High-efficiency photoreductive vapor generation of osmium

Richard M. de Oliveira, a Daniel L. G. Borges, a Patricia Grinberg b and Ralph E. Sturgeon a b

A novel, high yield (91 ± 5%) photochemical vapor generation (PVG) method is reported for Os, achieved via photo-reduction reactions in a 1% CH₃COOH medium containing 50 mg L⁻¹ Fe²⁺/²⁺. A sample flow rate of 2 mL min⁻¹ delivered to a flow-through photoreactor provided a 21 s irradiation time prior to passage of the volatile product to an inductively coupled plasma mass spectrometer for detection at m/z 192. A method detection limit of 0.16 pg mL⁻¹ was achieved, a 10-fold enhancement over that obtained using parallel photo-oxidation synthesis of OsO₄ from a 5% HNO₃ medium. Precision of replicate measurement was 4% (RSD) at 10 ng mL⁻¹. Although the identity of the product has not yet been ascertained by GC-MS, based on the chemistry of Os and the reaction conditions, as well as its difference in volatility from OsO₄, a carbonyl or alkyl-substituted carbonyl is suspected e.g., Os(CO)₄(CH₃)₂ and Os(CO)₄H₂.

1. Introduction

Photochemical vapor generation (PVG) is evolving into an elegant technique for enhancing analyte introduction efficiency with atomic and mass spectrometries, including atomic absorption (AAS), fluorescence (AFS), as well as inductively coupled plasma optical emission (ICP-OES) and mass spectrometry (ICP-MS). PVG has been demonstrated for transition metals, halogens as well as numerous metalloid elements amenable to conventional chemical vapor generation (CVG).

PVG typically relies on the generation of a highly reducing environment arising from production of solvated electrons (e⁻(aq)), H⁻ and CO₂⁻ radicals produced by the UV photolysis of low molecular weight carboxylic acids (RCOOH) or alcohols (ROH). Co-production of R⁻ and CO provides additional reactants to generate volatile hydrided, alkylated and carbonylated adducts of the analyte species. Exceptionally, the PVG of Os has been reported using UV photo-oxidation processes, resulting in the efficient production of (presumably) OsO₄. Several powerful oxidizers, including, HO⁻ and O⁻ are produced during photolysis of H₂O and HNO₃, permitting efficient generation from both dilute HNO₃ and pure H₂O. Zhu et al. utilized a home-made flow-through photoreactor interfaced to an ICP-OES for detection of Os, achieving a PVG generation efficiency of 96% and a limit of detection (LOD) of 0.2 ng mL⁻¹. The same group earlier reported a 51% generation efficiency for OsO₄ from pH 1.0 HNO₃ based on plasma mediated reactions in a solution cathode glow discharge source. Most recently, Gao et al. attained an LOD of 0.8 pg mL⁻¹ using a commercial flow-through photoreactor interfaced to an ICP-MS detection system. Both PVG studies highlighted the impact of solution temperature in that 90–100 °C was required to facilitate efficient phase transfer of OsO₄ from the irradiated medium, likely due to its relatively high solubility (60 mg mL⁻¹) in water.

Synthesis of volatile osmium species using typical PVG photo-reduction conditions employing carboxylic acids has not been reported. Based on the chemistry and the radical mediated mechanism of PVG, it is expected that a carbonylated product will be generated. Carbonylation of metals involves reduction of the metal center and is often performed at high temperatures and pressures of CO in an autoclave (Hieber process). Norton et al. have discussed the variety of mono- and poly-nuclear hydrido, alkyl and carbonyl complexes of osmium, including such species as Os(CO)₄(CH₃)₂ and Os(CO)₄H₂. Analogous carbonyl-, alkyl- and hydride-Os compounds likely constitute the potential volatile product(s) of this study, which remain unconfirmed at this time.

2. Experimental

The PVG system components are schematically illustrated in Fig. 1.

2.1 Instrumentation

Two photoreactors were examined. The performance of a low-pressure 19 W Hg discharge lamp (Beijing Titan Instrument Co. Ltd., Beijing, China) fitted with an internal channel of...
synthetic quartz (0.72 mL internal irradiated volume) through which the sample was pumped to expose the analyte to (primarily) 185 and 254 nm radiation (herein referred to as a flow-through lamp) was compared to that of a conventional Hg low-pressure 15 W germicidal lamp (Spectroline, USA). This latter photoreactor utilizes an externally wrapped 3 m length of 1.1 mm i.d. PTFE tubing (2.0 mL internal irradiated volume) through which the sample was pumped while being exposed to (primarily) 254 nm photons and has earlier been described elsewhere.31

Generated Os species were detected using an ELAN DRC II ICP-MS (PerkinElmer SCIEX, USA) operating in standard mode (i.e., no collision gas in the reaction cell) and fitted with conventional Ni sampler/skimmer cones. PVG analyte vapor emerging with the Ar carrier gas supplied to the GLS was directed to the base of the ICP torch via thin-walled PTFE tubing terminating in a ball and socket glass joint. All other conduits in contact with the PVG products comprised PTFE tubing. The dry plasma was sustained at 1150 W using 15 and 1.2 L min\(^{-1}\) Ar as plasma and auxiliary gas flows, respectively. Both 192Os and 190Os as well as 57Fe (and isotopes of other pertinent elements) were continuously monitored in peak hopping mode. Typical ICP-MS operating conditions are summarized in Table 1.

Sample solutions were propelled through either reactor at initially 2 mL min\(^{-1}\) via a Gilson Minipuls peristaltic pump (Mandel Scientific, Villiers, Le Bel, France), providing a sample irradiation time of 21 s in the flow-through device and 60 s in the germicidal unit. The irradiated solution was transported from the photoreactor to a glass thin-film GLS sourced from a model 2600 Tekran Instruments Corporation mercury analyzer (Toronto, Canada) to enable phase separation of the volatile analyte from the liquid for transport to the base of the ICP torch. A model 5830 Brooks mass flow controller (Emerson Electric Co., Hatfield, PA) provided an optimized flow of Ar to the GLS for this purpose.

Digestion of several Certified Reference Materials (CRMs) was undertaken using a Multiwave 3000 microwave system (Anton Paar GmbH, Austria).

UV-vis spectra of solutions were acquired on a Cary 5000 UV-Vis-NIR spectrometer (Varian Australia Pty Ltd.) using a matched set of 1 cm path length quartz cuvettes for reference (blank) and sample compartments.

2.2 Reagents and solutions

Working standards containing 100 µg L\(^{-1}\) Os(IV) were prepared by dilution of a 1000 mg L\(^{-1}\) stock solution (as (NH₄)₂OsCl₆) obtained from Sigma-Aldrich (St. Louis, USA). ACS-grade glacial acetic acid (99.7%), formic acid (≥88%) and hydrogen peroxide (35%) were sourced from Anachemia Chemicals (Quebec, Canada) and HF (ACS grade, 48%) was obtained from Thermo Fischer Scientific. In-house sub-boiling distillation of reagent grade feedstocks in a quartz still provided high-purity HNO₃ and HCl. Stock solutions of 5000 mg L\(^{-1}\) FeSO₄·6H₂O, Fe(NO₃)₃·9H₂O (Alfa Aesar), CuSO₄ (BDH Inc., Toronto), NiSO₄·6H₂O and CoSO₄·7H₂O (Baker Chemical Co., Philadelphia) were used as sources of transition metal ion sensitizers. All solutions were prepared in, and working solutions diluted with, 18 MΩ cm high-purity water generated in a Milli-Q Advantage system (Millipore Sigma, USA).

Three water samples, i.e., commercial bottled drinking water, local municipal tap water and freshly melted clean snow collected in Ottawa (January, 2021) were used to assess response. In addition to these simple, essentially matrix-free samples, several CRMs (available from the NRC), i.e., DORM-4 (Dogfish Muscle Tissue), MESS-4 (a moderately-contaminated marine sediment from the Beaufort Sea, Canada) and PACS-3 (a highly-contaminated marine sediment from Esquimalt harbor, BC, Canada) were also examined to determine Os spike recoveries from solutions of their digests, thereby providing an assessment of interference from concomitant species.

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**Table 1 ICP-MS operating conditions**

<table>
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<th>Parameter</th>
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<tr>
<td>RF power (W)</td>
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<tr>
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<tr>
<td>Isotopes monitored (m/z)</td>
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</tbody>
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**Fig. 1** Schematic of the PVG-ICP-MS experimental system: photolysis of the flowing sample occurs in a 19 W low-pressure flow-through Hg discharge lamp which is then directed to a gas-liquid separator (GLS) for transport of the volatile Os product in a stream of Ar via thin-walled PTFE tubing terminating in a ball and socket glass joint mated to the base of the central channel of the ICP-MS.
2.3 Procedures

A multielement solution covering the full m/z range was used for tuning the ICP-MS, as recommended by the manufacturer. After instrumental optimization, plasma parameters were set for detection of $^{192}$Os and $^{57}$Fe (as well as isotopes of other metal ion sensitizers subsequently tested) using conventional pneumatic nebulization (PN) sample introduction with a Meinhard nebulizer mated to a cyclonic spray chamber. Subsequently, the plasma was powered off, the nebulizer-spray chamber removed and the base of the ICP torch connected to the outlet of the GLS.

Test solutions containing 1 $\mu$g L$^{-1}$ Os(IV), 1% (v/v) CH$_3$COOH and 50 mg L$^{-1}$ Fe$^{2+}$ were used for the optimization of final PVG parameters. Samples (3 replicates) were introduced into either photoreactor by manually pipetting a 300 $\mu$L volume of analyte solution into the uptake of the peristaltic pump delivery line bracketed between leading and trailing aliquots of a solution of 1% (v/v) CH$_3$COOH. In this manner, sample irradiation time was independently and conveniently controlled while maintaining a constant, optimized supply rate of photolyzed sample to the GLS by simply stopping the delivery pump for desired time intervals once the total sample volume had rapidly entered the photoreactor. The impact of added Fe$^{3+}$ (5–100 mg L$^{-1}$) was studied in detail. Optimization of typical PVG parameters was undertaken, including sample irradiation time and GLS Ar gas flow rate. Both peak-height and area measurement modes were initially evaluated to characterize the transient signal profile.

Test solutions of the water samples were prepared to contain 1% CH$_3$COOH and 50 mg L$^{-1}$ Fe$^{2+}$. CRMs were subjected to digestion using an in-house procedure designed to effect total matrix dissolution (i.e., microwave assisted digestion). Replicate subsamples ($n = 3$) of nominally 0.25 g of each CRM were transferred to individual pre-cleaned Teflon digestion vessels. Aliquots of 10 mL HNO$_3$ (69%), 1 mL HCl and 3 mL HF were added to MESS-4 and PACS-3 samples, whereas 7 mL HNO$_3$ and 0.5 mL H$_2$O$_2$ were added to the DORM-4 samples. Digestion was undertaken at a microwave power of 1400 W using a 15 min ramp and 30 min hold time. Subsequently, the digests were placed on a hot plate in a laminar flow fume hood to remove residual HF and excess HNO$_3$ by evaporating them to near dryness followed by dilution to a final volume of 25 mL using 0.5% HNO$_3$. An aliquot of each sample was further diluted 10-fold with 1% CH$_3$COOH and spiked to contain 50 mg L$^{-1}$ Fe$^{2+}$. Unfortunately, no certified, reference or information values are available for Os in any of these CRMs.

2.4 Safety considerations

The full range and identity of compounds produced by the photochemical reactions is unknown. Standard safety precautions should be taken during all experiments and an adequate ventilation/exhaust system should be used.

3. Results and discussion

3.1 Reductive PVG media

Volatile oxidation products of Os produced by PVG reactions in pure water$^{31}$ and 5% (v/v) HNO$_3$ $^{30}$ have been earlier reported. In both scenarios, OsO$_4$ was assumed to be the generated species. Notably, sensitivity was increased at higher solution temperatures needed to enhance the phase separation efficiency, since OsO$_4$ is very soluble in water (6.2 g/100 mL at 25 $^\circ$C). As such, Zhu et al.$^{31}$ heated the photolysed sample in a 100 $^\circ$C oil bath prior to delivery to the GLS, whereas the lengthy irradiation time required in the procedure developed by Gao et al.$^{30}$ provided a solution temperature of 90 $^\circ$C upon its exit from the photoreactor. Neither study suggested the possibility of utilizing...
“typical” PVG photo-reduction conditions to generate a volatile Os species, relying instead on classical approaches requiring a strongly oxidizing environment.36

The feasibility of utilizing photo-reduction reactions was thus investigated in solutions containing 1 μg L⁻¹ Os(iv) prepared in either dilute CH₃COOH or HCOOH. The impact of added Fe²⁺, Fe³⁺, Ni²⁺, Co²⁺ or Cu²⁺ as a sensitizer was also examined. Generation from oxidizing media [presumably yielding OsO₄], including pure H₂O₂, 1% (v/v) H₂O₂, 5% (v/v) HNO₃, and 1% (v/v) H₂O₂ + 50 mg L⁻¹ Fe²⁺, was undertaken for performance comparisons. Sample flow rate was typically 2 mL min⁻¹ with the flow-through photoreactor and 1 mL min⁻¹ for comparison experiments using the germicidal photoreactor.

Results for the flow-through photoreactor, shown in Fig. 2, confirm the high PVG efficiency reported for Os in 5% (v/v) HNO₃.38 Surprisingly, an equivalently efficient process was evident when using 1% CH₃COOH in the presence of added Fe²⁺, Fe³⁺ (not shown for brevity) or Co²⁺. Signal intensities in the presence of these metals were 2.4-fold greater than that achieved in a 1% CH₃COOH solution alone. Although the reaction medium comprising 50 mg L⁻¹ Cu²⁺ in 1% CH₃COOH resulted in significant generation of a volatile form of Os, response remained 2-fold lower than that obtained using either Fe²⁺ or Fe³⁺ (Fe³⁺ for brevity). Attempts to undertake PVG of Os in 1% HCOOH (despite addition of Cu³⁺ or Fe³⁺) or 1% (v/v) H₂O₂ (even in the presence of Fe⁵⁺) were significantly less attractive compared to the CH₃COOH (Fe³⁺ or Co²⁺) and HNO₃ media. The presence of Fe³⁺ in 1% CH₃COOH generated ~4-fold greater efficiency than a solution of Fe³⁺ in 2% HCOOH. Using the germicidal photoreactor, PVG of Os from solutions of CH₃COOH containing Fe³⁺ or Co²⁺, and from 5% HNO₃ provided ~2-fold lower responses than those obtained with the flow-through photoreactor. Sample delivery to the GLS was maintained at 2 mL min⁻¹ for the flow-through photoreactor for all photo-reduction experiments. However, optimal irradiation times needed for processing the pure water system were longer than those for all other media, i.e., 80 s (corresponding to sample flow rate of 0.5 mL min⁻¹) in the flow-through photoreactor. These were in functional agreement with the conditions used by Zhu et al.,39 in that PVG efficiency increased with elevated solution temperature. Nevertheless, generation efficiency in pure water remained poor, i.e., 5-fold lower than that obtained in either 5% HNO₃ or the acetic acid/Fe⁵⁺ medium. Despite equivalent performance achieved with addition of either Fe³⁺ or Co²⁺ in 1% CH₃COOH, Fe²⁺ was arbitrarily selected for further investigation.

3.2 Optimization of PVG conditions

3.2.1 Impact of GLS performance. To ensure maximum transmission efficiency of the generated product to the ICP, operation of the GLS must also be optimized, specifically the flow rate of Ar carrier gas. Based on a photolyzed sample feed rate of 2 mL min⁻¹, Ar flow was varied from 150–800 mL min⁻¹. Transfer efficiency to the ICP was poor in the 100–200 mL min⁻¹ range. Enhanced phase separation/vapor transport efficiency was achieved using flow rates of 500–700 mL min⁻¹ with an optimum condition selected as 600 mL min⁻¹. The decrease in signal beyond 700 mL min⁻¹ is likely due to dilution of the volatile product. Note that any change in the depth of sampling initially established for detection of Os using PN sample introduction induced by optimization of the GLS Ar flow was not investigated as the selected flow rate was not significantly different from the nebulizer gas flow used for PN.

3.2.2 Optimization of irradiation time. Sample irradiation times from 5–84 s (corresponding to sample flow rates of 8.4 to 0.5 mL min⁻¹) were evaluated using the flow-through photoreactor. This study was conducted using rapid introduction of a 300 μL volume of test solution into the irradiation zone, allowing it to remain there for varying periods of time, and subsequently delivering it to the GLS at a constant flow of 2 mL min⁻¹. This procedure ensured that the efficiency of the GLS was not a variable affecting the results. The photoreactor was powered off to achieve an irradiation time of 0 s. Fig. 3A shows that in the range 5–21 s, response increases significantly with irradiation time. Times < 21 s were insufficient to drive the reaction to completion. However, excessive exposure of the sample caused signals to dramatically decrease, possibly due to either thermal- or photo-decomposition of the generated analyte species (discussed below). An optimal irradiation time of 21 s was selected for further study and reflects a balance between rates of generation and decomposition, which in this photoreactor corresponds to a sample flow rate of 2 mL min⁻¹. Surprisingly, Os species were also most efficiently generated in a 5% (v/v) HNO₃ medium using an irradiation time of only 21 s,
considerably shorter than the 150 s reported by Gao et al.,30 despite use of an identical flow-through photoreactor. Increasing irradiation time to 150 s resulted in a very significant decrease in signal, 170-fold lower than that achieved at 21 s, possibly a consequence of higher sample irradiance achieved in this study (potentially newer lamp) leading to photodecomposition of the product. It has been demonstrated that the presumed OsO₄ generated in this medium is stable and benefits from elevated solution temperature.36,31

Fig. 3B illustrates the influence of irradiated sample flow rate to the GLS on response with the flow-through photoreactor. The optimal irradiation time of 21 s was fixed (Fig. 3A) and the delivery of the irradiated sample to the GLS was varied from 0.5–8.4 mL min⁻¹. A substantially linear relationship between flow rate and response occurs in the range 0.5–2 mL min⁻¹, beyond which the efficiency of the GLS unit rapidly declines and the majority of the analyte is passed to waste as there is insufficient time for complete phase separation to occur. Optimum conditions were thus established as 2 mL min⁻¹ for irradiation of the sample and its delivery to the GLS for phase separation.

Vapor generation of Os was similarly evaluated using the germicidal lamp; irradiation times from 5–180 s were examined. Good response (no figure shown) was achieved in the range 60–120 s (corresponding to sample flow rates of 2 and 1 mL min⁻¹, respectively). At shorter times, the photo-reduction reactions were incomplete due to the comparatively low irradiance available with this photoreactor. This system uses PTFE for transport of sample during irradiation (35% absolute transmittance at 254 nm), which occurs external to the low-pressure discharge and further shielded from it by standard quartz housing (i.e., no 185 nm radiation and reduced irradiance from 254 nm). At 120 s, response was 4.5-fold higher than that at 5 s, but decreased thereafter to a level of 40% using a 180 s irradiation time, likely due to photo-decarbonylation, a favorable mode of decomposition with metal carbonyls57 (note that the temperature of the irradiated solution in this reactor never rises above ambient). As the germicidal photoreactor provided an optimal response some 2.3-fold smaller than that of the flow-through reactor, its further characterization was discontinued during this study. It is significant to conclude that 185 nm radiation does not play a major role in the synthesis of the volatile Os product.

3.2.3 Effect of solution temperature. Considering that both prior PVG studies of Os noted the importance of reaction temperature on response during photo-oxidation,36,31 this parameter was also evaluated for its effect during photo-reduction. A controlled temperature water bath was positioned between the outlet of the flow-through reactor and the inlet of the GLS in order to subject irradiated solutions to variable temperatures in the range 25–100 °C. This was accomplished by delivering the irradiated solution to a small quartz coil immersed in the water bath. As shown in Fig. 4, and in agreement with earlier reports,38 elevated temperature results in an increase in signal intensity by over 60% when PVG is undertaken in 5% (v/v) HNO₃. Surprisingly, a completely opposite thermal effect is evident for PVG of Os generated under photo-reducing conditions, (1% (v/v) CH₃COOH in the presence of 50 mg L⁻¹ Fe(III)] with response decreasing by up to 90% at a bath temperature of 100 °C. Clearly, a different volatile Os compound is generated during photo-reduction reactions, e.g., Os[Co]₄(CH₃)₂H₅; product identification by GC-MS is yet required for confirmation.

3.2.4 Reduction medium. Optimization of the composition of the generation medium was undertaken by examining PVG response from Os over a range of 0.5 to 30% (v/v) CH₃COOH containing 5–100 mg L⁻¹ Fe(III); results are summarized in Fig. 5. PVG was evident even in 0.5% CH₃COOH, but optimal response was achieved at 1% CH₃COOH, wherein a 50-fold enhancement occurred compared to the signal generated in pure water (0% CH₃COOH). This was followed by decreased response at higher concentrations of CH₃COOH, possibly due to a UV shadowing effect of the strongly absorbing acetic acid limiting the penetration depth of photons into the solution at higher concentrations, or the sequestering of CO (presumably needed for synthesis of the volatile species) by its reaction with H₂C=CH₂ to yield acetyl radicals,38 altering chemical synthesis of the desired product.

3.2.5 Effect of added iron on PVG. The impact of added iron sensitizer is shown in Fig. 5B. The presence of 5 mg L⁻¹ Fe(III) in 1% CH₃COOH resulted in a doubling of the signal intensity. Thereafter, response increased more slowly with increasing Fe(III), reaching a maximum at 50 mg L⁻¹. An optimal concentration of 50 mg L⁻¹ was thus selected, with the constraints that adding more may potentially lead to an increase in analyte contamination as well as induce a UV shadowing effect due to strong UV absorption by iron complexes.

Although metal ion sensitizers have become more widely utilized as effective agents for increasing PVG yields of many
analysts, apart from their role in the PVG chemistry of the halogens, little is understood of their mechanism of action in other systems. The precise role played by added iron (or other sensitizers) in this system is unknown. It is well-recognized that photochemical reactions of transition metal ions and their carboxylate complexes contribute to enhancing the reduction properties of the sample solution. UV-induced charge-transfer-to-solvent (CTTS) processes result in oxidation of metals such as Fe(II) to Fe(III), Cu(II) to Cu(III), charge-transfer-to-solvent (CTTS) processes result in oxidation of metals such as Fe(II) to Fe(III), Cu(II) to Cu(III), etc., with the release of an aquated electron (e\(^{aq}\)), available for direct reduction reactions or subsequent creation of H\(^+\) by scavenging H\(^2\). Additionally, transition metal carboxylate complexes are readily photolyzed by UV-B radiation, induced by ligand-to-metal charge transfer (LMCT) processes, and lead to additional production of highly reducing CO\(_2\)\(^-\). responsible for driving the redox chemistry in PVG media. In the present system, Os can be reduced from its IV oxidation state to zero, followed by attack with H\(_2\)C\(^\cdot\), H\(^+\) and CO present in the solution, leading to volatile (unknown) organometallic species. As a chloride complex of Os was investigated in this study, it is possible that through sequential reductions, alkylations and/or carboxylations, the final steps of the full synthesis may be realized by the added transition metal ion serving as an acceptor for the remaining chloride ligands during potential redox reactions of this metal center. Note that no significant signals could be detected for \(^{57}\)Fe or any of the other added transition metals as experimental conditions are far from optimal for PVG of these elements. Investigation of the UV-vis spectra of unphotolysed solutions of Os(IV) in 1% CH\(_3\)COOH with and without the various added metal ion sensitizers revealed no apparent alteration in the characteristic absorption bands readily seen and attributed to only Os(IV).

3.3 Interference from NO\(_3^–\) and NO\(_2^–\)

The presence of either NO\(_3^–\) and NO\(_2^–\) is known to cause severe interference with many PVG photo-reduction systems due to their high affinity for the reducing radicals that drive the desired analytical reactions. The impact of added NO\(_3^–\) and NO\(_2^–\) on the generation efficiency of Os was thus evaluated in the range 0.1 to 15 mmol L\(^{-1}\) in a medium comprising 1 \(\mu\)g L\(^{-1}\) Os, 50 mg L\(^{-1}\) Fe\(^{3+/2+}\) and 1% CH\(_3\)COOH. Results are presented in Fig. 6, showing >20% suppression occurs in the presence of only 0.1 mmol L\(^{-1}\) NO\(_3^–\) or NO\(_2^–\). With higher concentrations, up to 60% loss in generation efficiency occurs. In addition to the consumption of needed reducing radicals by these oxidizing anions, both absorb strongly at 254 nm, reducing the effective irradiance of the solution, further contributing to decreased availability of reducing radicals due to their shadowing effect. Clearly, this shortcoming is not present when oxidative PVG is undertaken to generate OsO\(_4\) from pure water or 5% nitric acid and is further evidence of synthesis of a distinctly different compound under reducing conditions.

Interferences of this magnitude from the presence of NO\(_3^–\) or NO\(_2^–\) can be managed using several different pretreatment approaches. 3.4 Analytical figures of merit

Table 2 summarizes relevant figures of merit achieved under optimal generation conditions (i.e., 1% CH\(_3\)COOH, 50 mg L\(^{-1}\) Fe\(^{3+/2+}\) with the flow-through photoreactor. Comparative performance figures for oxidative PVG in 5% HNO\(_3\) are also presented. Calibration functions using peak-height recording (y = ng mL\(^{-1}\)) were evaluated over a concentration range 0.2–3 ng
mL⁻¹, yielding: y = 1 834 00x – 2 100 (R² = 0.9993) for the CH₃COOH/Fe³⁺ medium and y = 2 001 00x – 9 800 (R² = 0.9988) for the 5% HNO₃ medium, revealing a difference in sensitivity of ~8%. Based on a comparison of the signals achieved with a 1 ng mL⁻¹ solution of Os totaling (~10⁻¹²) using either PVG (2 mL min⁻¹) or PN (1 mL min⁻¹) introduction techniques, enhancements of 25- and 27-fold in sensitivity relative to PN were obtained using the CH₃COOH/Fe³⁺ and 5% HNO₃ generation media, respectively. Although calibration functions using the germicidal lamp were also evaluated, the flow-through photoreactor provided an approximately 2.3-fold greater response, attributable to its enhanced sample irradiance as well as availability of the 185 nm radiation increasing production of reducing radicals, which may enhance yields.

Limits of detection (LODs) with the flow-through reactor, calculated as 3 times the standard deviation of the blank solution (s₀, n = 10), were 0.16 and 1.6 pg mL⁻¹ using the CH₃COOH/Fe³⁺ and 5% HNO₃ media, respectively. Limits of quantitation (LOQ, calculated as 10 s₀), were 0.5 and 5 pg mL⁻¹ respectively, with these two different PVG media. Despite similar sensitivity for both, the blank signal intensity at m/z 192 arising from the reductive system was 5.5-fold lower, corresponding to an absolute concentration of 2 pg mL⁻¹. The LOD achieved herein with the reductive PVG medium and ICP-MS detection presents a 5-fold improvement over that reported by Gao et al., following oxidative PVG in a solution of 5% HNO₃. As the instrumental background at m/z 192 was negligible, the measured intensities appeared to be due to contamination by Os in the blank solutions. Note that significant memory effects occur using the 5% HNO₃ generation medium and thus, despite careful washing, elevated signals may still be present during assessment of blank contamination, giving rise to the elevated LOD in 5% HNO₃ reported in this study and, by comparison, in that reported by Gao et al.,³⁸ Relative standard deviation (RSD, n = 10), expressing the precision of replicate peak-height measurements of a 1 ng mL⁻¹ standard, was typically 4% in both PVG media. For comparison, the RSD arising from signal integration of replicate (n = 10) introduction of the same Os concentration into the photoreactor was degraded to approximately 7%, hence the preference for characterization using peak-height measurements.

PVG generation efficiency was estimated following determination of residual Os content in the photolyzed waste solution carefully harvested from the GLS system. Samples of this waste were analysed using PN sample introduction with intensities compared to the identical matrix-matched but non-photolyzed feed sample. Reductive PVG efficiencies of 91 ± 5% (n = 3) were obtained characterizing the flow-through photoreactor.

Attempts to estimate oxidative PVG efficiency from the 5% HNO₃ medium were unsuccessful due to high and variable memory effects. Efforts to decontaminate the photoreactor and GLS system with a solution of 5% NH₄OH, as recommended by Gao et al.,³⁸ were ineffective. Perhaps for this reason these authors were unable to independently provide an estimated generation efficiency, whereas Zhu et al.,³¹ reported a value of 96% for oxidative PVG of Os from a pure water medium. Note that the 91% estimated herein is based on the assumption that all Os depleted from the photolyzed waste solution actually enters the ICP and contributes to response. Other loss mechanisms following photolysis include decomposition/deposition in the transfer lines or on other intermediate surfaces, which would serve to bias the estimate to a more favorable overall generation efficiency.

### 3.5 Application to real samples

Analytical application of the methodology was evaluated by assessing Os spike recoveries from three water samples (commercial bottled drinking water, local municipal tap water and freshly melted clean snow collected during January, 2021 in Ottawa), as well as several digested samples of CRMs. A spike recovery test was undertaken following addition of 1 ng mL⁻¹ Os(iv) to each sample subjected to PVG. As shown in Table 3, the Os concentrations in all six samples were below the procedural LOQ. Spike recoveries from 94 to 109% were obtained, measured against response from a matrix-free calibration standard, thereby revealing no significant signal perturbation due to concomitants typical of such digested sediment and biological tissue sample matrices. Although estimated upper concentrations of Os are presented for the CRMs, their digestion was not validated for potential losses or complete solubilization of endogenous Os species despite the use of closed vessels for digestion. Thus, the data presented in Table 3 may

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<th>Recovery/%</th>
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<tr>
<td>Snow</td>
<td>0</td>
<td>&lt;0.5⁶</td>
<td>95 ± 5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.95 ± 0.05⁶</td>
<td></td>
</tr>
<tr>
<td>MESS-4</td>
<td>0</td>
<td>&lt;0.5⁶</td>
<td>94 ± 2</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.94 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>DORM-4</td>
<td>0</td>
<td>&lt;0.5⁶</td>
<td>109 ± 9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.09 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>PACS-3</td>
<td>0</td>
<td>&lt;0.5⁶</td>
<td>94 ± 1</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.94 ± 0.01</td>
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</tr>
</tbody>
</table>

⁴ Limit of quantitation (LOQ), pg mL⁻¹. ⁵ Os concentration, ng mL⁻¹. ⁶ Os concentration in the solid CRM (ng g⁻¹), accounting for 10⁵-fold dilution arising from sample preparation.
only realistically be used to conclude that the PVG process itself is unperturbed by concomitant elements in such digests, reflecting a degree of freedom from interference.

4. Conclusions

This is the first report of the high yield synthesis of a volatile organo-osmium species under ambient laboratory conditions and should be of significant interest to not only the analytical and geo-analytical communities, but also synthetic inorganic and organic chemists. Reductive PVG of Os from a 1% CH₃COOH/Fe³⁺ medium versus its oxidative PVG from 5% HNO₃ and the opposing impact of solution temperature on response in these two systems strongly implicate synthesis of different volatile species. It remains to identify the compound generated and undertake additional analytical application of the methodology using samples of known and quantifiable Os content.

The presently developed system offers several advantages over its oxidative counterpart, including: faster throughput of samples due to the significantly shorter required irradiation time; no need for elevated temperatures to assure efficient phase transfer; improved LOD and no issues relating to memory effects. However, as a consequence of the use of a reductive PVG system, the presence of oxidizing species, such as nitrate and nitrite, may lead to potential signal suppression. This shortcoming needs to be considered when applications to real samples are undertaken, but effective pretreatment procedures exist to deal with this as has been demonstrated herein.

Conflicts of interest

There are no conflicts of interest to declare.

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