

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band: 77 (1997)
Heft: 1

Artikel: "Plug in" Os distillation
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DOI: <https://doi.org/10.5169/seals-58474>

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"Plug in" Os distillation

by Thomas F. Nägler¹ and Robert Frei¹

Abstract

We have developed a simple, easy to assemble distillation line for the efficient recovery of Os from geological samples. We repeatedly attained Os procedural yields of > 85%. The procedure involves a single distillation from HNO₃–HCl used for the digestion in conventional carius tubes, directly into HBr. The distillation assembly is composed solely of off-the-shelf Teflon® material, and no extra cooling system is needed. Besides being time and cost efficient, this design allows the plugging in of additional lines for the simultaneous distillation of a larger number of samples. Further, it enables a direct and subsequent low blank Re-recovery from the distillation residue. The latter is achieved by anion column exchange procedures. Following a simple micro-distillation step, the organic-free, purified Os fraction is ready for N-TIMS. Our technique can be easily copied and ensures high quality, high yield and low blank Os separation for geochemical, cosmochemical and geochronological studies.

Keywords: geochemistry, Os separation, distillation, Re–Os system.

Introduction

The increased interest in the Re–Os isotope system as an important tool to geochemical, cosmochemical and geochronological issues has led to a rapid development of the separation and mass-spectrometric techniques and analyses of Re–Os isotopes are now performed in an increasing number of laboratories.

Because the abundances of Re and Os in most geological samples are very low (usually in the ppb to ppt range), the chemical separation of these elements is a rather difficult venture. Crucial to the recovery of Re and Os for N-TIMS isotopic analyses is (i) an extraction procedure with an enormous enrichment factor and at the same time with a high recovery yield, and (ii) a small procedural blank to minimize the uncertainty in the concentration and isotope composition of Re and Os in the sample. Large-scale distillation techniques are applied to recover Os from sample amounts of up to tens of grams. Conventionally, Pyrex® glass distillation equipment is being used, in which H₂SO₄ is added to a sample, previously digested in aqua regia or in HF–HCl–EtOH mixtures, and Os is distilled as OsO₄ into reducing trapping solutions (NaOH, HCl–EtOH; WALKER,

1988, SHIREY and WALKER, 1995; HBr, KRÄHENBÜHL et al., 1992, ROY-BARMAN et al., 1996). Complete oxidation of Os can be achieved by adding an oxidant (ceric sulfate, CrO₃, etc.), particularly necessary if a reducing sample digestion solution was applied. Advantages of these distillation procedures clearly lie in the high chemical yields for Os, usually around 80%. Disadvantages of these procedures are (I) a slow procedural handling and (II) problems with extracting Re from the residual solutions. Separation of Re is achieved via either anion exchange chromatography or solvent extraction. The chromatographic extraction of Re from the distillation solution is complicated by significant volumes of H₂SO₄. In order to obtain a H₂SO₄ free Re-fraction – a prerequisite for N-TIMS analyses – large amounts of flushing acids usually have to be used on the separation columns. This may lead to a significant increase of blank contribution. Furthermore, the use of large quantities of H₂SO₄ itself may introduce high Re blanks. The same holds true for alternative techniques, in which Re is partitioned from the digestion or distillation solution into organic liquids (e.g., tribenzylamine; WALKER, 1988) and subsequently into ammonium hydroxide. Small quantities of sulfuric acid and rock components in-

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evitably coextract during solvent separations (WALKER, 1988). This usually calls for subsequent purification procedures with associated blanks, and thus makes the final extraction of a Re-fraction for isotopic analyses a complicated task.

In a recent publication, COHEN and WATERS (1996) report an alternative method for the separation of Os from geological materials. It basically builds on a solvent extraction procedure in which OsO_4 is partitioned directly from aqua regia digest solution into CCl_4 or CHCl_3 , and recovered by back-extraction into concentrated HBr . This new approach circumvents the use of ion exchange or large scale distillation techniques for Os while offering a simple handling procedure and ensuring minimum blank contributions. A significant disadvantage of this technique is a loss of ~ 40 to 50% of the sample Os during the extraction procedure. This is a major point of concern especially when crustal (i.e., extremely Os-poor) material is separated. Furthermore, the technique is susceptible to coextraction of ReCl_3 with OsO_4 from aqua regia into the organic liquids. Also, the authors state that Re-recovery may be suppressed by the presence of residual sample Cl^- or NO_3^- .

Here we present results from our efforts in developing a modified distillation procedure which allows for a user-friendly and simple Re and Os recovery from geological materials. Our distillation apparatus can be easily assembled from off-the-shelf components, and at the same time ensures fast processing with minimal blank levels.

Analytical descriptions

DIGESTION OF SAMPLES

In order to achieve complete spike-sample homogenization and dissolution of the sample material, we prefer digestion in a carius tube, which was recently re-described by SHIREY and WALKER (1995). In contrast to the proposed aqua regia ($\text{HCl} : \text{HNO}_3 = 2 : 1$) as digest solution we use reversed volume shares in our approach ($9 \text{ N HCl} : 14 \text{ N HNO}_3 = 1 : 2$). This significant change is essential to our technique, as it ensures complete oxidation of Os to OsO_4 at 220°C in the tube prior to distillation. This has to be achieved because distillation from pure HNO_3 at ca. 120°C (temperature of constant boiling) does not efficiently and rapidly oxidize Os (WALKER, 1988). We have confirmed this by our own experiments, in which Os from our standard solution ($(\text{NH}_4)_2\text{OsCl}_6$ in 6 M HCl , $50\text{--}100 \mu\text{l}$) practically did not distill into the trapping solution during two hours at constant

boiling temperature of HNO_3 . An alternative method, in which the sample digestion is performed in PTFE bombs under reducing conditions in a mixture of HF-HCl-EtOH (WALKER, 1988; ROY-BARMAN and ALLÈGRE, 1995), is not suitable for our simple distillation as Os in the digest solution is still present in a reduced form. Oxidation of Os in this case can only be achieved by addition of a strong oxidant, with the potential risk to increase the Re blank. Usually this problem is circumvented by aliquoting the digestion solution, but at the expense of both Os and Re yields. Furthermore, sporadic problems with Os memory effects of the bombs have been reported by the same authors. This problem does not apply for one-use carius tubes.

APPARATUS AND DISTILLATION PROCEDURE

The schematic sketch in figure 1 depicts the distillation apparatus. The sample digestion solution is transferred from the chilled carius tube into a 33 ml SAVILLEX® vial. The vial is inserted into a metal heating jacket and placed onto a hot plate previously heated to 115°C . The temperature is measured by a simple meat roast thermometer in an aluminium-block. This allows measurement of the effective temperature on the hot-plate, which is more accurate than using an internal thermostat. The vial is closed with a cap with two $1/8''$ ports, originally designed for taking solution to dryness in a closed cell. Through the inlet port N_2 is supplied via a $1/8''$ Teflon® FEP tube. To allow this tube to be extended to the bottom of the vial, the inner section of this port had to be slightly enlarged. The N_2 flow is controlled by a valve (one for each vial in multi sample distillation). A 65 cm long Teflon® FEP tube is plugged into the outlet port and inserted into a cylinder containing 10 ml of chilled 8.8 M HBr . In our experiments the culmination point of this tube was about 30 cm above the hot plate level. Note that no cooling system is applied along the tube. At this stage the N_2 bubble rate in the trapping solution receptacle can be controlled and adjusted (c. 3 bubbles per second). This can be easily achieved because the narrow (1.5 mm wide) tube supports a laminar flow. After the sample has been distilled at a temperature of 115°C for 100 minutes, the Os bearing HBr is transferred into a SAVILLEX® 15 ml vial and placed for one hour in an oven heated to 70°C . This ensures complete reduction of Os to the stable OsBr_2^- complex. Subsequently, the HBr is evaporated to dryness under an infra-red light at 70°C . Purification of this Os fraction is achieved

by a micro-distillation after ROY-BARMAN and ALLÈGRE (1995).

Re can be recovered from the remaining digestion solution. After drying down, Re is separated from the residue via conventional anion exchange procedures.

TEST-EXPERIMENTS

In the procedure described above part of the HBr trapping fluid may be oxidized by portions of HNO_3 which may be transferred during the distillation. In order to quantify the amount of transferred HNO_3 -HCl mixture, we repeatedly distilled into 10 ml of H_2O under the above men-

tioned distillation parameters (115 °C, 100 min). Subsequent titration of this H_2O consistently yielded a total acid molarity < 2 . This corresponds to a total amount of < 20 mmol of $\text{HCl} + \text{HNO}_3 + \text{HNO}_2$ which is significantly below the amount of HNO_3 needed to oxidize 10 ml of 8.8 M HBr ($= 88$ mmol HBr). Consequently, reducing conditions in the trapping solution are preserved during the whole process.

In order to optimize the yield of our distillation, we attempted in a first experiment to trace the amounts of OsO_4 transferred in successive time intervals (Tab. 1, yields 1a to 1c). A spike was introduced directly into the receptor liquid. The remaining Os in the digestion solution was subsequently recovered by liquid extraction techniques

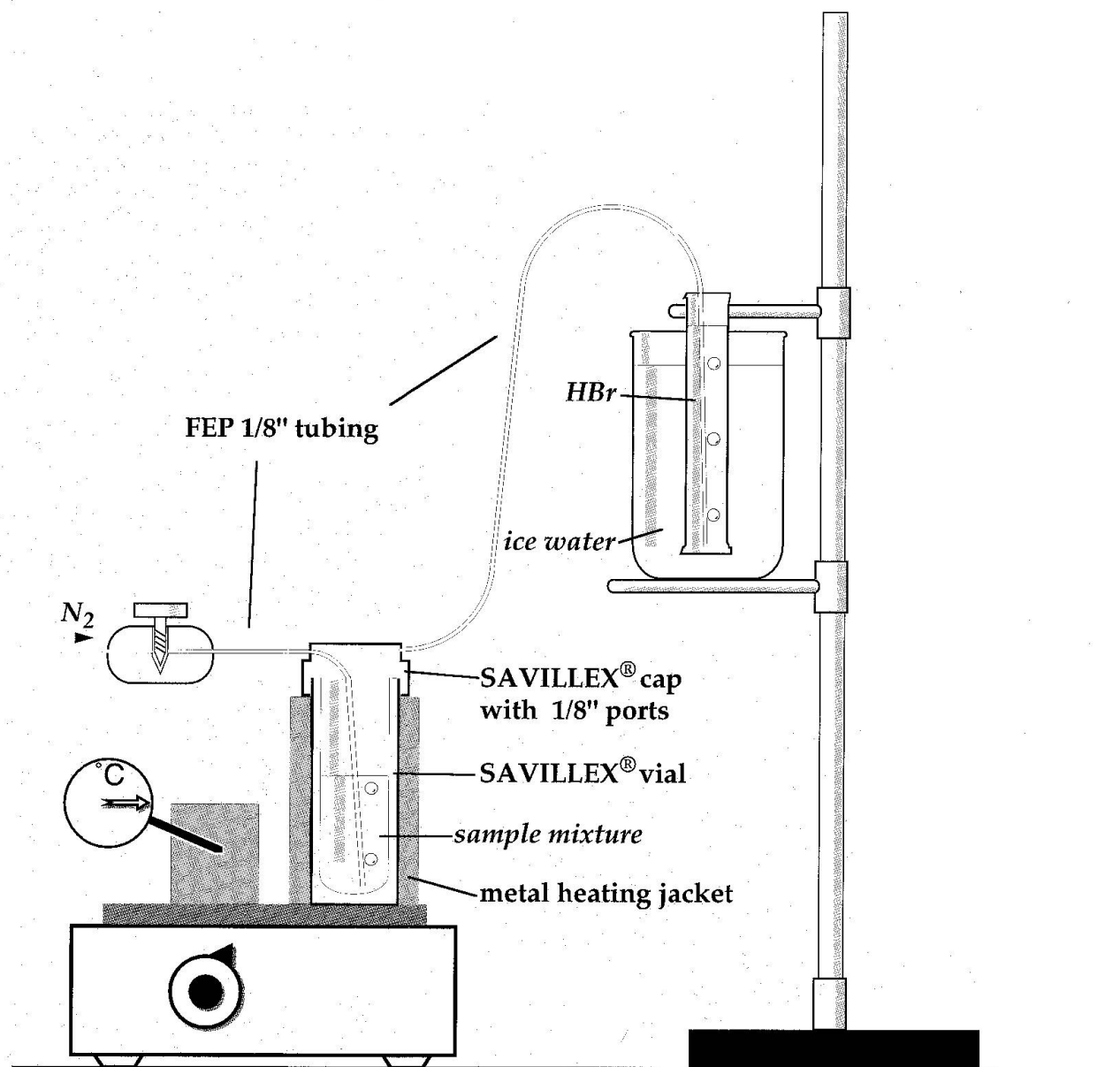


Fig. 1. Schematic sketch of the distillation apparatus (not to scale).

Tab. 1 "Plug in" osmium distillation yields.

Yield No	T (°C)	dist. period in min.	% Os recovered	step x of y
1a	110	0–60	35	1/4
1b	110	60–120	20	2/4
1c	110	120–180	20	3/4
1d		not dist.*	10	4/4
2	115	0–100	95	1/1
3	115	0–100	100	1/1
4	115	0–100	85	1/1
5	115	0–100	90	1/1
6	115	0–100	85	1/1

All fractions recovered in 8.8 M HBr. Yield percentages rounded to the closest figures in multiples of five. Data represent total yields from carius tube to end of distillation.

* Os recovered by liquid extraction from remaining solution, corrected for our liquid extraction yield (40%). The first experiment (yields 1a–1d) have been done without addition of 8 M HNO₃ to the sample mixture. For yield-experiments 1, 2 and 3 spike and standard-dosage was done volumetrically with pipettes, which may explain the unrealistic high value of yield 3. For yields 4–6 dosage was done precisely by weight, leading to more consistent results.

Os and Re concentrations have been determined by isotope dilution and measured as oxides with N-TIMS techniques on an AVCO 9000 mass-spectrometer. Os was measured from Pt filaments, and Re using our Ta filament technique (FREI et al., 1996).

(yield 1d) (COHEN and WATERS, 1996). The sum of detected Os in this experiment (1a–1d) adds to 85%, indicating, that a maximum of 15% of the total Os could have escaped the system. Part of this apparent loss may be explained by incomplete homogenization of distilled Os and the subsequently added spike solution, and by the uncertainty of the liquid extraction yield (Tab. 1). During this experiment the HBr trapping solution turned dark brown already during the first couple of minutes, due to the formation of Br₂. This indicates that HNO₃ was preferentially distilled relative to H₂O. In order to obtain the reverse effect, i.e. a preferential evaporation of H₂O (\pm HCl) relative to HNO₃ in the beginning of the distillation, we diluted the digestion solution with 5 ml of 8 M HNO₃ in the subsequent experiments. The color of the HBr turned only light brown within the first 15 min. Three parallel yields (4–6, Tab. 1) performed under these optimized conditions (i.e., keeping 115 °C during the entire distillation interval of 100 min.; slight dilution of the digestion solution) consistently gave recovery rates \geq 85%.

We successfully tested our distillation procedure for chromites (NÄGLER et al., in prep.) and

ore minerals (FREI and NÄGLER, 1996). Silicates have not been assessed yet but SHIREY and WALKER (1995) concluded that Re and Os are sufficiently extracted from silicates in the carius tube digestion. Similarly, FREI et al. (1997) monitored in detail, that metal cations (with some limitations to high-field strength elements) are efficiently leached by HNO₃ from silicates. We therefore are confident, that once Os is present in an oxidized state (achieved in the carius tube), our distillation is suitable for silicate material also.

BLANK LEVELS

One of the most crucial points to Re–Os analytics is the Re blank level. In our separation procedure the Re-bearing digest solution is only in contact with Teflon® material. In order to exclude cross contamination, the inlet tubing is replaced after each separation. We used double subboiling distilled HNO₃ (< 0.1 pg Re/ml) and Suprapur® HCl for sample digestion and ion-chromatography. Our total Re procedure blanks consistently remained below 30 pg. Most of this blank can be traced back to contributions from the column chemistry.

Our experiments involved the use of commercially available Suprapur® HBr (MERCK™) as the trapping liquid for Os. It is a potential major source for foreign Os in this procedure. However, its blank level was measured to be below 1 pg in the needed volumes.

Dissolution of samples under elevated temperatures and pressures in PTFE Teflon bombs occasionally produced memory effects for OsO₄ (ROY-BARMAN and ALLÈGRE, 1995). Up to now we have not observed cross contamination from our multiply re-used PFA Teflon® vials. Measured procedural blanks for Os remained below 1 pg. As a precaution, it may be advisable to separate different sets of vials for radiogenic, low concentration Os samples, and primitive high concentration samples.

Conclusions

The simplicity of our procedure and apparatus may contribute to a more efficient Re–Os isotope data acquisition. Its advantages are as follows:

- 1) The apparatus is composed solely of "off-the-shelf material" and can therefore be easily copied. Its "plug in" assembly simplifies the handling procedure. Furthermore, the number of parallel lines for simultaneous distillations can be conveniently increased to the needs of a laboratory.

2) It is time saving, because only one major distillation step for Os (from 2 : 1 HNO₃-HCl directly into HBr) has to be performed. When combined with carius tube digestion it avoids the use of extra oxidants and thus aliquotation of a Re fraction prior to distillation (e.g., LUCK and ALLÈGRE, 1991) or complicated oxidant purification (e.g., WALKER, 1988).

3) The narrow (1.5 mm inner diameter) tube supports laminar flow of N₂. Therefore, a constant bubble rate in the trapping solution receptacle can be easily adjusted. Further, no extra cooling system along the tube is needed.

4) Os recoveries compare to those reached by conventional Os distillations (> 80%), but are significantly better than those of liquid extraction techniques (≤ 50%, COHEN and WALTERS, 1996, and our own experiments).

Acknowledgements

We are thankful to Th. Meisel whose spike and standard solution were used in this study. Further his constructive review as well as the one of J. E. Snow were of great help. We are appreciative towards A.S. Cohen and F.G. Waters, Open University at Milton Keynes, who supplied us with a pre-print of their manuscript. Furthermore, we acknowledge support by Swiss National Foundation, grant No. 20-40442.94 to J.D. Kramers.

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Manuscript received November 14, 1996; revised manuscript accepted January 14, 1997.