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Detection of Bromine by ICP-*oa*-ToF-MS Following Photochemical Vapor Generation

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ABSTRACT: A unique flow-through photochemical reactor is utilized for the generation of volatile methyl bromide from aqueous solutions of bromide and bromate ions in a medium of 2% acetic acid containing 3000 $\mu g/mL$ NH$_4$Cl. The volatile product is transported to a thin-film gas–liquid phase separator and directed to an inductively coupled plasma (ICP) tine-of-flight mass spectrometer for detection and quantitation using either of the ^{79}Br or ^{81}Br isotopes. Utilizing a sample flow rate of 3.3 mL/min and a 13 s irradiation time, a detection limit of 0.14 ng/mL is achieved, yielding a 17-fold enhancement over conventional solution nebulization. The estimated generation efficiency of 95% provides for a significant increase in analyte transport efficiency to the ICP. Precision of replicate measurement is 2.5% (RSD) at 20 ng/mL. The methodology was validated by successful determination of bromine in reference materials, including IRMM (BCR-611) low level bromide in groundwater, NIST SRM 1568b Rice Flour, and SRM 1632 bituminous coal.
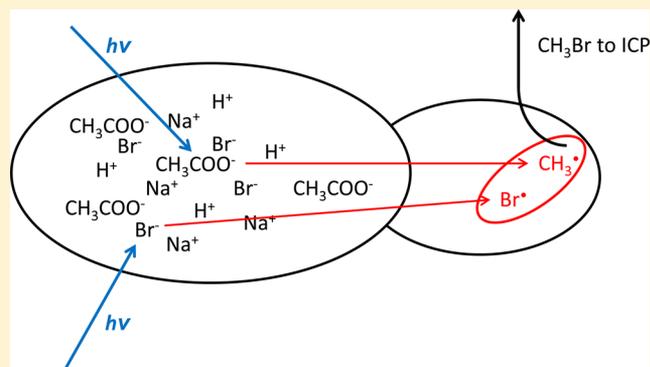
Only recently has bromine been identified as an essential trace element, important for the development of collagen in mammals.[1] Current major interest in this element arises from its widespread usage in industrial materials, including fire retardants, agricultural pesticides and pharmaceuticals. Treatment of groundwater by ozonolysis[2] to ensure potability raises concerns over production of bromate disinfection byproducts which, as a consequence of potential carcinogenic activity, has resulted in maximum permissible levels of 10 ng/mL being mandated in such waters in the US and several European countries.[3] Brominated organic compounds from natural and anthropogenic sources are widely dispersed in the atmosphere[4−7] and regarded as "hazardous", as bromine is 50−60-fold more effective than chlorine in destroying ozone and CH$_3$Br is estimated to be responsible for approximately 15% of halogen-catalyzed ozone destruction in the upper atmosphere.[8,9]

Recently, Flores and colleagues[10] comprehensively reviewed methodologies utilized for sample preparation and detection of bromine (and the halogens in general). Special precautions are required with most preparation procedures as use of mineral acids must be avoided to prevent losses of volatile halogen species; reliance on combustion bombs, pyrohydrolysis and alkaline solubilization techniques has emerged as preferable alternatives. Interestingly, solid sampling with the graphite furnace, when combined with inductively coupled plasma mass spectrometry (ICP-MS) for detection, is free of this limitation and provides one of the most sensitive of techniques available for detection of bromine, characterized by a limit of quantitation of 30 ng/g.[11] Although ICP-MS constitutes the majority of instrumental approaches for subsequent quantita-

tion, the high ionization potential of Br (11.8 eV) yields a low degree of ionization[12] (∼10%) and method detection limits, even with sector field instrumentation, are typically no better than 20 ng/g.[13]

It is well-recognized that sample introduction with pneumatic nebulization suffers poor efficiency, with typically only 1−3% of the generated aerosol reaching the plasma when sample flow rates of 1 mL/min are used to feed concentric nebulizers.[14] Consequently, it has been noted that the ideal sample for an ICP would be gaseous.[15] Vapor generation fulfills such an objective,[16−21] providing enhanced limits of detection not only as a result of increased analyte introduction efficiency but also as a consequence of the substantially increased mass flux of sample (several mL/min readily processed). Conventional chemical vapor generation utilizing powerful reductants such as sodium tetrahydroborate is ineffective for vapor generation of the halogens. However, recent work with photochemical vapor generation (PVG)[16,18,22] highlights promising applications for this purpose. Although iodine was readily amenable to PVG, generating methyl iodide upon irradiation of a dilute solution of acetic acid to yield an analyte introduction efficiency of 94% (40-fold enhancement in sensitivity),[23,24] bromine proved intractable under all experimental conditions investigated.

Recently, Qin et al. reported on use of a high efficiency flow-through UV reactor that has been demonstrated suitable for PVG of mercury,[25] and more recently for Sn,[26] as well as providing a relatively thin-film of sample for irradiation of

highly UV-absorbing gasoline to enable efficient reduction of mercury in this matrix.[27] It has been postulated[22] that efficient PVG of bromine may be possible if the sample can be irradiated with intense, deep UV radiation (185 nm); this flow-through lamp provides such access and was used herein to evaluate the feasibility of PVG of bromine.

■ EXPERIMENTAL SECTION

Instrumentation. Measurements were undertaken with inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometry (ICP-*oa*-ToF-MS, GBC Optimass8000, GBC Scientific Equipment Pty Ltd., Australia). System parameters were individually optimized for response when using either solution nebulization[28] or PVG for sample introduction. This was conveniently implemented with use of a Conikal concentric 1 mL/min nebulizer coupled to a cyclonic spray chamber having an auxiliary port for introduction of vapor generated species (Twister, P/N 20-809-0380HE, Glass Expansion, Pocasset MA). Both ^{79}Br and ^{81}Br were monitored in analog mode using integration times ranging from 1 to 5 s, depending on the sample concentration and its mode of introduction. Sample solution was delivered to the nebulizer at a nominal flow of 1 mL/min using a Gilson Minipuls 3 peristaltic pump (Mandel Scientific, Villiers, Le Bel, France), which also served to evacuate waste from the spray chamber.

The principal PVG reactor was composed of a low pressure flow-through 19 W mercury discharge lamp (Beijing Titan Instrument Co. Ltd., Beijing, China) having an internal solution channel volume of approximately 0.72 mL.[25] Effluent from the PVG reactor was directed to a glass thin-film gas liquid separator (GLS) from a model 2600 Tekran Instruments Corporation (Toronto, Canada) mercury analyzer. Solution delivery to the PVG reactor and waste evacuation from the GLS was accomplished using a separate Gilson Minipuls 3 peristaltic pump typically operating so as to provide a solution feed of 3 mL/min. A flow of Ar passing through the GLS via a Brooks model 5850 mass flow controller (Emerson Electric Co., Hatfield, PA) typically in the range of 300 to 600 mL/min, served to strip the volatile bromine species from the liquid phase and transport it to the gas inlet of the spray chamber. With the PVG in operation, no solution was delivered to the nebulizer but the nebulizer gas was maintained at 0.8 L/min so that the sampling depth in the plasma could be set by adjusting the torch position once the combined nebulizer and GLS flows were optimized. Figure 1 provides a schematic of the experimental system.

Secondary PVG systems that were also examined for performance included a combined UV spray chamber[29] successfully used for PVG of iodine[23,24] and a 15 W germicidal lamp wound with 2 m of thin wall Teflon tubing, as earlier described for use with mercury vapor generation.[30] The latter was connected to the thin-film GLS.

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.

Compressed air was used to feed a model RMU16 ozone generator (Azco Industries Ltd., Langley, BC) to undertake ozonolysis of aqueous samples of bromide in an effort to oxidize the species to bromate. Generated ozone (16 g/h) was passed through a sintered glass disk immersed in the solution to ensure saturation. Varying periods of reaction time were investigated.
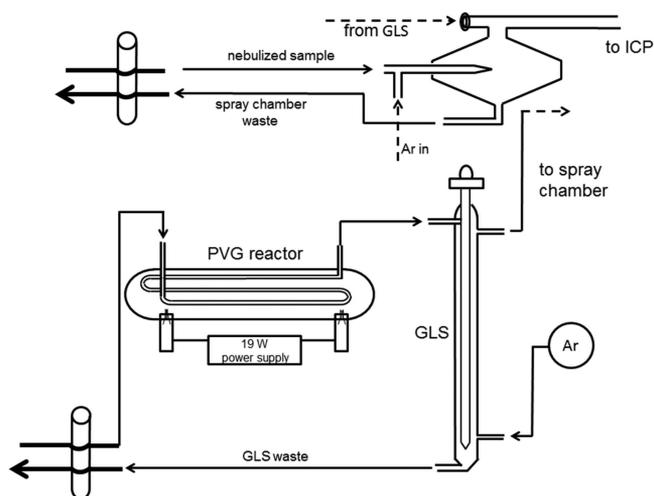

Figure 1. Schematic of experimental system. Rapid change from solution nebulization to PVG vapor generation sample introduction is achieved utilizing a dual inlet cyclonic spray chamber.

Reagents and Materials. ACS grade sodium bromide and bromate were sourced from Anachemia Chemicals Ltd. (VWR international, Ville Mont-Royal, Quebec, Canada). Formic acid (Veritas grade, 88%) was purchased from GFS Chemicals (Powell, OH), propionic acid (99%,) was sourced from Thermo Fisher Scientific and several grades of glacial acetic acid were examined, including ACS and high-purity Optima grades (>99.7%, Thermo Fisher) as well as high-purity baseline grade (Seastar Chemicals Inc., Sydney, BC, Canada). All solutions were prepared in 18 MΩ·cm resistivity high-purity water (DIW) available from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feedwater (Barnstead/Thermolyne Corp., Dubuque, IA). Ammonium carbonate (ACS grade, >99.5%) and zinc oxide (99.9%, −200 mesh powder) were purchased from Sigma-Aldrich (Steinheim, Germany) and Alfa Aesar (Ward Hill, MA), respectively. High-purity hydrochloric acid was prepared by sub-boil distillation of reagent grade feedstock using a quartz still; environmental grade (20−22%) ammonium hydroxide was sourced from Anachemia (Lachine, QC, Canada). A solution of ammonium chloride modifier was prepared by mixing 10 mL of sub-boil distilled HCl with 7 mL of high-purity NH₄OH followed by addition of 13 mL of DIW. ACS grade phosphoric acid (Fisher Scientific) was used for pH adjustment of some solutions prior to PVG.

Method validation was performed using a suite of reference and certified reference materials, including IRMM BCR-611 low level bromide in groundwater, (Geel, Belgium), NIST SRM 1568b Rice Flour and NIST SRM 1632 bituminous coal (Gaithersburg, MD).

Procedure. Optimization and mass calibration of the ICP-*oa*-ToF-MS was undertaken using solution nebulization sample introduction with 200 ng/mL feed solutions of Br⁻ or BrO₃⁻ as well as a mixed 10 ng/mL multielement tuning solution, as described by Sturgeon et al.[28] With mass spectrometer parameters optimized, generation of volatile bromide species was undertaken using the PVG reactor, and experimental conditions yielding maximum response and stability were identified, including solution matrix composition and irradiation time (flow rate through the PVG reactor) as well as Ar gas transfer flow rate through the GLS. Once established, calibration functions were derived and limits of detection

estimated, permitting performance metrics relative to solution nebulization to be compared.

Relative response from Br^- or BrO_3^- was noted for both solution nebulization and PVG sample introduction under optimum conditions of each. Bromide salts were dried at 105 °C in an air convection oven for 2 h prior to gravimetric preparation of their 1000 mg/mL stock solutions in DIW. Working spikes were prepared by serial dilution in DIW.

A sintering agent was prepared from $NaCO_3$ and ZnO according to the directions of Österlund et al.[31] Nominal 0.3 g subsamples of SRM 1568b Rice Flour and SRM 1632 bituminous coal (Gaithersburg, MD) were prepared in precleaned porcelain boats and sintered in a muffle furnace for 2 h at 560 °C following the procedure of Österlund et al.[31] The cooled residue was transferred to a clean screw-capped polypropylene bottle and dissolved in 20−40 mL DIW. Excess salt was allowed to precipitate by standing overnight at room temperature before a subsample of the supernatant was further diluted with a 2% solution of acetic acid for analysis by standard additions using PVG sample introduction. A dry weight correction factor for moisture content (drying over magnesium perchlorate for several days) was undertaken for these samples. For IRMM BCR-611 (low level bromide in groundwater), an ampule was opened and the contents diluted 5-fold with 2% acetic acid and submitted to analysis by PVG. Corresponding blanks were prepared for all samples. The impact of addition of an ammonium chloride "modifier" to all sample solutions was examined and analyses by PVG were conducted following spiking of all solutions to ∼3000 μg/mL NH_4Cl by the addition of 1 mL of the stock modifier to 50 mL of sample.

The identity of the photochemical reaction product was established by directing the gas phase from the outlet of the GLS to a clean, Ar-flushed 1 L glass cylinder fitted with stopcocks at either end and a septum port in the center. A 10 mg/L solution of either bromide or bromate was continually processed through the UV reactor, allowing the effluent to flush the gas sampling bulb (ultimately directed to a fume cupboard). After several minutes, the stopcocks were closed. A 250 μL aliquot of the contents was sampled with a gas sampling syringe and injected into a gas chromatography−mass spectrometry (GC−MS) instrument fitted with a DB-624 column (length, 60 m; stationary phase, 6%-cyanopropyl-phenyl-94%-dimethyl polysiloxane; 0.25 mm inner diameter; 1.40 mm coating). The inlet liner temperature was 200 °C, and the injection was performed in split mode (20:1). A temperature program comprising 10 min at 35 °C, rising at 20 °C/min to 240 °C with a hold for 2 min was undertaken in a constant He flow of 1 mL/min. The temperature of the transfer line was 240 °C and the mass spectrum was acquired over the range m/z 35−150 with EI at 70 eV.

Safety Precautions. The vapor phase bromine species produced in the presence of acetic acid has been identified as methyl bromide. PVG with real sample matrices may result in generation of additional potentially toxic volatile metal species. Standard good laboratory practice is required in preparing all reagents and solutions. The volatile product issuing from the PVG reactor is directed to either the ICP spray chamber for safe exhaust, or to a fume cupboard when the products are being captured for subsequent GC−MS identification.

■ **RESULTS AND DISCUSSION**

Nebulization of solutions of either Br^- or BrO_3^- in both DIW and 2% acetic acid media provided the same response, within

their precision of measurement, confirming equivalent (and accurate) preparation of the solutions from either of the dried salts as well as no impact arising from the anionic form of bromine. Using a 5 s integration time and steady-state pneumatic sample introduction at 1 mL/min (optimum nebulizer gas flow rate of 800 mL/min), an estimated limit of detection (LOD) based on measurements of Br^- at m/z 79 was 2.4 ng/mL with a relative standard deviation of 1.9% at a concentration of 40 ng/mL. The abundance sensitivity of the ToF instrument is approximately an order of magnitude poorer than that of a quadrupole,[28] creating an elevated background on m/z 79 from the rising edge of $^{80}Ar_2^+$ (and also on m/z 81 from the tail of $^{80}Ar_2^+$). Monitoring m/z 81 was also feasible but the substantially increased background due to the isobaric Ar_2H^+ molecular ion at this mass raised the detection limit some 7-fold. Use of either a quadrupole or sector field instrument[13,32] should serve to significantly improve these LODs, due to the enhanced sensitivities and abundance sensitivities afforded such instruments in comparison to the ICP-*oa*-ToF-MS used herein.

PVG Sample Introduction. Based on conditions developed for successful PVG of iodine,[23,24] acetic acid was initially selected as the medium of choice for vapor generation of bromine. Introduction of 100 ng/mL solutions of Br^- or BrO_3^- in acetic acid media to the PVG reactor equally enhanced sensitivity of both m/z 79 and 81 isotopes. Using an initially arbitrary sample flow rate of 3.3 mL/min to the PVG reactor (13 s UV irradiation time), and a flow rate of 400 mL/min Ar to the GLS, the effect of acid concentration on relative response was evaluated, as shown in Figure 2 (note that solution
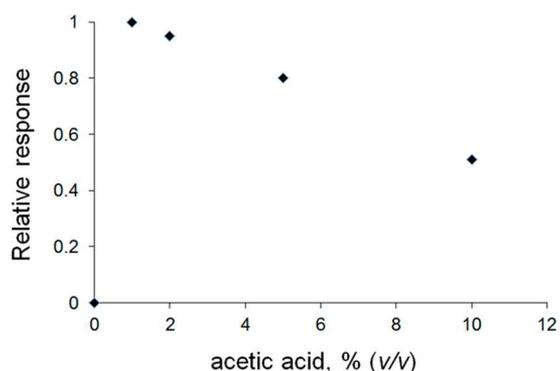
Figure 2. Effect of acetic acid concentration on relative response from 200 ng/mL Br^- using PVG sample introduction at a flow rate of 3.3 mL/min through the reactor. Precision of replicate measurement ($n = 3$) is embedded within the marker point.

introduction through the nebulizer was stopped during vapor generation but the nebulizer gas flow was maintained at its optimized 800 mL/min flow rate). A 2% (v/v) solution was selected for further work, based on considerations of robustness and minimization of potential contamination from the reagent blank. By comparison, equivalent solutions of formic and propionic acids generated relative responses of 2% and 50% of that from acetic acid, much as noted for PVG of iodine;[23,24] formic acid generates HBr which, being ionized, remains in solution and produces no enhancement in transfer efficiency whereas propionic acid gives rise to ethyl bromide, possibly with poorer generation efficiency and/or reduced GLS separation efficiency. Headspace GC−MS detection confirmed that ethyl bromide was the generated species. Comparison of PVG response from solutions of Br^- in 2% acetic acid with that

from their conventional pneumatic nebulization revealed a 7-fold enhancement for the former and a corresponding LOD of 0.71 ng/mL (monitoring m/z 79). Although net response at m/z 81 was the same as that at m/z 79 (within measurement precision), the enhanced background arising from $^{81}Ar_2H^+$ and tailing from $^{80}Ar_2^+$ degraded the LOD 7-fold.

PVG performance with solutions of BrO_3^- was different from that of Br^-. Under identical experimental conditions, response from this anion was ~4-fold larger than that generated by Br^-. As the product, methyl bromide is the same in both cases;[33] this is a consequence of the kinetics of the reaction and suggests an altered mechanism. Response from PVG of BrO_3^- was enhanced 21-fold relative to its solution nebulization and the corresponding LOD, 0.22 ng/mL, reflected a nearly 10-fold improvement. Taking into account the relative flux of analyte to the two introduction systems wherein supply to the PVG reactor was 3.3 mL/min and that to the nebulizer was 1 mL/min, and further assuming that the nominal efficiency for sample introduction with the nebulizer is 2%,[14] corresponding sample introduction efficiencies for PVG of Br^- and BrO_3^- are nominally 4% and 13%, respectively. The latter figure does not appear to be a remarkable improvement in analytical performance for PVG but when substantial increases in flow rate of sample to the ICP can be utilized without degrading efficiency of generation, significant performance improvements accrue, as evidenced from the above.

Photochemical vapor generation of CH_3Br is consistent with the radical mediated mechanism of this process discussed by Sturgeon and Grinberg.[22] Jortner and others[34−36] have presented evidence for the role of the solvated electron and charge transfer to solvent (CTTS) processes during photochemical reactions of the halogens in aqueous media and proposed intermediate cage complexes comprising the halogen atom (radical) and solvated electron from which final reaction products devolve, i.e., in the case of bromine:

$$Br^-_{(aq)} \xrightarrow{h\nu} (Br^-)^*_{CTTS} \rightarrow \rightarrow [{}^{\cdot}Br_{(aq)} + e^-_{(aq)}] \qquad (1)$$
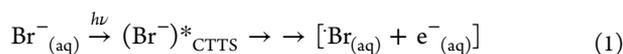
The $^{\bullet}Br_{(aq)}$ radical may briefly avoid recombination in the cage as the electron escapes and reacts with a suitable scavenger, following which $^{\bullet}Br_{(aq)}$ may also interact with solvent, with other bromide radicals or with those generated in the medium, i.e., methyl radicals from photolysis of the acetic acid. Jortner et al.[34] argue that production of excited state Br atoms arising from use of 184 nm radiation behave differently from ground state bromine atoms produced by 254 nm radiation ($^2P_{3/2}$ vs $^2P_{1/2}$ states, respectively); quantum yields for bromine atom generation are wavelength dependent with up to 5-fold greater yield at 184.9 nm. Such results have led to the suggestion that "conventional" PVG of Br was earlier unsuccessful because the UV sources used were primarily limited to wavelengths of 254 nm and above and even in the case of the UV spray chamber,[29] wherein the Hg line at 184.5 nm is available, the extremely short residence time for irradiation (~2 s) coupled with the low intensity of the source (3 W) precluded significant yield.[22] Availability of the high intensity (19 W) flow-through lamp comprising the current PVG reactor subjects the sample to 185 nm radiation and possibly aids in the enhanced photochemical yield of CH_3Br. However, understanding of the mechanism is far from clear, considering the significantly enhanced response from BrO_3^-, indicating multiple factors are involved.

Consistent with the above, the response from BrO_3^- was enhanced only 3-fold when using the UV spray chamber as its UV source was turned on, and that from Br^- increased only 20% with the lamp on compared to response from standard solution nebulization (lamp off). Although variable irradiation time is possible when the 15 W germicidal lamp is used as the PVG reactor, signal intensities equivalent to those generated with the flow-through PVG reactor were only asymptotically achieved when the irradiation time approached 35 min for solutions of Br^- (160-fold longer than with the flow-through PVG reactor), rendering practical use of either source intractable under such conditions.

The impact of sample irradiation time on PVG signals from Br^- was investigated using an intermittent stop - flow sequence for sample introduction along with integration of discrete signal transients. A fixed 700 μL volume of a 200 ng/mL solution of Br^- in 2% acetic acid was rapidly delivered to the PVG reactor whereupon the solution flow was stopped for controlled periods of time, i.e., irradiation time, before it was rapidly expelled into the delivery line to the GLS. Once in this delivery line, it was always pumped to the GLS at 3.3 mL/min. The resulting transient signal was integrated and the impact of irradiation time investigated over the range of 3−25 s. This approach to discern the impact of irradiation time was needed as it is impossible to undertake such an experiment in a continuous feed mode. Changing the irradiation time via changes in sample flow rate through the PVG simultaneously alters the rate of delivery of sample to the GLS, thus convoluting the impact of irradiation time and flux of sample to the torch. Within the precision of measurement (~4.8% RSD), no change in response was evident over the entire irradiation time, thereby permitting equally efficient generation of product over the equivalent flow rates of 1.7−14.4 mL/min. Despite the PVG reactor being capable of processing such large sample flow rates, limitations ultimately arise with the efficiency of separation of CH_3Br from the liquid phase. At a continuous delivery flow rate of arbitrarily 3.3 mL/min (13 s irradiation time), the best response, i.e., a trade-off between efficiency of gas−liquid separation and transport of CH_3Br and excessive dilution, was obtained using an Ar gas flow rate of 500 mL/min through the GLS.

Speciation and Effects of NH_4Cl Modifier. The limitation of unequal response from Br^- and BrO_3^- anions that may be present in real samples presents a severe impediment to accurate quantitation of total bromine. In such circumstance their separation by ion chromatography (IC)[10,37,38] prior to individual quantitation using PVG should provide a solution to this issue by simply directing the effluent from the IC to the PVG reactor.

As the LOD achieved with BrO_3^- was superior, attempts were made to undertake prior oxidation of samples of Br- in DIW using ozone[39] in accordance with the simple reaction:

$$Br^- + O_3 \rightarrow BrO_3^- \qquad (2)$$

Unfortunately, subsequent response was erratic and low, suggesting losses of analyte during ozonolysis. Yu et al.[40] have undertaken a detailed investigation of this (radical) reaction, suggesting that a number of intermediates are formed and that major products of the oxidation include Br_2 and Br_3^- with only a 10% yield of BrO_3^-.

Abandoning the possibility of a clean approach to oxidation, classical reduction of BrO_3^- to Br^- was attempted using a

mixture of hydrochloric acid and sodium iodide[41,42] in an effort to convert all species in a sample to a single ionic form, i.e.:

$$BrO_3^- + 9I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O + Br^- \qquad (3)$$
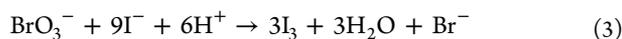
Severe signal suppression occurred during PVG, and blanks were elevated with the consequence that this approach was also abandoned.

An examination of the methodologies typically employed with IC to effect separation of the bromine species[10,37,38] reveals that the eluents most frequently encountered include NaCl, Na_2CO_3, Na_2SO_4 and $NaHCO_3$, all at typically <1000 μg/mL Na and compatible with the PVG process. Thus, IC ultimately provides a practical solution to this issue.

Studies by Jortner et al.[35] suggest that the presence in solution of an effective electron scavenger for the solvated electron (reaction 1), such as NH_4^+, may serve to enhance the overall efficiency of the photochemical reaction. To this end, solutions of Br^- and BrO_3^- were spiked with varying amounts of an ultrapure solution of NH_4Cl "modifier" prepared from sub-boil distilled HCl and environmental grade NH_4OH. Figure 3 shows the impact of the presence of this modifier
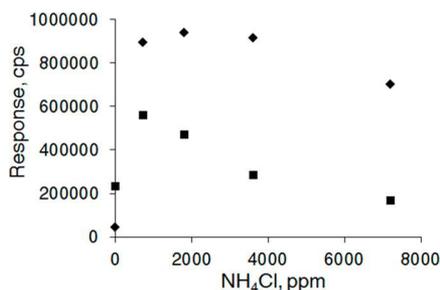
Figure 3. Response from PVG of 40 ng/mL Br^- and BrO_3^- in 2% CH_3COOH + NH_4Cl modifier. Sample flow rate of 3.3 mL/min (13 s irradiation time): ♦, Br^-; ■, BrO_3^-. Precision of replicate measurement ($n = 3$) is embedded within the marker point.

on PVG response from a 40 ng/mL solution of both species in 2% acetic acid. A UV exposure time of 13 s was used, in accordance with all earlier studies. It is evident that response is significantly enhanced for both anions, more so for Br^-. Moreover, there is a reversal in sensitivity in that response for Br^- now exceeds that for BrO_3^- when the modifier is present. This further highlights a difference in the fundamental mechanism of PVG of these two species, despite the same ultimate product being formed. UV–vis spectra of a 50 μg/mL solution of each anion in 2% acetic acid (vs 2% acetic acid in the reference cell) and in the presence of 3000 μg/mL NH_4Cl (against a reference solution of the same composition without the bromine species present) also revealed distinct differences. Figure 4 shows spectra for these solutions in the presence of the added NH_4Cl modifier. The strong UV absorption band that selectively occurs in a solution of Br^- below 250 nm is absent in that for BrO_3^- (note that 2% acetic acid is a strong nonselective absorber of UV in this region), suggesting an ammonia complex that may play a role in the selective absorption of deep UV radiation. In the absence of added NH_4Cl, neither species exhibits any specific absorption at wavelengths as low as 240 nm and is perhaps one reason why PVG of bromine is typically difficult with standard low pressure Hg discharge lamps that are ozone free, i.e., provide no access to the deeper UV wavelengths. The NH_4Cl modifier is acidic and its addition to the sample solutions results in a systematic
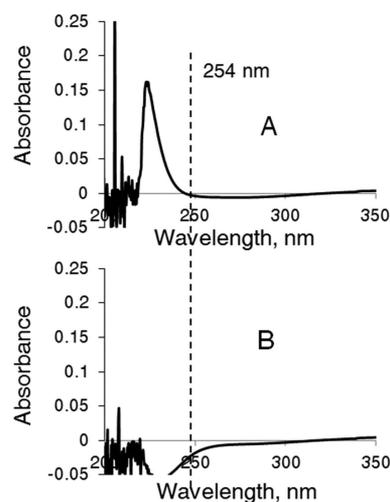
Figure 4. UV–vis spectra of 50 μg/mL Br^- (A) and BrO_3^- (B) in 2% CH_3COOH + 3000 ppm of NH_4Cl vs CH_3COOH + 3000 ppm of NH_4Cl.

decrease in their pH from 2.39 (no modifier) to 1.35 (7000 μg/mL). Subsequent experiments undertaken in the absence of the modifier but with corresponding pH adjustments made with H_3PO_4 revealed no impact of pH on response; the effect is entirely due to the presence of NH_4^+, possibly in the role of providing a photochemical ligand to metal charge transfer reaction that enhances PVG efficiency.[22]

Although addition of NH_4Cl was unable to resolve the issue of normalizing the response of the two species, it significantly enhanced not only the sensitivity (or generation efficiency) for both species but also altered the kinetics of PVG. Further, addition of NH_4Cl to solutions of 2% (v/v) formic acid increased response from 2% of that in acetic acid to 30%, suggesting its efficacy as a reagent to reduce potential interferences. Sensitivity for bromide with PVG is enhanced 21-fold in the presence of the modifier whereas that for bromate increases 2-fold. Relative to conventional pneumatic nebulization, PVG in the presence of the NH_4Cl modifier provides an increase in sensitivity of 143-fold. Recalling the factor of 3 difference in rate of supply of sample to the ICP and assuming a 2% efficiency for sample introduction by pneumatic nebulization, the PVG efficiency for Br^- is 95%. The corresponding LOD for Br^- is 0.14 ng/mL based on 3-fold the standard deviation of the blank, a 17-fold improvement over that achieved with pneumatic nebulization.

The substantial enhancements in generation efficiency afforded by the presence of NH_4Cl in the sample prompted a brief re-examination of the performance of the UV spray chamber as an integrated PVG reactor/GLS for convenient sample processing. In contrast to the initial investigation, wherein only a 20% enhancement in sensitivity was obtained when the UV lamp was on (at 1 mL/min neb flow rate), the presence of NH_4Cl enhanced sensitivity 25-fold for Br^- (8-fold for BrO_3^-), suggesting that a PVG generation efficiency of 50% can be achieved with a UV irradiation time as short as 2 s. Clearly, reaction kinetics is impacted by the presence of this modifier. Although the UV spray chamber offers an elegant means of accomplishing PVG, it is somewhat limited in application due to the constraints on sample flow rate being <1 mL/min and thus the benefit of utilizing higher flow rates with concomitant enhanced sensitivity is absent. In this regard, re-

examination of the germicidal lamp for PVG is warranted as higher flow rates may be utilized and the long irradiation time noted earlier may no longer be required.

Analytical Performance. Figures of merit are summarized in Table 1, from which the analytical advantages of undertaking

Table 1. Figures of Merit

blank[a], ng/mL	2.2
isotope ratio[b]	0.9813 (Br⁻); 1.0023 (BrO₃⁻)
mass discrimination factor[c]	0.023 (Br⁻); 0.013 (BrO₃⁻)
precision, %RSD @ 20 ng/mL	2.5
LOD[d], ng/mL	0.14 (2.4)
linearity[e] (upper range, ng/mL)	200
PVG efficiency[f], %	95

[a]For ^{79}Br; medium comprising 2% acetic acid containing 3000 μg/mL NH$_4$Cl. [b]Ratio of regression slopes of calibration functions (0−200 ng/mL) prepared from Br⁻ or BrO$_3$⁻ in 2% acetic acid containing 3000 μg/mL NH$_4$Cl. [c]Based on experimental isotope ratios vs IUPAC reference value of 1.0278.[43] [d]Based on a response equivalent to 3 times the standard deviation of the blank ($n = 15$); value in parentheses is LOD for solution nebulization (1 mL/min). [e]Upper limit of calibration function experimentally tested [f]Based on response from PVG of Br⁻ relative to optimized signal from solution nebulization, assuming nominal introduction efficiency of 2% for the latter.[14]

PVG sample introduction for bromine are amply evident. A relatively large blank is encountered in the present system when monitoring the m/z 79 isotope due, as noted earlier, to the poor abundance sensitivity of the ToF, leading to a significant contribution to the background from the leading edge of the intense ^{80}Ar$_2$⁺ molecular ion. Using high-purity HCl and NH$_4$OH to prepare the NH$_4$Cl modifier and ACS grade acetic acid, the gross blank was equivalent to 2.2 ng/g. Notable is the observation that the blank arising from the plasma background accounted for approximately 50% of this response. With the present detection system, there is little to be gained by using ultrapure acetic acid as blanks prepared with Baseline grade (Seastar chemicals) were insignificantly lower than those arising from use of the ACS reagent grade acid. It is assumed that a sector field instrument could take greater advantage of the high-purity acid and yield a lower blank. It is also possible that contributions to the blank arising from reagent contamination can be reduced for use in extreme situations by prephotolyzing the reaction mixture and degassing it to remove residual bromine contaminant prior to using such a reagent for sample preparation.

Isotope ratio capabilities of the ToF system are typically superior to those of a quadrupole. A precision of measurement of ^{79}Br/^{81}Br based on 15 replicate determinations (5 s averaging for each measurement) of the intensities of each isotope generated from a 200 ng/mL solution of Br⁻ was 0.48%. From the slopes of the calibration functions covering the range 10−200 ng/mL of both Br⁻ and BrO$_3$⁻, isotope ratios of 0.9813 and 1.0023 were obtained, respectively. Considering that the reference ratio is 1.0278,[43] mass discrimination factors are calculated to be 0.023 and 0.013 for Br⁻ and BrO$_3$⁻, respectively. These appear sufficiently different, within the precision of measurement, that one may conclude that a kinetic isotope effect may be manifesting itself during the PVG process as a consequence of the different oxidation state of bromine. More work would have to be undertaken using a multicollector instrument to unambiguously confirm this.

Precision of replicate measurement is on the order of 2.5% when undertaking PVG of a calibration standard of 20 ng/mL Br-. It is evident from Table 2 that the precision of determination of bromine in real samples is not significantly degraded from this value.

Table 2. Analytical Results

sample	determined ($n = 2$)[a]	certified (reference) value	ref
BCR-611 (μg/kg)	95.3 ± 4.6	93 ± 4	IRMM
NIST 1568b (mg/kg)	8.70 ± 0.40	8.31 ± 0.61	NIST
NIST1632a (mg/kg)	39.8 ± 2.4	(44.9 ± 0.9)	44
		(41 ± 4)	45
		(40 ± 3)	46
		(39.6 ± 1.9)	47

[a]Average and standard deviation calculated from analysis of two independently prepared subsamples of material.

A LOD, calculated as the concentration of a solution generating a response equivalent to 3 times the standard deviation of the blank ($n = 15$), of 0.14 ng/mL is achieved. This compares with a LOD of 2.4 ng/mL arising from sample introduction using conventional pneumatic nebulization with this instrument. The 17-fold enhancement in LOD highlights the significant benefit of PVG sample introduction. Based on the relative sensitivities of pneumatic nebulization and PVG vapor introduction of the same solution, and assuming that the introduction efficiency for the nebulizer is nominally 2%, the PVG efficiency is estimated to be 95%.

Applications to Environmental Samples. Optimized conditions for detection and PVG reaction were used along with the method of additions for quantitation. Following sintering of the solid reference materials, bromine was present as bromide in the prepared solutions as the evolved HBr$_{(g)}$ is trapped and neutralized by Na$_2$CO$_3$ in the sintering agent:[31]

$$2HBr_{(g)} + Na_2CO_{3(s)} \rightarrow 2NaBr_{(s)} + H_2O_{(g)} + CO_{2(g)}$$

(4)
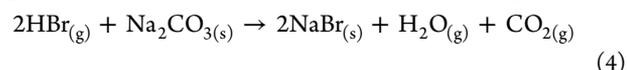
Spikes of Br⁻ were added to the solutions to double and triple the expected endogenous concentrations of analyte in the prepared samples, i.e., ∼20 ng/mL for IRMM BCR-611ground-water and ∼40 ng/mL for solutions of both SRM 1568b Rice Flour and 1632 bituminous coal, thereby ensuring linearity of the calibration functions. The ammonium chloride modifier (∼3000 μg/mL NH$_4$Cl) was added to all solutions to ensure enhanced response. Blanks were also quantitated by the method of additions and corrections made in concentration space rather than by simple subtraction from gross response. Table 2 summarizes analytical results for these materials, from which it is evident that excellent agreement is obtained with certified (for BCR 611 and SRM1568b) or well characterized external values derived from instrumental neutron activation analysis (i.e., for SRM 1632a[44−47]).

Based on $3s_{blank}$ ($n = 9$), the estimated method LOD for the sintered samples is 0.19 mg/kg, assuming a 0.5 g subsample. This compares with the value of 20 mg/kg reported by Österlund et al.[31] who utilized such a sintering technique but applied an additional cation-exchange cleanup of the matrix prior to analysis by solution nebulization coupled with sector field ICP-MS. In the case of the groundwater sample, a LOD of 0.12 ng/mL is achieved.

Applications to other sample matrices were not attempted. It is noteworthy that efficient alternative sample decomposition techniques, such as microwave induced combustion with absorption in an alkaline solution, do not promote formation of species other than bromide,[48,49] making quantitation for total bromine straightforward. Additionally, > 90% of bromine is in the form of bromide in most potable waters.[50] However, samples may be encountered wherein the speciation of bromine remains of interest. As response from the two species is significantly different, even in the presence of the NH_4Cl "modifier", it is prudent to rely on IC for prior separation.[10,37,38] Samples spiked with both Br^- and BrO_3^- can then be subjected to sensitive sequential quantitation by coupling the effluent from an IC column to the PVG reactor via a suitable chemical manifold to blend in the acetic acid and NH_4Cl modifier, particularly because the composition of popular effluents, i.e., NaCl, Na_2CO_3, Na_2SO_4 and $NaHCO_3$, should be compatible with the PVG process.

Interferences from concomitant elements present in samples were not specifically investigated in this study. Operationally, this is a laborious and relatively noninformative process whereby the impact of individual elements added at various concentrations to a standard is assessed. To be useful, all elements should be examined over substantial concentration ranges and in mixtures because of potential synergistic effects. Suffice to note that analysis by the method of additions was required for the above samples, wherein the groundwater material suffered a 40% signal suppression but response from the sintered coal sample was enhanced 20% relative to that obtained in the sinter blank; thus both positive and negative interferences are inevitable, depending on the mix of concomitant elements and their relative concentrations.

CONCLUSIONS

Although the mechanistic role of NH_4Cl in the photochemical medium is unknown at this time, it clearly serves to significantly enhance the PVG efficiency of generation of volatile methyl bromide from solutions of both Br^- and BrO_3^-. Although a significant difference remains in the relative response from these two anionic forms of bromine, this presents no impediment to utilization of the enhanced performance arising from vapor generation for analytical applications.

An estimated LOD using sector field instrumentation has been reported for ^{79}Br as being ~0.02 ng/mL[13], which is some 100-fold better than the value achieved with the ToF platform and pneumatic nebulization sample introduction used in this study. This opens the possibility for an equally significant improvement in the LOD achievable with PVG sample introduction when coupled to such an instrument.

Although simplification of the experimental approach appears feasible with use of the UV-spray chamber fulfilling the combined roles of PVG reactor and GLS, as high efficiency is achieved in the presence of the NH_4Cl modifier, the disadvantage of this approach is the limitation in flux of material delivered to the ICP in that the larger flow rates sustained with the flow-through PVG reactor cannot be attained.

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