



## Analytical Note

# Determination of Os by isotope dilution-inductively coupled plasma-mass spectrometry with the combination of laser ablation to introduce chemically separated geological samples



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## ABSTRACT

A method was developed for the determination of trace Os in geological samples by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) with the combination of chemical separation and preconcentration. Samples are digested using aqua regia in Carius tubes, and the Os analyte is converted into volatile OsO<sub>4</sub>, which is distilled and absorbed with HBr. The HBr solution is concentrated for further Os purification using the microdistillation technique. The purified Os is dissolved in 10 μl of 0.02% sucrose–0.005% H<sub>3</sub>PO<sub>4</sub> solution and then evaporated on pieces of perfluoroalkoxy (PFA) film, resulting in the formation of a tiny object (<3 × 10<sup>4</sup> μm<sup>2</sup> superficial area). Using LA-ICP-MS measurements, the object can give Os signals at least 100 times higher than those provided by routine solution-ICP-MS while successfully avoiding the memory effect. The procedural blank and detection limit in the developed technique are 3.0 pg and 1.8 pg for Os, respectively when 1 g of samples is taken. Reference materials (RM) are analyzed, and their Os concentrations obtained by isotope dilution are comparable to reference or literature values. Based on the individual RM results, the precision is estimated within the range of 0.6 to 9.4% relative standard deviation (RSD), revealing that this method is applicable to the determination of trace Os in geological samples.

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## 1. Introduction

Osmium is one of the platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt), which are highly compatible and siderophilic; therefore, they are important for understanding the petrogenesis of mantle-derived rocks [1–3]. In nature, Os consists of seven isotopes, i.e., <sup>184</sup>Os, <sup>186</sup>Os, <sup>187</sup>Os, <sup>188</sup>Os, <sup>189</sup>Os, <sup>190</sup>Os and <sup>192</sup>Os. Among these isotopes, <sup>186</sup>Os and <sup>187</sup>Os are radiogenic and are related to the decay of <sup>192</sup>Pt and <sup>187</sup>Re, respectively. Therefore, they can be used as isotopic tracers for investigating the evolution of earth and the interaction of crust and mantle [4–7]. Therefore, Os is significantly important for geochemical studies based on PGEs coupled with Pt–Os and Re–Os isotopic systems [3,8,9]. However, the accurate determination of Os is difficult due to its extremely low abundance in nature and its loss as volatile OsO<sub>4</sub> formed during the chemical pretreatment. Thus, analytical instrumentation and chemical pretreatments play important roles in obtaining high quality Os data. Currently, the commonly used techniques are negative thermal ionization-mass spectrometry (N-TIMS) and inductively coupled plasma-mass spectrometry (ICP-MS). Because the precise and accurate determination of Os isotopic compositions can be obtained

by N-TIMS [10], the application to geological investigation has become increasingly more common [8,11]. For N-TIMS measurements, however, the mass spectrum of Os molecular species is complex because it is detected as a negative trioxide ion, OsO<sub>3</sub><sup>−</sup>, arising from the reactions of Os and O isotopes. In contrast, Os is detected as a single charged ion, Os<sup>+</sup> with ICP-MS measurements, which offers a simple mass spectrum. In addition, ICP-MS has other advantages, such as high throughput and flexible sample introduction; therefore, it has been one of the most attractive techniques for the precise and accurate determination of Os [12–14]. Using the conventional solution introduction system of ICP-MS, however, there is only a small uptake that is ionized by ICP, whereas most of the uptake becomes waste liquid and is drained away. This disadvantage is difficult to accept for the analysis of trace elements, which must be separated and preconcentrated. However, the loss of Os can be effectively overcome by introducing volatile OsO<sub>4</sub> to ICP with either pure water in which Os exists as the OsO<sub>4</sub> form [14] or OsO<sub>4</sub> vapor generation devices [15,16]. Although the Os measurements by ICP-MS have a high sensitivity, a strong memory effect is encountered, and it is considered to be associated with the nebulizer and spray-chamber of the conventional solution introduction system where Os as the OsO<sub>4</sub> form can easily adhere to its surface [17,18]. Without involving the nebulizer and spray-chamber, the membrane desolvation device is coupled with ICP-MS, and Os is detected with high sensitivity; however, the memory

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effect remains strong [12]. The strong memory effect of Os has been the focus of many studies, and the Os measurement by ICP-MS has been attempted to avoid the nebulizer and spray-chamber of the solution introducing system. To address the volatility of  $\text{OsO}_4$ , its vapor phase is directly introduced into ICP by online sparging of the digested samples in which Os is changed into  $\text{OsO}_4$  [13,19] or by distilling Os via an oxidizing reagent in a mini-apparatus [20]. In practice, the former can be more readily handled than the latter, thus presenting more applications [21–23]. With sparging or distilling, however,  $\text{OsO}_4$  is slowly released from the target samples, and this can be clearly demonstrated even with an electrothermal ware for heating [24]. Currently, much attention is still required for both detection sensitivity and memory effect for the analysis of Os by ICP-MS.

As the most commonly used instrumentation, ICP-MS has great flexibility to be connected with different sample introduction systems. In addition to the conventional solution system, the laser ablation (LA) system has been widely employed for in-situ analysis. Using LA-ICP-MS, Os-rich minerals, such as iridosmines, Ru–Os sulfides and Ru–Os–Ir alloys, have been analyzed, and the memory effect of Os can be effectively overcome [25–29]. As an in-situ analysis technique, however, only a micro-quantity of samples is ablated; thus, analytes at high concentration levels are required to provide sufficient detection signals. Therefore, LA-ICP-MS has not been applicable to the majority of unknown samples for the direct analysis of Os due to its low abundance and heterogeneous distribution. To exploit the low memory effect of Os during LA-ICP-MS measurements, an attempt was made to combine the LA technique with chemical separation and preconcentration for the trace level analysis of Os by ICP-MS. The focus of this study is the introduction of the preconcentrated Os into ICP with maximum utilization, and the key strategies are 1) to find a supporting material on which the preconcentrated Os in a liquid state can be further evaporated into a tiny non-liquid object, and 2) to identify a host medium, which can make the remaining object adhere to the supporting material during laser ablation. To accomplish these goals, our efforts were primarily focused on searching for supporting materials and host media but not experimenting with the sample digestion conditions. Using the common Carius tube technique described by Shirey and Walker [30], 1–2 g reference samples were digested with  $\text{HNO}_3$  and HCl at 230 °C, and the applicability of our proposal was examined.

## 2. Materials and methods

### 2.1. Instruments

The instrumentation employed in this study is an ICP-MS (7500a, Agilent Technologies, USA) coupled with an ArF excimer LA system (193 nm Resolution M-50, Resonetics LLC, USA) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. As described in detail by Müller et al. [29], this LA system can wash out 99% of the signal in less than 1.5 s because of its innovative sample cell design. Helium gas carrying the ablated sample aerosol is mixed with an argon carrier gas and, finally, flows into the ICP. Prior to analysis, the LA-ICP-MS system was optimized using NIST610 ablated with a 33  $\mu\text{m}$  spot size, 10 Hz repetition rate and 6  $\mu\text{m s}^{-1}$  scan speed to achieve the maximum signal intensity for  $^7\text{Li}$ ,  $^{89}\text{Y}$  and  $^{238}\text{U}$ , as well as a low oxide formation level for  $\text{ThO}^+/\text{Th}^+$ . The detailed instrumentation and operating conditions are given in Table 1. In practical analysis, the sample targets with inclusion of common Os standards were ablated with a 43  $\mu\text{m}$  spot size and 8 Hz repetition rate, whereas the fluence was maintained at 4  $\text{J cm}^{-2}$  because changing it is inconvenient. The common Os standards were measured for every three samples to obtain the mass fractionation factors of Os isotopic ratios. In addition,  $^{187}\text{Os}$  was monitored because it has radiogenic characteristics, i.e., related to the  $\beta^-$  decay of  $^{187}\text{Re}$ . Thus, it is easy to evaluate the abundance levels of the radiogenic  $^{187}\text{Os}$  in unknown samples by comparing the measured ratio of  $^{187}\text{Os}/^{188}\text{Os}$  with

**Table 1**  
LA-ICP-MS instrumentation and operating conditions.

Resolution M-50 laser ablation system (ArF Excimer, Resonetics LLC, USA)	
Ablation cell & volume	Two-volume laser-ablation cell (Laurin Technic, Australia), effective volume $\sim 1\text{--}2\text{ cm}^3$
Laser wavelength	193 nm
Pulse width	$\sim 20\text{ ns}$
Fluence	4 $\text{J cm}^{-2}$
Repetition rate	8 Hz
Spot size	43 $\mu\text{m}$
Sampling mode/pattern	Line analysis
Scan speed	6 $\mu\text{m/s}$
Carrier gas	0.7 $\text{l min}^{-1}$ He
Ablation duration	60 s
Agilent 7500a ICP-MS	
Sample introduction	Ablation aerosol
Forward power	1250 w
Ar cooling gas flow rate	15 $\text{l min}^{-1}$
Ar auxiliary gas flow rate	1.0 $\text{l min}^{-1}$
Ni sampling cone orifice	1.0 mm
Ni skimmer cone orifice	0.7 mm
Acquisition mode	Peak jumping
Channel dwell time	20 ms
Channel per mass	1
Measured isotopes	$^{187}\text{Os}$ , $^{188}\text{Os}$ , $^{190}\text{Os}$ and $^{192}\text{Os}$
Other information	
Gas blank	30 s on-peak zero subtracted
Sample line	2.5 m from ablation cell to torch
Washing time	30 s after the laser ended firing

the value of 0.1474 derived from the relative abundances of  $^{187}\text{Os}$  (1.96%) to  $^{188}\text{Os}$  (13.3%) [31]. If the measured  $^{187}\text{Os}/^{188}\text{Os}$  ratio was much higher than the value, then the radiogenic  $^{187}\text{Os}$  should be considered. In the course of this study, a low resolution ICP-QMS was employed, and the  $^{187}\text{Os}/^{188}\text{Os}$  ratios measured only as reference values are  $0.146 \pm 0.011$  for WPR-1,  $0.171 \pm 0.010$  for UTM-1,  $0.176 \pm 0.012$  for GPT-7,  $0.192 \pm 0.018$  for GPT-4,  $0.201 \pm 0.028$  for WGB-1 and  $0.919 \pm 0.146$  for TDB-1. Among these  $^{187}\text{Os}/^{188}\text{Os}$  ratios, the highest  $^{187}\text{Os}/^{188}\text{Os}$  ratio was found for the TDB-1 reference material, and it is within the range of 0.7542 to 1.0477, as measured by precise N-TIMS [32]. Its radiogenic  $^{187}\text{Os}$  content was evaluated, but it only accounts for less than 10% of the total Os (see Table 2). Thus, the content level of the radiogenic  $^{187}\text{Os}$  is closely dependent on the abundances of Re and the geological age of the unknown samples. Generally, the amount of radiogenic  $^{187}\text{Os}$  is negligible due to its parent  $^{187}\text{Re}$  with low abundances and a long half-life.

### 2.2. Samples and reference materials

The PGE reference materials employed in this study are CANMET-CCRMP WGB-1 (gabbro rock), WPR-1 (altered peridotite), TDB-1 (diabase rock) and UMT-1 (ultramafic ore tailings). The Chinese national reference materials, GPT-4 (GBW07291, pyroxene peridotite) and GPT-7 (GBW07294, soil), are also used.

### 2.3. Reagents and standards

Water with a resistivity of 18.2  $\text{M}\Omega\text{ cm}$  was prepared using a Milli-Q system (Millipore, USA) and was used throughout the experimental preparation. Concentrated  $\text{HNO}_3$  and HCl (electronic grade, the Beijing Institute of Reagents), HBr (99.9999%, Alfa Aesar),  $\text{H}_3\text{PO}_4$  (guarantee reagent, Sinopharm Chemical Reagent Co. Ltd.), sucrose (biochemical grade, Fluka), and perfluoroalkoxy (PFA) film (0.06 mm thick, Shanghai Plastics Research Institute) were also used. Prior to use, the concentrated  $\text{HNO}_3$  and HCl were further purified by sub-boiling distillation in whole PFA systems (Savillex).

An enriched  $^{190}\text{Os}$  spike was purchased as metal powder from the Oak Ridge National Laboratory (USA), and its isotopic abundances

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