



Sensitive determination of osmium in natural waters by inductively coupled plasma mass spectrometry after photochemical vapor generation



Ying Gao^{a,b,*}, Shuzhen Li^c, Hongyan He^a, Tonglin Li^a, Ting Yu^c, Rui Liu^{b,c}, Shijun Ni^a, Zeming Shi^{a,*}

^a College of Earth Sciences, Chengdu University of Technology, Chengdu, Sichuan 610059, China

^b State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Chengdu University of Technology, Chengdu 610059, China

^c Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China

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ABSTRACT

Accurate analysis of osmium is important in geochemistry and geochronology. The current osmium analytical methods often suffer from low sensitivity, multi-step extraction, high procedural blank, and severe memory effect. In this work, a highly sensitive and simple method for the determination of osmium in natural waters was developed by coupling inductively coupled plasma-mass spectrometry with photochemical vapor generation. The procedural blank is low due to the needlessness of high concentration strong oxidant. What's more, the memory effect was successfully solved by using 5.0% ammonium hydroxide elution instead of using concentrated inorganic acid or oxidant reagent reported before. The influences of the concentration of nitric acid, the flow rate of carrier gas, the photo irradiation time on osmium detection were investigated. Under optimized conditions, the detection limit was 0.8 pg mL⁻¹. A precision of 3.2% (RSD, n = 5) was achieved at a concentration of 1 ng mL⁻¹. The accuracy is successfully validated in several natural water samples with spike recoveries from 97% to 106%. The proposed method is sensitive, simple, low blank, and memory effect-free, which has a great potential in relevant geochemistry and geochronology study.

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1. Introduction

The Re-Os isotopic system (¹⁸⁷Re decays to ¹⁸⁷Os via β decay with a 42 Ma half-life) is used increasingly for the study of processes occurring at the Earth's surface, as an isotopic tracer with chalcophile and siderophile properties and thus forms a unique complement to other lithophile radiogenic isotopic systems such as U-Pb, Sm-Nd, and Rb-Sr. [1] The system was successfully adopted in various applications, including constraining the ages of subcontinental lithospheric mantle and magmatic iron meteorite groups [2], examining the recycling of oceanic crust into the mantle [3], dating of hydrocarbon deposits [4], and tracing the influx of water sediment sources [5]. Generally, the major challenge in the analysis of Re-Os system, is attributed to the Os [6], mainly because of (I) the very low abundances of Os in most geological materials (typically 10 to 100 pg kg⁻¹ in environmental water [1], 10 to 100 pg g⁻¹ in crustal rocks, and 1 to 5 ng g⁻¹ in mantle peridotites [7]), requiring highly sensitive techniques and extremely low procedural blanks; (II) the volatility of OsO₄ at rather low temperature (boiling point of

130 °C at 10⁵ Pa), posing hindrances for the usage of classical pre-concentration and separation techniques.

The development of elemental mass spectrometry, especially inductively coupled plasma-mass spectrometry (ICP-MS) opens a great possibility for Os measurements. The advantages of ICP-MS as an elemental detector include low detection limits (pg mL⁻¹ level for most elements), low matrix effects, wide dynamic ranges, and high spectral resolution for elements and isotopes [8,9]. The procedure for ICP-MS-based Os analysis often involves Carius tube digestion, solvent extraction, multi-distillation, and solution nebulization [6,10]. The analytical sensitivity was greatly enhanced by the generation of volatile OsO₄, using high concentration of strong oxidizing agents, such as HNO₃ [11], H₂O₂ [12], H₅IO₆ [13], and K₂Cr₂O₇ [14]. However, these oxidizing procedures are often time- and labor-consuming and bring considerably high procedural blank [12,15]. Recently, photo-induced chemical vapor generation (photo-CVG) was demonstrated to be a simple, fast, interference-minimized and environmentally friendly technique [16–18], for sample introduction of Hg [19], Cd [20], conventional hydride-forming elements (As, Bi, Sb, Se, Te) [21–26], transition metals (Ni, Co, Fe) [27,28], non-metals (I, Br) [29,30], and also Os [31]. In photo-CVG, volatile species are generated from non-volatile precursors by ultraviolet irradiation with minimal reagent consumption. Recently, Zhu et al.

* Corresponding authors at: College of Earth Sciences, Chengdu University of Technology, Chengdu, Sichuan 610059, China.

E-mail addresses: ying.gao@gmail.com (Y. Gao), szm129@sina.com (Z. Shi).

developed a high efficiency photooxidation vapor generation method for the determination of Os by inductively coupled plasma optical emission spectrometry [31]. By using a flow-through and highly efficient photochemical reactor, Os is readily converted into volatile OsO_4 after 11 s UV irradiation [31]. Increasing the temperature of sample solution can efficiently enhance the transportation efficiency of Os to detector after oxidation. Therefore, a gas-liquid separator was immersed in a temperature controlled oil bath to separate OsO_4 from sample solution. Also, a condenser tube with cooling water was required to prevent huge amount of water vapor from transporting to ICP torch. The method is simple, with a limit of detection of 0.2 ng mL^{-1} . However, a severe memory effect of Os was observed in photo-CVG system, which also limited the throughput of sample analysis.

In this work, we developed a photo-CVG and ICP-MS-based method for Os determination in environmental water samples. A highly efficient photo-oxidation vapor generation reactor, similar as previous report but with longer irradiation path [32], was used for highly efficient production of OsO_4 . The use of oil bath and following cooling system for enhancing the transportation efficiency of Os is not necessary in the current experimental design. The comparisons of different washing reagents were carried out to eliminate the memory effect. The optimization of assay conditions, including oxidizing reagent concentration and instrument parameters, as well as analytical performance and method validation, were investigated and discussed in detail. River water, lake water, mineral water, and seawater were selected as models for Os determination. The characteristics of direct, fast, sensitive and low procedural blank provide a great potential in Re-Os isotopic dating system.

2. Experimental

2.1. Instrument

An ELAN DRC™-e ICP MS (Perkin Elmer, Inc., Shelton, CT, USA) equipped with quartz torch and alumina sample injector tube was used. The fitted Gem Tip cross-flow nebulizer and a corrosion resistant double pass Rytons spray chamber mounted outside the torch box were replaced by a PVG-system for Os determination in this work. A model FIA-3110 flow injection pump system (Vital Instruments Co. Ltd., Beijing, P.R. China) was used for the introduction of sample solutions to the PVG system. A schematic of the photo-CVG photoreactor interfaced to the ICP-MS is similar as described before (Fig. 1) [21]. The photo-CVG system consists of a 19 W thin film flow-through lamp (Beijing Titan Instruments Co., Beijing, China) loosely covered with aluminum foil to shield the operator from exposure to the UV. It can provide 185 nm and 254 nm irradiation. Compared to previous report [31], it has longer irradiation path as shown in Fig. 1. Argon carrier gas was introduced through a “T” connection between the outlet of the photoreactor and a tandem set of two homemade gas-liquid separators (GLSs, ~2 mL internal volume) maintained at 0°C by immersion in an ice bath to minimize any transport of liquid droplets derived from condensation of water vapor to the ICP. The generated analyte vapors were

directed from the outlet of the last GLS to ICP-MS via a 0.25 m length of Teflon lined Tygon tubing. Optimization of the ICP-MS parameters was performed as recommended by the manufacturer. ^{192}Os was monitored due to its high natural abundance and free of interferences arising from sample matrices. Optimum conditions for photo-CVG were investigated independently. Typical operating conditions are summarized in Table 1.

2.2. Reagents and solutions

All reagents were of at least analytical reagent grade. Deionized water (DIW) with resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was used throughout. Nitric acid and hydrogen peroxide of great reagent grade were obtained from Aladdin (Shanghai, P.R. China). A 1000 mg g^{-1} stock solution of Os was prepared from ammonium hexachloroosmate (99.99% metals basis) from Aladdin (Shanghai, P.R. China). 0.2308 g ammonium hexachloroosmate was dissolved in 50 mL HCl , and then diluted to 100 mL with DIW in volumetric flask. Working Os standard solutions were prepared by dilution of the stock solution with $5\% \text{ HNO}_3$ before use.

2.3. Sample preparation

Six environmental water samples were determined in this experiment, including 1 river water sample (from Dongfeng River, Chengdu, P.R. China), 1 lake water sample (from Yan Lake, Chengdu, P.R. China), 2 mineral water samples (from Emeishan City, P.R. China and Shenzhen City, P.R. China, respectively), 1 seawater sample (from Sanya, Hainan, P.R. China) and 1 artificial water sample (certified reference material, GBW 08608). The collected river water, lake water, sea water and mineral water samples were immediately filtrated through $0.22 \mu\text{m}$ membranes after sampling and stored in 4°C refrigerator.

3. Results and discussion

3.1. The memory effect

The memory effect in sample introduction system results in long washout times and deteriorates the precision and detection limits for the analyte, which affects the accuracy and the reliability of the analytical results. To reduce the influence of memory effect of Os, concentrated H_2SO_4 or H_2O_2 was used to clean used vessels or sample inlet tubes for several minutes [11,33]. To investigate the memory effect of Osmium in photo-CVG system, a $2 \mu\text{g L}^{-1}$ Os standard made up in $5\% \text{ HNO}_3$ was continuously introduced into the photo-CVG-ICP-MS system. The Os response gradually increases with time and does not achieve a maximum within 3.5 min (Fig. 2a). After that, 5% nitric acid was used to wash out osmium and the signal wasn't back to blank level after 15 min washing. The use of flow injection (FI) as sample introduction method can minimize the memory effect for determination of Hg and Os by ICP-MS [31, 34]. Therefore, FI was used in the work (Fig. 2b). Furthermore, more

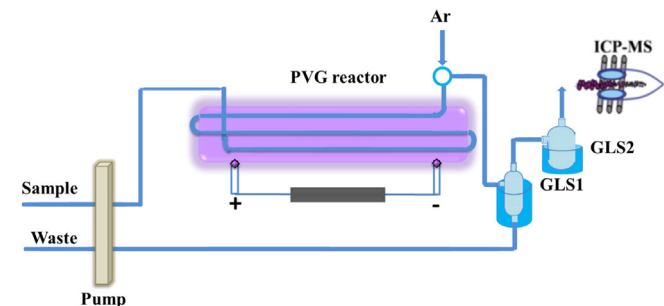


Fig. 1. Schematic diagram of the photo-PVG-ICP-MS determination of Os; GLS: gas liquid separator.

Table 1
ICP-MS instrumental operating parameters.

Parameters	Values
RF power/W	1175 W
Cool gas flow	15 L min^{-1}
Auxiliary gas flow	1.2 L min^{-1}
Nebulizer (Carrier) gas flow	1.00 L min^{-1}
Scanning mode	Peak hopping
Resolution	0.7 amu
Dwell time	30 ms
Dead time	50 ns
Sweeps per reading	1
Readings per replicate	1
Number of replicates	1000
Sampling pump rate	2.0 mL min^{-1}
Isotope monitored	^{192}Os

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