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A new low memory effect device for Os micro-distillation

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This paper reports a new Os micro-distillation device made of glass. We call this glassware a glass conical vial (GCV). The bottom and cover top of the GCV are designed to be pointed in order to hold small droplets of <math><20\ \mu\text{l}</math>. The recovery of Os exceeded 93% after micro-distillation of solutions containing as low as 0.6 ng of Os using GCVs. A simple $\text{HNO}_3\text{-H}_2\text{O}$ -baking procedure to clean the used GCV resulted in background levels of Os and Re below 0.37 and 0.36 pg, respectively, even though micro-distilled solutions in the GCV contained up to 750 ng or 350 ng of Os or Re, respectively. The new device has the advantages of high Os recovery, low Os and Re background, and easy cleaning, and is especially suitable for micro-distillation of samples with a low Os content.

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Introduction

The ^{187}Re - ^{187}Os system has been widely used in the fields of geochemistry and cosmochemistry.¹⁻⁷ As is well-known, most terrestrial materials and extraterrestrial samples have very low abundances of Re and Os. For example, the Os content is typically 10 to 100 pg g^{-1} in crustal rocks and 1 to 5 ng g^{-1} in mantle peridotites. The abundance of Os on some lunar basalts is only a few pg g^{-1} , and even less than 1 pg g^{-1} in lunar meteorites.^{8,9} Generally, either negative thermal ionization mass spectrometry (NTIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) is used to analyse the Os isotopic composition with high precision and accuracy. ^{187}Re is a significant isobaric interference of ^{187}Os , which can directly affect the accuracy and precision of ^{187}Os determination using either of these two types of mass spectrometry. For these reasons, the high precision and accuracy measurement of Os isotopic ratios requires a lower background of Re and Os and higher recovery of Os during the Os chemical purification procedure.

During analysis of Os isotopes, matrix elements, organics, and isobaric interferences are all potential factors that could seriously affect the precision and accuracy of Os isotopic ratios. Therefore, Os in samples must be chemically separated before being

measured by NTIMS/MC-ICPMS. The commonly used method for the chemical purification of Os is to dissolve the sample with inverse aqua regia ($\text{HNO}_3 : \text{HCl} = 3 : 1, \text{v/v}$) and then purify the Os using a two-step process. In the first step, liquid-liquid extraction of OsO_4 (e.g., CCl_4 or CHCl_3)¹⁰⁻¹³ or distillation¹⁴⁻¹⁸ is used to extract OsO_4 from the solution of the digested sample. In the second step, the OsO_4 extracted from the first step is further purified by a micro-distillation method.¹⁹⁻²² The second step of micro-distillation separates Os from interfering elements such as Re as much as possible, which is significant for Os isotopic ratio measurement with high accuracy and precision.

Birck *et al.* (1997),²⁰ first reported the micro-distillation of Os in a vial of perfluoroalkoxy (PFA) material with a conical bottom and a flat top. In subsequent experiments, it was found that the PFA material could be permeated by OsO_4 , thus presenting a potential risk of Os loss^{23,24} as well as cross-contamination when reusing the containers. Therefore, the PFA vials have to be cleaned by a complicated process for repeated use^{10,15,20,25,26} and it still has a serious memory effect when relatively high Os was distilled. Compared with the PFA material, the glass material could avoid these disadvantages easily.

In this study, we designed a special glass conical vial (GCV) for Os micro-distillation. Using this new device for Os micro-distillation, the Os recovery could be larger than 93%, and the background of Os and Re could be less than 0.37 pg and 0.36 pg respectively. As well as the vial cleaning procedure was simpler and less time-consuming.

Experimental

Instrumentation

An inductively coupled plasma mass spectrometer (ICP-MS, Plasma Quant MS, Jena Company) was used to analyze the Os

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Table 1 ICP-MS operating parameters

Parameter	Value
RF power	1100 W
Plasma gas	15 l min ⁻¹
Aux gas	1.20 l min ⁻¹
Nebulizer gas	0.78 l min ⁻¹
Sweeps	20
Readings	1
Replicates	3
Scan mode	Peak hopping
Dwell time per AMU (ms)	50
Sampling cone (Ni)	1 mm
Skimmer cone (Ni)	0.8 mm

and Re recoveries as well as the vessel background after micro-distillation using GCVs at the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). During the determination of Re and Os, the calibration solution of Rh was used as an internal standard and the calibration solutions of Re and Os were used as external standards. Background of 2% HNO₃ solutions was normally <50 counts per second (cps) for Re and Os. The sensitivity of the instrument to 10 ng g⁻¹ In–Th tuning solution was adjusted to more than 2 × 10⁵ cps for ¹¹⁵In and 1 × 10⁵ cps for ²³²Th. The measurement parameters are shown in Table 1. Osmium isotopic ratios were measured using a thermal ionization mass spectrometer (TIMS, Triton Plus, Thermo Fisher Scientific Inc.) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). The Os isotopic measurements are described in the literature by Wang *et al.* (2017 and 2023).^{27,28}

Reagents and reference materials

High purity water (HPW) was obtained from a Millipore purification system with a resistivity of 18.2 MΩ cm⁻¹. Concentrated HCl (12 mol l⁻¹), HNO₃ (16 mol l⁻¹) and HBr (8.8 mol l⁻¹) were purified by double sub-boiling distillation. The high purity oxidant solution CrO₃–H₂SO₄ was a mixed solution with CrO₃ (8% m/v) and H₂SO₄ (6 mol l⁻¹), heated at 100 °C to remove potential Os in the solution.²⁹

The calibration solutions of Os, Re and Rh (1000 μg g⁻¹) were purchased from NCS Testing Technology Co., Ltd. The geological reference materials WPR-1 and BIR-1a were purchased from CANMET-CCRM, and USGS, respectively. The information about WPR-1 and BIR-1a is shown in Table 2.

Laboratory ware

In this study, a novel glassware was designed for Os micro-distillation, and its usability was assessed using calibration solutions of Os, Re and geological reference materials. The glassware consisted of a cup with a base as the main body and a cap. Both the cup bottom and the cap top were pointed in order to hold small drops. The cup was shaped like a Chinese shot glass. We called the glassware a glass conical vial (GCV). The GCV volume was approximately 3 ml. The upper part of the cup body was smaller and the lower part was larger, which facilitated the maintenance of temperature during micro-distillation. The diameter of the base was slightly larger than that of the largest section of the bowl so that it could be securely placed. The thickness of the GCV wall was around 2 mm. A schematic of the GCV structure is shown in Fig. 1. Because the electric heating plate was plane heating, in order to improve the efficiency of heat conduction, the distance between the cup body and the cup base should be as short as possible. The tip to hold 20 μl solution was a cone with a base diameter of 5 mm and 10 mm in height. To ensure sealing, the upper 2/3 of the outer surface of the cup body and the lower 1/2 of the inner surface of the cap were frosted.

Separation procedure

To assess the availability of the GCVs, a 200 μl calibration solution containing 750 ng of Os in HBr medium, which is much larger than the amount of Os for routine analysis (<40 ng), was pipetted into the GCV. The GCV was then placed in a perforated electric heating plate and evaporated at 80 °C until dry. The size of the heating plate used was 50 × 25 cm² with 50 holes arranged in 10 columns and 5 rows. Each hole has a diameter of 25 mm and a height of 30 mm. At this time, Os remained in the reduced state of OsBr₆²⁻ at the bottom of the GCV. 20 μl CrO₃–H₂SO₄ was added to the evaporated sample in the GCV, and the cap was quickly closed, with a loop of PTFE tape wrapped around the frosted outer surface of the main body to ensure tightness. The tip of the cap contained 20 μl of 8.8 mol l⁻¹ HBr. The GCVs were placed on a heating plate at 80 °C for 3 h. The Os would first be redissolved in CrO₃–H₂SO₄ and converted to OsO₄ in the oxidized state and volatile OsO₄ was transferred in the gas phase to the top of the cap where it was reduced to OsBr₆²⁻ by HBr. To maintain a uniform temperature inside the GCV, aluminium foil was covered around the GCV during micro-distillation, while the tip of the cap with HBr was exposed without aluminium foil to keep a lower temperature of HBr. After the Os micro-distillation, the 20 μl HBr solution of extracted Os at the top of the GCV was

Table 2 The information about geological reference materials used in this study

Name	Lithology	Mass fraction		Weight (g)	Os amount ^a (ng)	¹⁸⁷ Os/ ¹⁸⁸ Os (2SD)
		Re ^b (ng g ⁻¹)	Os ^c (ng g ⁻¹)			
WPR-1	Mineralized serpentinite	10.8	13.3	1.10	14.630	0.14430 ± 10 ^c
BIR-1a	Basalt	0.661	0.35	1.10	0.385	0.13358 ± 31 ^c

^a The Os amount was calculated from the weight and the Os mass fraction. ^b Data source from Chu *et al.* (2015).³⁷ ^c Date source from Wang *et al.* (2019).³⁵

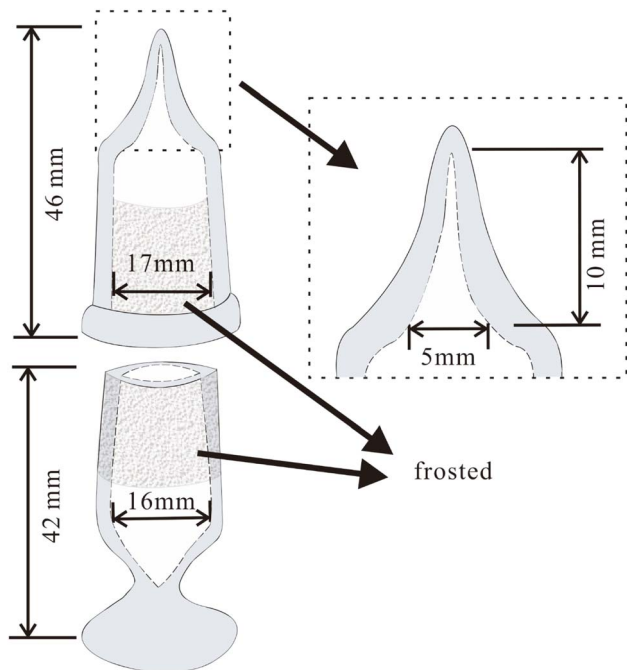


Fig. 1 The schematic of the glass conical vial.

diluted to 0.6 ml (equivalent to 0.29 mol l^{-1} of HBr medium), and measured by ICP-MS.

For comparison, the PFA conical vials (PFAVs) were also used for Os micro-distillation. 200 μl of calibration solution containing 750 ng of Os was concentrated to less than 20 μl first in HBr medium in a PTFE cup at 80 $^{\circ}\text{C}$. Subsequently, it was transferred to the centre of the PFAV cap and dried at 80 $^{\circ}\text{C}$. The evaporated residue was dissolved in 20 μl $\text{CrO}_3\text{-H}_2\text{SO}_4$. Then, the PFAV with 20 μl 8.8 mol l^{-1} HBr in the tip and PFAV lid was screwed tightly and placed turned upside down on a heating plate at 80 $^{\circ}\text{C}$ for 3 h. In the micro-distillation process, the PFAV was wrapped in aluminium foil with the exception of the tip. Finally, the HBr solution containing the extracted Os was diluted to 0.6 ml, (0.29 mol l^{-1} HBr medium) and the Os concentration was analyzed by ICP-MS. The used PFAVs continued to be used for background experiments after cleaning (see section “Os background”).

Two geological reference materials WPR-1 and BIR-1a were weighed 1.10 g (Table 2) each and put in Carius tubes. The reverse-aqua regia solution of 8 ml (6 ml 16 mol l^{-1} HNO_3 at $-18 \text{ }^{\circ}\text{C}$ and 2 ml 12 mol l^{-1} HCl at room temperature) was

added to the Carius tube. The tubes were immediately sealed with glass stoppers and then heated in an oven at 190 $^{\circ}\text{C}$ for 32 h. This step was the same as Qi *et al.* (2013).³⁰ After slowly cooling down in air to room temperature, the Carius tubes were further cooled in a refrigerator at $-18 \text{ }^{\circ}\text{C}$ for 2 h. Subsequently, Os was separated by a distillation method^{17,31} and collected in 1.5 ml of 8.8 mol l^{-1} HBr solution. After distillation, the Os was transferred to a GCV for micro-distillation as described above. Finally, the Os-HBr solution in the GCV tip was concentrated to approximately 2 μl at 80 $^{\circ}\text{C}$ and loaded on a Pt ribbon, which was then covered with $\text{Ba}(\text{OH})_2$ activator for Os isotopic measurements by NTIMS.

Results and discussion

Cleaning procedure for the GCVs and Os background

In order to evaluate the cleaning procedure and background of the PFAV and GCV after Os micro-distillation, 9 GCVs and 6 PFAVs were used to carry out Os micro-distillation as described in the section of “Separation procedure”. All cups were then divided into three groups for cleaning, labelled as group I, group II, and group III. The cleaning procedure for each group is shown in Table 3.

Group I included 3 GCVs and 3 PFAVs, all of which were washed using a 3-step washing process. In step 1, all six vials were immersed in concentrated HNO_3 and boiled on a hot plate at 165 $^{\circ}\text{C}$ for 2 h; in step 2, all the cups were rinsed 6 times with HPW and then boiled at a set temperature of 165 $^{\circ}\text{C}$ for 2 h; in step 3, all cups were allowed to dry naturally at room temperature.

Group II, like group I, consisted of 3 GCVs and 3 PFAVs, along with a 3-step cleaning process. The difference was that in step 3, all vials were baked in an oven at 185 $^{\circ}\text{C}$ for 2 h instead of drying naturally at room temperature as in group I.

Group III had only 3 GCVs and these cups were subjected to a 5-step cleaning process: the first 3 steps were the same as in group II; in step 4, after step 3, 2 ml concentrated HNO_3 was added to the GCVs and refluxed on an electric hot plate at 120 $^{\circ}\text{C}$ for 1 h; step 5, the GCVs were rinsed 3–5 times with HPW, and then baked again in an oven at 185 $^{\circ}\text{C}$ for 2 h.

The Os remaining in the cleaned cup was extracted by a micro-distillation process, which was the background of the cup. The results show that the background of PFAVs was significantly higher than that of GCVs after the same washing process (Fig. 2). When the vials were dried at room temperature after washing step 1 and step 2, the Os background of PFAVs

Table 3 Cleaning procedures for GCVs and PFAVs

Group	Vial	Step 1	Step 2	Step 3	Step 4	Step 5
		HNO_3	Water	Dry	Refluxed	Dry
I	3 GCVs and 3 PFAVs	165 $^{\circ}\text{C}$	165 $^{\circ}\text{C}$	25 $^{\circ}\text{C}$	—	—
II	3 GCVs and 3 PFAVs	165 $^{\circ}\text{C}$	165 $^{\circ}\text{C}$	185 $^{\circ}\text{C}$	—	—
III	3 GCVs	165 $^{\circ}\text{C}$	165 $^{\circ}\text{C}$	185 $^{\circ}\text{C}$	120 $^{\circ}\text{C}$	185 $^{\circ}\text{C}$

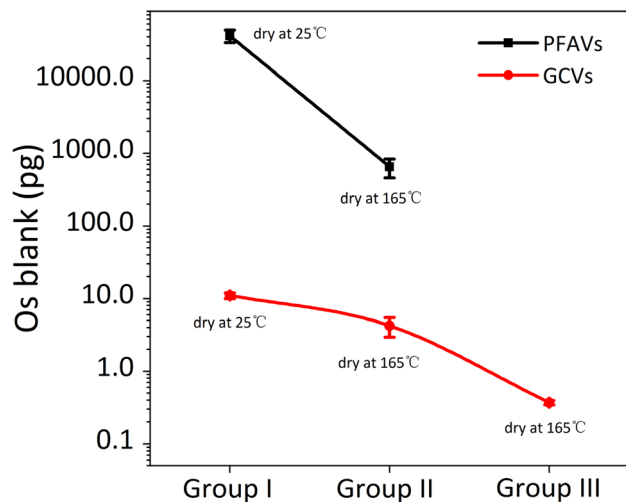


Fig. 2 Os blank of two different material cups after different cleaning procedures. Each analysis point represents the mean value of three cup backgrounds for the same cleaning procedure. The error bar is 2SD.

was about 4000 times higher than that of GCVs. After baking at 185 °C for 2 h in step 3, the Os backgrounds of both vials were significantly reduced, from about 41 ng to 0.6 ng for PFAVs and from 11 pg to 4 pg for GCVs, but the PFAV background after baking was still 150 times higher than that of the GCV. This result also indicates that our new GCV device has significant advantages over the traditional PFAV.

To further reduce the background of GCVs, the cleaning process of group III was designed. The results suggest that the Os background of GCVs cleaned by the above 5 steps could be as low as 0.37 pg. The total time taken to complete the 5-step cleaning of GCVs is approximately 10 h. In previous studies, aqua regia, $\text{CrO}_3\text{-H}_2\text{SO}_4$, HBr and nitric acid have been employed in combination to clean PFAVs sequentially, and the cleaning time was even up to 24 h.^{10,15,20,25,29,32} Compared to the conventional PFAV cleaning procedure, the GCV cleaning procedure is simpler and less time-consuming.

Micro-distillation extraction rate and background of Re

In order to assess the extraction rate of Re in solution accompanying Os into HBr during Os micro-distillation, and the effect of high Re-content solution on the GCV background, a two-group experiment was designed. Six GCVs were prepared and divided into two groups. In group I, 175 μl of 2 $\mu\text{g g}^{-1}$ (350 ng) Re calibration solution and 200 μl of 8 mol l^{-1} HBr were applied to micro-distillation as described previously. The GCVs would then be cleaned using the method of group II in the previous section. After cleaning, the micro-distillation was carried out again.

In group II, 10 μl of 2 $\mu\text{g g}^{-1}$ (20 ng) Re calibration solution and 200 μl of 8 mol l^{-1} HBr were subjected to the same micro-distillation technique to examine the extraction of Re by HBr on the tip of the GCV cap. Finally, the droplet of HBr at the tip of 6 GCVs was diluted to 0.6 ml (0.29 mol l^{-1} HBr medium) for ICP-MS determination.

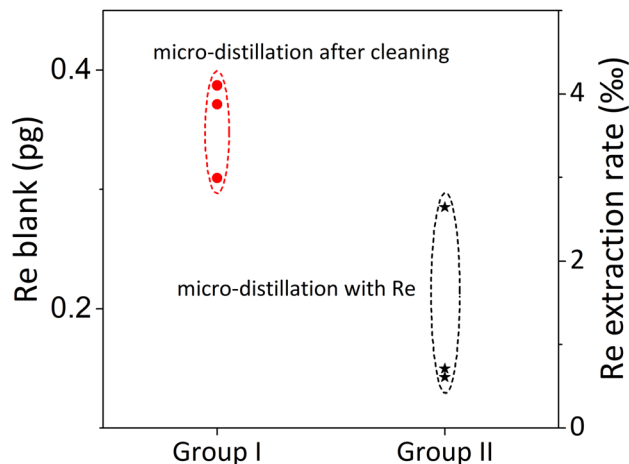


Fig. 3 Re background and Re extraction rate in GCVs during micro-distillation. The left vertical axis corresponds to the Re blank for group I. And the right vertical axis corresponds to the Re extraction rate for group II.

The analysis of Re in group I shows that despite the amount of Re in solution being as high as 350 ng, the background after micro-distillation and cleaning in the GCVs is below 0.36 pg (see Fig. 3, red solid circles). This result demonstrates that very low Re backgrounds can be achieved with a simple cleaning process and confirms that the new GCVs are easier to clean than conventional PFAVs.

The results of Re analysis in group II show that the extraction rate of Re by micro-distillation for a solution with a total content of 20 ng of Re was only 0.6–2.6‰ (see Fig. 3, black solid stars). Considering that most of the Re has been removed from the original solution of the actual sample after the first step of Os separation, the amount of Re in the solution before micro-distillation should be much smaller than the amount of Os. Therefore, after micro-distillation, the effect of the Re extracted along with the Os during the Os isotopic measurement could be negligible.

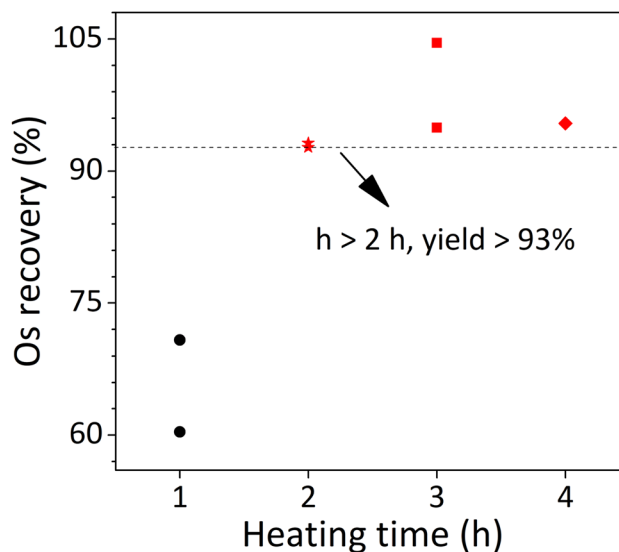


Fig. 4 Os recovery versus micro-distillation duration.

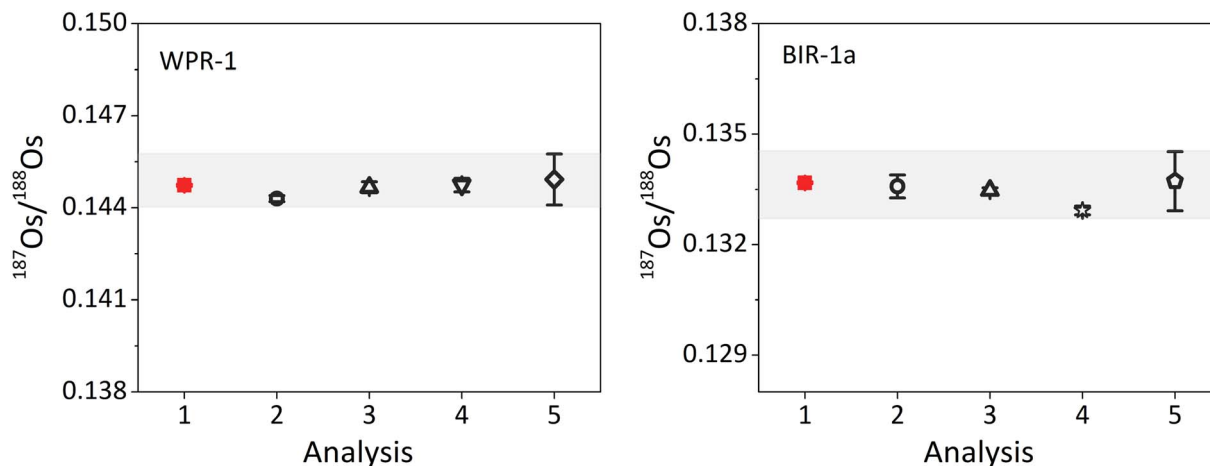


Fig. 5 The $^{187}\text{Os}/^{188}\text{Os}$ ratios of WPR-1 and BIR-1a measured by NTIMS after Os micro-distillation using GCVs. Red solid square: the data from this work; open circle: the data from Wang *et al.* (2019);³⁵ open regular triangle: the data from Chu *et al.* (2015);³⁷ open inverted triangle: the data from Genske *et al.* (2016);³⁸ open diamond: the data from Day *et al.* (2016);²¹ open star: the data from Nakanishi *et al.* (2019);²² open pentagon: the data from Ishikawa *et al.* (2014).³⁶ The gray rectangle is the range of all $^{187}\text{Os}/^{188}\text{Os}$ ratios in the literature cited in this paper. The error bar is 2SD.

Os recovery by micro-distillation using the GCV

It is especially important to obtain high Os recoveries for small-size/low-content samples. Seven GCVs with the Os calibration solution were performed micro-distillation to determine the recovery of Os. Each 50 μl of 13.4 ng g^{-1} (0.67 ng) Os calibration solution was pipetted to the bottom of the GCV, followed by the addition of 20 μl of concentrated HBr and evaporated to dryness at 80 $^{\circ}\text{C}$. Micro-distillation was then carried out as described in the “Separation procedure”. All cups were heated at the same temperature (80 $^{\circ}\text{C}$) during the micro-distillation process and the heating duration was divided into four groups of 1 h, 2 h, 3 h, and 4 h each. After micro-distillation, the Os-extracted HBr solution at the top of the cap was dissolved to 1 ml with HPW, while Rh was added as an internal standard, and the solution was measured by ICP-MS in 0.29 mol l^{-1} HBr medium.

The results show that the Os recovery was only 60–70% for a micro-distillation duration of 1 h, and up to 93% for a micro-distillation duration of 2 h. Continuing to increase the micro-distillation duration resulted in a non-significant increase in the Os recovery, and even up to 4 h, the Os recovery of about 95% was approximately the same as that for 3 h of micro-distillation (Fig. 4).

Results for geological reference materials

In this study, two reference materials, WPR-1 and BIR-1a, were chosen to verify the utility of the GCV used for Os micro-distillation, as they represent geological rocks with higher and lower Os content, respectively. Previous studies have also confirmed that PGE and Re are more homogeneous in these two rocks than in other geological reference materials.^{21,22,29,33–36} The powdered samples were digested and analysed using the method described in the “Separation procedure”. The total procedure blank values for Re and Os were 1.3 ± 2.1 and 0.4 ± 0.3 pg (2SD, $n = 2$), respectively.

The results show that the $^{187}\text{Os}/^{188}\text{Os}$ ratio measured for the two rocks in this study is consistent with the published data within the error range (Fig. 5). The $^{187}\text{Os}/^{188}\text{Os}$ ratio of BIR-1a is

0.133680 ± 20 (2SD, $n = 3$), which is consistent with the ratio of 0.133184 ± 19 (2SD, $n = 3$) and 0.133763 ± 61 (2SD, $n = 3$) previously measured in our laboratory with the same sample size (1 g) and by the conventional purification method. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of WPR-1 is 0.144743 ± 33 (2SD, $n = 5$), which is slightly higher than the ratio of 0.144302 ± 99 (2SD, $n = 2$) previously measured in our laboratory. The weighing sample sizes of the two rocks used by the two micro-distillation methods (GCVs and PFAVs) in our laboratory are small (0.5–1 g). Therefore, the heterogeneity of Os caused by the nugget effect might be obvious. Although the ratio of WPR-1 was slightly higher than that of previous data in our lab, it was consistent with those published values^{21,37,38} analysed by another lab in the error range.

Summary

A newly designed GCV for the micro-distillation of Os is reported, which offers the following advantages compared to the conventional PFAV:

- (1) The glass material avoids the disadvantage that the PFA material may be penetrated by OsO_4 .
- (2) The GCV is easier to clean and has a lower background than the PFAV.
- (3) Higher Os recoveries can be obtained. When the duration of micro-distillation is longer than 2 h, the recovery of Os can reach more than 93%.

In short, the newly designed GCV is more suitable for micro-distillation of Os in low-content/small-size samples as it is easier to clean to achieve the low background requirements for Re and Os. It is worth noting that the GCV made of glass is clearly more economical than the PFAV.

Author contributions

Yuling Zeng: writing – original draft, data curation, validation; Guiqin Wang: conceptualization, writing – review & editing,

data curation, funding acquisition, project administration; Liang Qi: resources, methodology; Jianfeng Gao: methodology; Zhaofeng Zhang: supervision.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 S. B. Shirey and R. J. Walker, *Earth Planet. Sci.*, 1998, **26**, 423–500.
- 2 J. Xu, G. Wang, J. Li and J. Chen, *Geochimica*, 2010, **39**, 142–148.
- 3 Y. Kadlag and H. Becker, *Geochim. Cosmochim. Acta*, 2016, **172**, 225–246.
- 4 M. Paquet, J. M. D. Day, A. Udry, R. Hattingh, B. Kumler, R. R. Rahib, K. T. Tait and C. R. Neal, *Geochim. Cosmochim. Acta*, 2021, **293**, 379–398.
- 5 A. Dubiella-Jackowska, Z. Polkowska and J. Namieśnik, *Pol. J. Environ. Stud.*, 2007, **16**, 329–345.
- 6 Z. Chu, M. Wang, D. Liu, J. Liu, J. Guo, H. Zhang and C. Cai, *Chem. Geol.*, 2023, **620**, 121342.
- 7 R. J. Walker, J. W. Morgan, M. F. Horan, G. K. Czamanske, E. J. Krogstad, V. A. Fedorenko and V. E. Kuniilov, *Geochim. Cosmochim. Acta*, 1994, **58**, 4179–4197.
- 8 J. M. D. Day and R. J. Walker, *Earth Planet. Sci. Lett.*, 2015, **423**, 114–124.
- 9 J. M. Day, D. G. Pearson and L. A. Taylor, *Science*, 2007, **315**, 217–219.
- 10 A. S. Cohen and F. G. Waters, *Anal. Chim. Acta*, 1996, **332**, 269–275.
- 11 J. J. Shen, D. A. Papanastassiou and G. J. Wasserburg, *Geochim. Cosmochim. Acta*, 1996, **60**, 2887–2900.
- 12 J. Zhang, J. Li, X. Long, S. Sun, L. Yin and M. Dai, *Geostand. Geoanal. Res.*, 2017, **41**, 649–658.
- 13 N. Phelan, J. M. D. Day, J. K. Dhaliwal, Y. Liu, C. A. Corder, C. Strom, E. Pringle, N. Assayag, P. Cartigny, K. Marti and F. Moynier, *Geochim. Cosmochim. Acta*, 2022, **318**, 19–54.
- 14 J. W. Morgan and R. J. Walker, *Anal. Chim. Acta*, 1989, **222**, 291–300.
- 15 S. B. Shirey and R. J. Walker, *Anal. Chem.*, 1995, **67**, 2136–2141.
- 16 Y. Sun, M.-F. Zhou and M. Sun, *J. Anal. At. Spectrom.*, 2001, **16**, 345–349.
- 17 L. Qi, M.-F. Zhou, J. Gao and Z. Zhao, *J. Anal. At. Spectrom.*, 2010, **25**, 585.
- 18 X. Jin, W. Li, P. Xiang, P. A. Sakyi, M. Zhu and L. Zhang, *J. Anal. At. Spectrom.*, 2013, **28**, 396–404.
- 19 M. Roy-Barman, PhD thesis, Université de Paris VII, 1993.
- 20 J. L. Birck, M. R. Barman and F. Capmas, *Geostand. Geoanal. Res.*, 1997, **21**, 19–27.
- 21 J. M. D. Day, C. L. Waters, B. F. Schaefer, R. J. Walker and S. Turner, *Geostand. Geoanal. Res.*, 2016, **40**, 49–65.
- 22 N. Nakanishi, T. Yokoyama and A. Ishikawa, *Geostand. Geoanal. Res.*, 2019, **43**, 231–243.
- 23 E. E. Ilia Rodushkin and D. C. Baxter, *Geostand. Geoanal. Res.*, 2007, **31**, 27–38.
- 24 S. Czerczak, J. P. Gromiec, A. Pałaszewska-Tkacz and A. Świdwińska-Gajewska, in *Patty's Toxicology*, 2012, pp. 653–768.
- 25 D. G. Pearson and S. J. Woodland, *Chem. Geol.*, 2000, **165**, 87–107.
- 26 J. Li, X. Jiang, J. Xu, L. Zhong, X. Wang, G. Wang and P. Zhao, *Geostand. Geoanal. Res.*, 2014, **38**, 37–50.
- 27 G. Wang, T. Sun and J. Xu, *Rapid Commun. Mass Spectrom.*, 2017, **31**, 1616–1622.
- 28 G. Wang, Y. Zeng, L. Qi, W. Liu and J. Xu, *Anal. Chim. Acta*, 2023, 1278.
- 29 J. Li, P.-p. Zhao, J. Liu, X. Wang, A. Y. Yang, G. Wang and J.-F. Xu, *Geostand. Geoanal. Res.*, 2015, **39**, 17–30.
- 30 L. Qi, J.-F. Gao, M.-F. Zhou and J. Hu, *Geostand. Geoanal. Res.*, 2013, **37**, 345–351.
- 31 L. Qi, J. Gao, X. Huang, J. Hu, M.-F. Zhou and H. Zhong, *J. Anal. At. Spectrom.*, 2011, **26**, 1900–1904.
- 32 I. R. Dmitry Malinovsky, B. Douglas and B. Öhlander, *Anal. Chim. Acta*, 2002, **463**, 111–124.
- 33 T. Meisel and J. Moser, *Chem. Geol.*, 2004, **208**, 319–338.
- 34 T. Meisel and J. Moser, *Geostand. Geoanal. Res.*, 2004, **28**, 233–250.
- 35 G. Wang, H. Vollstaedt, J. Xu and W. Liu, *Geostand. Geoanal. Res.*, 2019, **43**, 419–433.
- 36 A. Ishikawa, R. Senda, K. Suzuki, C. W. Dale and T. Meisel, *Chem. Geol.*, 2014, **384**, 27–46.
- 37 Z. Chu, Y. Yan, Z. Chen, J. Guo, Y. Yang, C. Li and Y. Zhang, *Geostand. Geoanal. Res.*, 2015, **39**, 151–169.
- 38 F. S. Genske, C. Beier, A. Stracke, S. P. Turner, N. J. Pearson, F. Hauff, B. F. Schaefer and K. M. Haase, *Geochim. Cosmochim. Acta*, 2016, **172**, 76–92.