by subboiling-point distillation. Ir solution was diluted from iridium standard solution (1000 $\mu$g L$^{-1}$, Merck). High-purity deionized water (18 MΩ, produced with a Milli-Q Plus water purification system) was applied for the dilution of the samples.

### 2.3. Sample preparation

The amount of 2.4–4.2 mg of metallic osmium was dissolved in closed vessels (XP-1500) in a microwave oven (Microwave Activated Reaction System Mars 5, CEM Corporation, USA) under temperature and pressure control in a mixture consisting of 1 mL HCl (30%) and 0.25 mL subboiled $HNO_3$ (64%) (supragrade purity). Digestion parameters are summarized in Table 2. Only one sample was completely digested at a temperature of 80 °C (method 1). Digestion of other samples required a temperature of 150 °C (method 2). Digested samples were transferred to clean polypropylene tubes (15 mL, Falcon) and made up to 10 mL with Milli-Q water. Specpure $(NH_4)_2OsCl_6$ was dissolved in 0.1N $HNO_3$.

### 2.4. ICP-MS measurement procedure

The experimental parameters of all ICP-MS were first optimized at the best precision of isotope ratio measurements and at a maximum ion intensity of $^{192}$Os$^+$ in natural osmium solution with respect to torch position and choosing the optimal rf-power and cooling, auxiliary and nebulizer gas flow rates.

The isotopic composition of Os samples was measured in 1:100 diluted samples using HEX-ICP-MS. The data were acquired in six runs, monitoring all isotopes for 5 min in each run, i.e., a total of 30 min. The measured isotopic ratios in Os samples were corrected with account to background, the mass discrimination factors determined experimentally by measuring Ir isotope and osmium hydride ratio OsH$^+$/Os$^+$.

Isotope ratio measurements were subsequently performed in 1:10,000 diluted samples by ICP-SFMS. The data were acquired in five blocks of six runs, monitoring all isotopes for 5 min in each run. The measured isotopic ratios were corrected as those measured with HEX-ICP-MS and with taking account to dead time. Possible Pt and W impurities in osmium samples, which could interfere with $^{184}$Os, $^{186}$Os and $^{192}$Os, were monitored by measuring isotopes $^{183}$W and $^{194}$Pt.

In MC-ICP-MS an isotopic ratio result represents the acquisition of a run comprising 5 blocks of 10 ratio measurements, i.e., 50 ratios are accumulated. The ratio values for the JMC sample of osmium presented are the means of seven runs at different Os concentrations: 600, 200, 200, 50, 50, 10 and 10 $\mu$g L$^{-1}$. Because of material scarcity (at GSI) only one run (50 ratios) of the natural Os metal sample could be accumulated. The total time for one run is approximately 15 min, which includes zero and ion intensity measurements and the duration of peak centering between each block. Therefore, the element consumption in the case of a 10 $\mu$g L$^{-1}$ per sample is ~0.45 $\mu$g osmium for MC-ICP-MS analysis (0.18 $\mu$g in ICP-SFMS and 1.35 $\mu$g in HEX-ICP-MS).

Ten out of twelve Faraday collectors were used in this work, in the simultaneous data collection mode of operation. The osmium isotopes and the possible Pt, Re and W isobaric interferences were adjusted to the various Faraday collectors as shown in Table 3. The double mass unit dispersion between High6 (H6), H5 and H4 collectors (compare to other detectors) is intrinsic to the detection system. This adjustment was

Table 3
Adjustment of the Faraday collectors for natural osmium isotopic measurements

| H6 | H5 | H4 | H3 | H2 | H1 | Axial | L1 | L2 | L3 |
|---|---|---|---|---|---|---|---|---|---|
| | $^{192}$Os | $^{190}$Os | $^{189}$Os | $^{188}$Os | $^{187}$Os | $^{186}$Os | | $^{184}$Os | |
| $^{194}$Pt | $^{192}$Pt | $^{190}$Pt | | | $^{187}$Re | $^{186}$W | $^{185}$Re | $^{184}$W | $^{182}$W |

Table 4
Adjustment of the Faraday collectors for enriched $^{197}$Os isotopic measurements

| H5 | H4 | H3 | H2 | H1 | Axial | L1 | L2 | IC-0 | L3 | IC-1 | L4 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^{192}$Os | | $^{190}$Os | $^{189}$Os | $^{188}$Os | $^{187}$Os | $^{186}$Os | | $^{184}$Os | |
| $^{195}$Pt | $^{193}$Ir | $^{192}$Pt | $^{191}$Ir | $^{190}$Pt | | | $^{187}$Re | $^{186}$W | $^{187}$Re | $^{184}$W | $^{183}$W |

used for natural osmium measurements. Table 4 shows the collector adjustment when iridium was added to the high-enriched $^{187}$Os samples. Twelve collectors (10 Faraday and 2 ion counters) were used for these measurements. Zero measurements were made in both cases at half masses by deflecting the potential of the electrostatic analyzer before each block measurement. The following isotope ratios were used for discrimination and interference corrections [26].

(a) for natural osmium measurements: $^{192}\mathrm{Os}/^{188}\mathrm{Os} = 3.08271$; $^{190}\mathrm{Pt}/^{194}\mathrm{Pt} = 0.000386$; $^{186}\mathrm{W}/^{182}\mathrm{W} = 1.0725$; $^{184}\mathrm{W}/^{182}\mathrm{W} = 1.15636$ and $^{187}\mathrm{Re}/^{185}\mathrm{Re} = 1.674$;

(b) for $^{187}$Os enriched solutions: $^{192}\mathrm{Pt}/^{195}\mathrm{Pt} = 0.02308$; $^{190}\mathrm{Pt}/^{195}\mathrm{Pt} = 0.000376$; $^{184}\mathrm{W}/^{183}\mathrm{W} = 2.14078$; $^{186}\mathrm{W}/^{183}\mathrm{W} = 1.98594$ and $^{191}\mathrm{Ir}/^{193}\mathrm{Ir} = 0.59399$.

It should be noted that according to IUPAC, the iridium ratio has an uncertainty of 0.7%. This may slightly affect on the $^{192}$Os abundance in the enriched samples.

Between each run the nebulizer was washed with a 1% (in MC-ICP-MS) or 0.1% (in HEX-ICP-QMS and ICP-SFMS) solution of hydroxylamine hydrochloride, to facilitate the osmium washout [27].

## 3. Results and discussion

In the following discussion we will refer to osmium samples of unknown origin with enriched $^{187}$Os as osmium-187 samples, and samples with isotopic composition close to that for natural Os given in [24] as natural osmium samples. Table 5 presents the isotope ratios in the natural metallic osmium sample measured

Table 5
Isotope ratios of natural metallic osmium and $(NH_4)_2OsCl_6$ samples

| Isotope ratio | Metallic osmium | | | | $(NH_4)_2OsCl_6$ (JMS) | | Metallic osmium | |
|---|---|---|---|---|---|---|---|---|
| | ICP-SFMS | | HEX-ICP-MS | | MC-ICP-MS | | MC-ICP-MS | |
| | Ratio | 2RSD (%) | Ratio | 2RSD (%) | Ratio | 2RSD (%) | Ratio | 2RSD (%) |
| $^{184}$Os/$^{192}$Os | 0.000525 | 0.83 | 0.000385 | 5.5 | 0.000422 | 3.8 | 0.00042 | 0.21 |
| $^{186}$Os/$^{192}$Os | 0.0390 | 0.16 | 0.0390 | 0.13 | 0.03893 | 0.09 | 0.03894 | 0.0032 |
| $^{187}$Os/$^{192}$Os | 0.0567 | 0.093 | 0.0566 | 0.20 | 0.05642 | 0.09 | 0.05642 | 0.0033 |
| $^{188}$Os/$^{192}$Os | 0.3247 | 0.090 | 0.3255 | 0.083 | 0.324390[a] | | 0.324390[a] | |
| $^{189}$Os/$^{192}$Os | 0.3964 | 0.13 | 0.3967 | 0.098 | 0.39565 | 0.004 | 0.39566 | 0.001 |
| $^{190}$Os/$^{192}$Os | 0.6436 | 0.092 | 0.6449 | 0.096 | 0.64352 | 0.002 | 0.64353 | 0.001 |

[a] Normalization factor.

Table 6
Isotope abundance (at.%) calculated from isotopic ratios

| Isotope | Literature data | | Measurement results (metallic osmium) | | $(NH_4)_2OsCl_6$ (JMS) (MC-ICP-MS) |
|---|---|---|---|---|---|
| | N-TIMS [24] | ICP-SFMS | HEX-ICP-MS | MC-ICP-MS | |
| $^{184}Os$ | 0.0197 | 0.021 | 0.016 | 0.01728 | 0.01742 |
| $^{186}Os$ | 1.5859 | 1.58 | 1.58 | 1.584 | 1.584 |
| $^{187}Os$[a] | 1.9644 | 2.30 | 2.30 | 2.294 | 2.294 |
| $^{188}Os$ | 13.2434 | 13.19 | 13.21 | 13.192 | 13.194 |
| $^{189}Os$ | 16.1466 | 16.11 | 16.11 | 16.090 | 16.092 |
| $^{190}Os$ | 26.2584 | 26.15 | 26.18 | 26.171 | 26.161 |
| $^{192}Os$ | 40.7815 | 40.64 | 40.60 | 40.667 | 40.673 |

[a] The differences in the isotope abundance of this isotope are addressed in Section 3.

Table 7
Isotopic composition of $^{187}Os$ sample 1

| Isotopic ratio | MC-ICP-MS | | ICP-SFMS | | HEX-ICP-MS | |
|---|---|---|---|---|---|---|
| | Ratio | 2RSD (%) | Ratio | 2RSD (%) | Ratio | 2RSD (%) |
| $^{184}Os/^{187}Os$ | 0.0000014 | – | <0.00001 | | <0.00001 | |
| $^{186}Os/^{187}Os$ | 0.00016 | 0.8 | 0.00016 | 3.1 | 0.00016 | 6.9 |
| $^{188}Os/^{187}Os$ | 0.00148 | 0.04 | 0.00146 | 0.07 | 0.00149 | 0.52 |
| $^{189}Os/^{187}Os$ | 0.00177 | 0.04 | 0.00177 | 0.08 | 0.00177 | 0.55 |
| $^{190}Os/^{187}Os$ | 0.00288 | 0.03 | 0.00289 | 0.07 | 0.00284 | 0.49 |
| $^{192}Os/^{187}Os$ | 0.00449 | 0.03 | 0.00451 | 0.08 | 0.00440 | 0.22 |

Table 8
Isotopic composition of $^{187}Os$ sample 2

| Isotopic ratio | MC-ICP-MS | | ICP-SFMS | | HEX-ICP-MS | |
|---|---|---|---|---|---|---|
| | Ratio | 2RSD (%) | Ratio | 2RSD (%) | Ratio | 2RSD (%) |
| $^{184}Os/^{187}Os$ | <1.0E−7 | – | <0.00001 | | <0.00001 | |
| $^{186}Os/^{187}Os$ | 0.000070 | 0.7 | 0.000072 | 2.5 | 0.000074 | 3.1 |
| $^{188}Os/^{187}Os$ | 0.00065 | 0.04 | 0.00065 | 0.21 | 0.00071 | 0.35 |
| $^{189}Os/^{187}Os$ | 0.000766 | 0.03 | 0.00077 | 0.06 | 0.00075 | 0.48 |
| $^{190}Os/^{187}Os$ | 0.00124 | 0.02 | 0.00124 | 0.08 | 0.00122 | 0.43 |
| $^{192}Os/^{187}Os$ | 0.00193 | 0.02 | 0.00195 | 0.07 | 0.00190 | 0.29 |

Table 9
Isotopic composition of $^{187}Os$ sample 3

| Isotopic ratio | MC-ICP-MS | | ICP-SFMS | | HEX-ICP-MS | |
|---|---|---|---|---|---|---|
| | Ratio | 2RSD (%) | Ratio | 2RSD (%) | Ratio | 2RSD (%) |
| $^{184}Os/^{187}Os$ | 0.00000062 | – | <0.00001 | | <0.00001 | |
| $^{186}Os/^{187}Os$ | 0.000071 | 0.7 | 0.000065 | 4.6 | 0.000070 | 3.7 |
| $^{188}Os/^{187}Os$ | 0.00066 | 0.06 | 0.00065 | 0.11 | 0.00066 | 0.27 |
| $^{189}Os/^{187}Os$ | 0.00077 | 0.04 | 0.00076 | 0.08 | 0.00075 | 0.39 |
| $^{190}Os/^{187}Os$ | 0.00125 | 0.03 | 0.00124 | 0.12 | 0.00121 | 0.27 |
| $^{192}Os/^{187}Os$ | 0.00195 | 0.02 | 0.00194 | 0.07 | 0.00188 | 0.19 |

Table 10
Isotope abundance (%) calculated from isotopic ratios in enriched $^{187}$Os samples 1–3

| Isotope | Sample 1 | | | Sample 2 | | | Sample 3 | | |
|---|---|---|---|---|---|---|---|---|---|
| | MC-ICP-MS | ICP-SFMS | HEX-ICP-MS | MC-ICP-MS | ICP-SFMS | HEX-ICP-MS | MC-ICP-MS | ICP-SFMS | HEX-ICP-MS |
| $^{184}$Os | 0.00014 | <0.001 | <0.001 | <0.00001 | <0.001 | <0.001 | 0.000062 | <0.001 | <0.001 |
| $^{186}$Os | 0.0158 | 0.0160 | 0.0162 | 0.00692 | 0.00714 | 0.00734 | 0.00709 | 0.00645 | 0.00701 |
| $^{187}$Os | 98.934 | 98.932 | 98.945 | 99.537 | 99.534 | 99.536 | 99.533 | 99.537 | 99.545 |
| $^{188}$Os | 0.146 | 0.144 | 0.148 | 0.0650 | 0.065 | 0.071 | 0.0656 | 0.0643 | 0.065 |
| $^{189}$Os | 0.175 | 0.175 | 0.175 | 0.0762 | 0.076 | 0.075 | 0.0768 | 0.0761 | 0.074 |
| $^{190}$Os | 0.285 | 0.286 | 0.281 | 0.123 | 0.123 | 0.121 | 0.124 | 0.123 | 0.120 |
| $^{192}$Os | 0.444 | 0.447 | 0.436 | 0.192 | 0.194 | 0.189 | 0.194 | 0.193 | 0.187 |

with different ICP-MS techniques and $(NH_4)_2OsCl_6$ sample measured with MC-ICP-MS. The identity of the isotope ratios of both samples indicate that the metallic osmium is also a JMC product. Table 6 shows the isotopic composition of these osmium samples in comparison to the "Best Measurement from a Single Terrestrial Source" from literature [24]. It should be noted that the value involving the $^{187}$Os isotope in this work is higher than the value quoted in [24], 1.964 vs. 2.294 at.%. Natural samples of higher $^{187}$Os abundance are well known [18], they are typical for geological old or Re-rich ores. The $^{187}$Os abundance in metallic osmium of 2.3 at.% measured both with the ICP-SFMS and HEX-ICP-MS coincide well with $^{187}$Os abundance observed the JMC sample (Table 6). This fact may point to the same origin of the natural metallic osmium and JMC osmium.

A precision (2RSD) of 0.21–0.001, 0.83–0.09 and 5.5–0.083% for osmium isotope ratios depending on isotope abundance in metallic osmium sample was observed in MC-ICP-MS, ICP-SFMS and HEX-ICP-QMS, respectively. The measured $^{186}$Os/$^{192}$Os, $^{188}$Os/$^{192}$Os, $^{189}$Os/$^{192}$Os and $^{190}$Os/$^{192}$Os isotope ratios in both natural osmium samples correspond well to literature data. The uncertainty of $^{184}$Os/$^{192}$Os determination was relatively high due to the low abundance of $^{184}$Os (2RSD of 0.83% in ICP-SFMS and 2RSD of 5.5% in HEX-ICP-MS). Furthermore, the results of HEX-ICP-MS and ICP-SFMS did not coincide within experimental error. The systematically lower result of HEX-ICP-MS may be due to losses of a weak peak of a low-abundant isotope when applying the threshold for minimizing detector noise. This effect was also observed in [28] when measuring uranium isotopic ratios. Hence, a special correction algorithm of isotopic ratios for low-abundant isotopes is required in HEX-ICP-MS.

Tables 7–10 present the isotopic ratios and calculated isotopic composition in three enriched $^{187}$Os samples measured by different ICP-MS techniques. Experimental results of MC-ICP-MS and ICP-SFMS coincided within experimental errors. Two RSD of 0.02–0.04 and 0.07–0.12% for osmium isotope ratios with abundances above $10^{-3}$ were observed in MC-ICP-MS and ICP-SFMS, respectively. The $^{186}$Os/$^{187}$Os isotope ratio varying from $7 \times 10^{-5}$ to $1.6 \times 10^{-4}$ in the three samples analyzed was measured with a precision of 0.8 and 2.5–4.6% in MC-ICP-MS and ICP-SFMS, respectively. HEX-ICP-MS yielded a precision of 0.19 (2RSD) to 6.9% depending on isotope abundance.

$^{187}$Os abundance reached 98.934% in sample 1 and 99.53% in samples 2 and 3. The isotopic composition of the last two samples coincided within experimental errors, hence it was possible to conclude the identity of these samples. Isotopic abundance of $^{186}$Os, $^{188}$Os, $^{189}$Os, $^{190}$Os and $^{192}$Os was approximately 2.3 times higher than the abundance of the same isotopes in samples 2 and 3 pointing to a different origin of sample 1. In addition, the $^{186}$Os/$^{192}$Os, $^{188}$Os/$^{192}$Os, $^{189}$Os/$^{192}$Os and $^{190}$Os/$^{192}$Os isotope ratios in all three enriched samples were close to those reported in [24]. This confirms the natural origin of all analyzed samples, because in the case of electromagnetic enrichment $^{192}$Os should be separated from the sample to a greater extent thus increasing isotopic ratios $^{186}$Os/$^{192}$Os, $^{188}$Os/$^{192}$Os and $^{189}$Os/$^{192}$Os.

## 4. Conclusions

Os isotope abundances were determined in several $^{187}$Os enriched samples, using different ICP-MS techniques. In general, for all methods, a good agreement of isotopic abundance was found. There is an excellent agreement for isotope ratios between the natural metallic and $(NH_4)_2OsCl_6$ measured by MC-ICP-MS. Comparing the measured ratios in the natural metallic sample with the three different instruments, it may be concluded that the agreement for the abundant isotope ratios is good. There are differences for the low isotope ratio values. This is not surprising regarding the superiority of MC-ICP-MS over other instruments in isotope ratio measurements. Nevertheless the overall conclusion is that the ICP-SFMS and HEX-ICP-MS data and the MC-ICP-MS data support each other in the characterization of the $^{187}$Os enriched samples.

MC-ICP-MS allowed the Os isotopic abundance to be determined with a high accuracy and precision. ICP-SFMS yielded slightly lower precision. The osmium isotopic results presented here demonstrate that the ICP-MS is a powerful tool for the high-precision determination of isotopic composition in low amounts of Os.

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