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UV Vapor Generation for Determination of Selenium by Heated Quartz Tube Atomic Absorption Spectrometry

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A new vapor generation technique utilizing UV irradiation coupled with atomic absorption for the determination of selenium in aqueous solutions is described. In the presence of low molecular weight organic acid solutions, inorganic selenium(IV) is converted by UV irradiation to volatile selenium species, which are then rapidly transported to a heated quartz tube atomizer for detection by atomic absorption spectrometry. Optimum conditions for photochemical vapor generation and interferences from concomitant elements were investigated. Identification of the volatile products using cryotrapping GC/MS analysis revealed that inorganic selenium(IV) is converted to volatile selenium hydride, selenium carbonyl, dimethyl selenide, and diethyl selenide in the presence of formic, acetic, propionic, and malonic acids, respectively. In acetic acid solution, the efficiency of generation was estimated to be 50 ± 10%. No interference from Ni^{2+} and Co^{2+} at concentrations of 500 and 100 mg L^{-1}, respectively, was evident. A detection limit of 2.5 μg L^{-1} and a relative sensitivity of 1.2 μg L^{-1} (1% absorption) with a precision of 1.2% (RSD, $n = 11$) at 50 μg L^{-1} were obtained.

The use of vapor generation as a means of sample introduction for atomic spectrometry offers unique advantages for real sample analysis, which arise as a result of the separation and concentration of the analyte from the complex matrix. Higher sample introduction efficiency and improved limits of detection can also be achieved. By selectively forming volatile species, vapor generation enables the analysis of problematic samples having high dissolved salt, acid concentrations, or other species, which would otherwise cause serious spectroscopic or matrix interferences. Among the existing methods that use various media for vapor generation[1,2] (i.e., hydridization, cold vapor generation, halination, ethylation, propylation, oxidization, etc.), and electrons[3] (electrochemical hydride generation), hydride generation using borohydride reduction is the most widely used. As a result, other generation methods are rather limited in scope, not only to a few elements but to generation conditions that may also be rather critical. However, the principal problem with current hydride generation techniques is that of interference arising from the presence of transition metals,[1] notably Ni, Co, and Cu, caused by their interaction with the $NaBH_4$ reductant or their catalytic decomposition of the analyte hydride on the reduced interference metal surface. These are especially severe for the generation of H_2Se or H_2Te. In addition, $NaBH_4$ is a potential source of contamination, and its aqueous solution is unstable. The development of new vapor generation systems for the determination of trace elements therefore remains a fascinating research area in atomic spectroscopy.

In the past few decades, UV-induced photooxidation for the decomposition of organic material in samples has been widely described in the literature. Often, a strong oxidizing agent, such as O_3, $K_2S_2O_8$, and $K_2Cr_2O_7$, as well as HNO_3 or H_2O_2, is added to the system[4−7] and intermediate radicals (mainly $OH^•$), formed during UV irradiation, play a crucial role in the process of oxidation. Although UV irradiation itself is catalytic in nature,[5] in the presence of some organic substances it can result in formation of radicals (such as $H^•$, $CO^•$) that elicit "photoreduction", such as for production of hydrogen,[8] instead of stimulating oxidation. As a typical example, volatile mercury species formed by photochemical processes have been reported in earlier studies.[9] Synthetic seawater, spiked with organoselenium compounds and exposed to sunlight, produced methylated selenium, which was not the case with spikes of inorganic selenium.[10] Kikuchi and Sakamoto[11] reported formation of volatile species of selenium, (presumably SeH_2) when photolyzing aqueous solutions fortified with formic acid in the presence of TiO_2 photocatalyst. Despite such progress, little is known in this area as there is too little effort expended in clarifying UV "photoreduction" reactions so as to permit their routine use in analytical chemistry.

This study was undertaken to characterize a new technique for vapor generation based on UV irradiation of samples for

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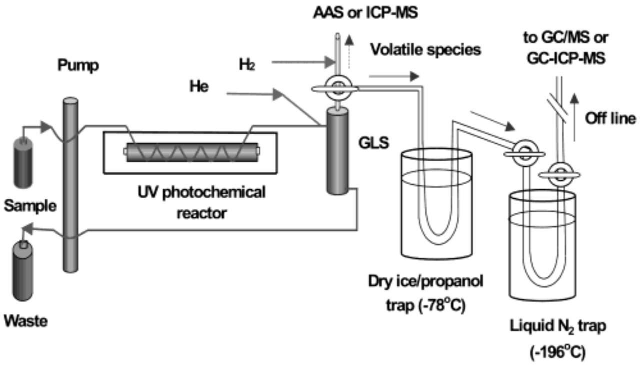

Figure 1. Schematic of the experimental system.

determination of selenium by atomic absorption spectrometry. Optimum conditions for photochemical vapor generation and interferences by concomitant elements were investigated. Although the reported figures of merit do not yet compare favorably with other techniques currently used for detection of selenium, there are several advantages associated with this approach, not the least of which is a tolerance toward high concentrations of Ni^{2+} and Co^{2+}.

EXPERIMENTAL SECTION

Instrumentation. A flow-through photoreactor, consisting of a 5-m length of 18-gauge poly(tetrafluoroethylene) (PTFE) tubing (Alpha Wire Corp.) of dimensions 1.74 mm o.d × 1.10 mm i.d. wrapped around either of two low-pressure Hg vapor UV lamps (254 nm, 3 or 15 W, Cole Parmer, Vernon Hills, IL), was constructed. A schematic of this system is illustrated in Figure 1. Samples were propelled through the tubing with the aid of a Minipuls 2 peristaltic pump (Gilson, Middleton, WI) operating at a speed of 50 revolutions min^{-1}, corresponding to a solution flow rate of 2 mL min^{-1} and solution irradiation times of 2 min. UV vapor generation was accomplished in a continuous-flow mode as the sample was passed through the PTFE tube for irradiation. A 55 mL min^{-1} flow of He purge gas was introduced into a gas−liquid separator, where the effluent from the UV photoreactor was directly merged with the He flow. The resultant volatile species were transported by the He flow from the gas−liquid separator either directly to a heated quartz tube atomizer via a 10-cm length of PTFE transfer tubing or through an intermediate cryogenically cooled U-shaped glass condensation tube. The quartz tube atomizer temperature was maintained at 900 °C. This was accomplished using a Perkin-Elmer FIAS-400 flow injection accessory to provide the power and temperature feedback for the quartz tube. The former was controlled with the use of a dedicated, separate PC. A flow rate of 15 mL min^{-1} H_2 was introduced via a second line into the atomizer to aid in the atomization of selenium.

The quartz tube atomizer with mounted in the burner (optical) compartment of a Perkin-Elmer model 5000 atomic absorption spectrometer fitted with a Perkin-Elmer electrodeless discharge lamp, which was operated at 5-W power. Radiation was detected at the resonance wavelength of 196.0 nm using a band-pass of 0.2 nm (low slit). Simultaneous deuterium background correction was applied for all measurements. Both peak height and integrated absorbance measurements were recorded.

Measurements were made in a continuous on-line mode to characterize the yield of the reaction products and also in an off-line manner to trap the volatile species in an effort to subsequently characterize them via GC/MS and GC/ICPMS techniques. For this latter purpose, a series of cryogenically cooled Pyrex U-tube traps (0.8 cm o.d. × 0.6 cm i.d. × 13 cm deep × 4 cm across) were occasionally placed between the generator and the detector to condense the generated analyte species, as described below.

To avoid clogging of the cryogenically cooled Pyrex U-tube and possible decomposition of any volatile Se compounds by concomitant water, a dry ice−methanol trap (−78 °C), into which a "guard" Pyrex U-tube (1.7 cm o.d. × 1.5 cm i.d. × 13 cm deep × 6 cm across) was immersed, was used to remove any water vapor carried over from the UV photochemical reaction system. Continuous monitoring of the AAS signal for selenium confirmed that there were no losses of volatile selenium species incurred by passage through this dry ice trap. The second U-tube, packed with glass wool and immersed in liquid nitrogen (−196 °C), was used for trapping the volatile species swept from the dry ice bath. Continuous on-line monitoring of the AAS signal revealed that the volatile selenium species were completely trapped in this second U-tube. High-purity helium was chosen as the carrier gas as it is not condensed in the U-tube at liquid nitrogen temperatures and does not introduce any mass spectral interference during the subsequent identification of trapped species using GC/ICPMS and GC/MS. Prior to commencing the trapping experiment, the U-tubes were flushed with He for 10 min at room temperature.

A Hewlett-Packard (HP) model 6890 gas chromatograph was interfaced to an HP 5973 mass-selective detector (mass range 60−270 Da). Selenium compounds were separated on a 30 m × 0.25 mm i.d. × 0.25 mm film (J&W Scientific) DB1 capillary column (1% phenyl, 99% poly(dimethylsiloxane)) using UHP helium carrier gas and a head pressure of 12.5 psi. Splitless sample injection was used. Sample aliquots of 250 μL were manually injected. The transfer line temperature was 280 °C. A carrier gas flow rate was set at 0.8 mL min^{-1}. An 18-min temperature program was used with an initial temperature of 60 °C and a hold time of 10 min followed by a ramp of 90 °C min^{-1} to a temperature of 280 °C, which was held for 10 min.

A Perkin-Elmer Sciex Elan 6000 (Concord, ON, Canada) ICPMS instrument was interfaced to a Varian 3400 GC (Varian Canada, Georgetown, Canada) equipped with a 15-m length of DB-1 column (0.32 mm) through an in-house heated transfer line.[12] The sampling process and GC conditions were similar to those used above for GC/MS measurements. The ICPMS was operated in accordance with the manufacturer's recommendations with the ^{78}Se isotope selected for detection.

Reagents and Samples. All solutions were prepared using 18 MΩ·cm deionized, reverse osmosis water (DIW) obtained from a mixed-bed ion-exchange system (NanoPure, model D4744, Barnstead/Thermoline, Dubuque, IA). Calibration solutions were prepared daily by diluting the stock solutions. Selenium stock solutions (1000 mg L^{-1}) were prepared from selenite (Na_2SeO_3 99%, Aldrich) and selenate (Na_2SeO_4 99%, Aldrich). Solutions of low molecular weight acids were prepared from analytical reagent grade materials: formic acid (23 M, Anachemica), acetic acid (6.3 M, BDH), propionic acid (13 M, BDH), and malonic acid (BDH). Solutions of H_2O_2 were prepared from 30% H_2O_2 (9.8 M, Anachem-

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ica). High-purity HNO_3, $NaNO_3$, and $NaNO_2$ (Fisher Scientific) were used, except where indicated otherwise. Titania (Tinano 40 HPC-D, lot 149, 99% TiO_2) was obtained from Altair Technologies, Inc. All gases (H_2, Ar, He) were of high purity and obtained from Praxair Products Inc. (Mississauga, ON, Canada).

Samples of Ottawa River water were obtained as needed from the shore of the river by sampling aliquots into precleaned polypropylene screw-capped bottles and directly transporting them to the laboratory for immediate study. Certified Reference Materials CASS-4 (coastal seawater) and NASS-5 (open ocean seawater) were obtained from the National Research Council of Canada, Ottawa, and used to investigate generation of volatile selenium compounds from a saline matrix.

Procedure. Volatile selenium compounds were generated when the selenium standard solutions containing various low molecular weight acids at different concentrations were pumped through the PTFE tubing of the photoreactor. The gaseous products were separated from the liquid phase in the gas−liquid separator and flushed into the heated quartz tube atomizer for AAS measurements or passed through the successive U-tubes using a stream of He carrier gas. Following cryocondensation, the second U-tube was closed at both ends by rubber septa, removed from the liquid nitrogen bath, and allowed to equilibrate to room temperature for ~15 min. A 0.250-mL volume of the gas phase containing the volatile Se species was sampled through the septum of the U-tube using a gastight syringe and injected into the GC/MS for species identification.

Initial experiments were undertaken using a batch reactor consisting of a silicone septum-sealed vial into which a 4-W low-pressure penlight mercury lamp had been inserted (sheathed in a quartz finger). The vial was spiked with a solution of ~10 mL of DIW containing 0.5 mg L^{-1} Se(IV) and 0.7 mol L^{-1} formic acid to which 1 g L^{-1} TiO_2 was added, in accordance with the protocol described by Kikuchi and Sakamoto.[11] Following exposure of the batch sample to the UV source, the volatile selenium species so formed were conducted to a heated quartz tube by argon gas, which was bubbled through the vial.

Table 1 summarizes all optimized experimental conditions used for this study.

Safety Considerations. Some organoselenium compounds may be toxic (e.g., SeH_2), and the full range of such compounds produced in these studies may not be known. Essential safety precautions must be taken during all manipulations and an adequate ventilation/exhaust system used.

RESULTS AND DISCUSSION

Optimization of Photochemical Reactor System. Preliminary experiments revealed that the presence of TiO_2 in the reaction cell was unnecessary for the generation of a volatile selenium product. However, a batch reactor cannot ensure that the tested solution receives homogeneous UV light irradiation, and the resulting signal suffered serious tailing and was not suitable for analytical purposes. A flow-through photoreactor, as described above, was thus used in all further work. By using a flow-through photoreactor, the volatile selenium species were rapidly formed, giving rise to relatively sharp atomic absorption signals in a matter of only a few minutes.

The carrier gas flow rate and composition were found to have a significant impact on response, as they influence not only the process of gas−liquid separation and analyte transport but atomization in the heated quartz tube as well, especially peak height response. With a 60 mL min^{-1} flow rate of only argon as the carrier gas, signals were irreproducible and consisted of multiple spikes, as shown by the resulting absorbance trace in Figure 2b. Such a phenomenon is well known to quartz tube AAS and is indicative of an insufficient hydrogen radical population needed for complete atomization in the cell. Periodic availability of bursts of hydrogen generate the necessary free radical population needed to atomize SeH_2. To confirm this, an auxiliary flow of hydrogen was introduced through a bypass line to the atomizer, as shown in Figure 1. Although a flow of 15 mL min^{-1} was adequate, rates ranging from 5 to 50 mL min^{-1} did not significantly change the sensitivity, but higher flow rates caused serious dilution effects and were avoided. Figure 2a illustrates the typical response obtained from a solution of 0.7 M formic acid spiked with a 0.1 μg mL^{-1} solution of Se(IV). An Ar gas flow rate of 60 mL min^{-1} was found to give maximum signal intensities for determination of selenium. Response from the processing of a blank solution containing acetic acid but no added Se(IV) is evident in Figure 2c. The noise associated with the steady-state signal arising from the continuous processing of a 0.050 mg L^{-1} solution of Se^{4+} is 5.9% (1 σ, $n = 39$ data points) in the presence of H_2.

Table 1. Optimized Experimental Conditions

	Generation
source lamp	Hg vapor UV lamps, 254 nm, 3 or 15 W, incident radiation of ~48 mW cm^{-2} (Cole Parmer)
tubing	5-m length of 1.10-mm-i.d., 1.74-mm-o.d PTFE tubing (Cole Parmer)
irradiation time	2 min
sample flow rate	2 mL min^{-1} (Minipuls 2 peristaltic pump (Gilson), 50 revolutions min^{-1})
carrier gas	high-purity Ar: 55 mL min^{-1}
acetic acid	0.7 mol L^{-1}
Se concn	less than 50 mg L^{-1}
	Detection
AAS	Perkin-Elmer model 4100 AAS; Perkin-Elmer EDL current, 350 mA; wavelength, 196.0 nm; band-pass:, 0.2 nm; deuterium background correction quartz tube atomizer temperature, 900°C
H_2 auxiliary gas flow	15 mL min^{-1} (to atomizer)
	Species Identification
water trap	dry ice−methanol trap, −78 °C
volatile species trap	liquid nitrogen, −196 °C
carrier gas	He, high purity, 55 mL min^{-1}
GC/MS	Hewlett-Packard (HP) model 6890 gas chromatograph, HP 5973 mass-selective detector
column	30 m × 0.25 mm i.d. × 0.25 mm film (J&W Scientific) DB1 capillary column (1% phenyl, 99% poly(dimethylsiloxane))
injection vol	0.25 mL; splitless mode
Injector temp	280 °C
carrier gas	high-purity He, 0.8 mL min^{-1}
column temp	60 °C, 10 min; 90 °C min^{-1} to 280 °C, 10 min
transfer line	280 °C
GC/ICPMS	Perkin-Elmer Sciex Elan 6000
GC	Varian 3400
m/z GC column temp program	^{78}Se isotope, 15-m length of DB-1 colum (0.32 mm) as for GC/MS

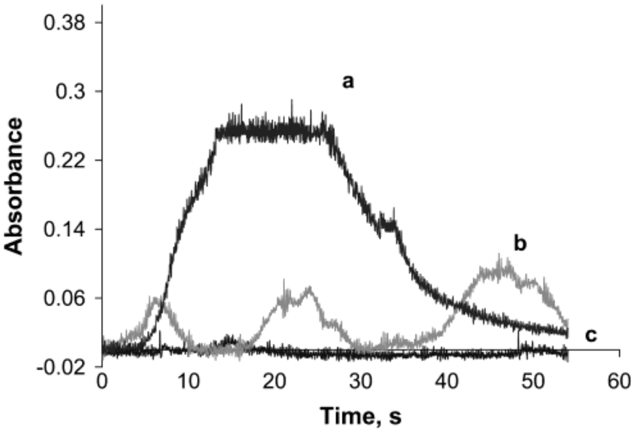

Figure 2. Typical background-corrected steady-state signal obtained for the photochemical vapor generation of Se from a solution of 0.7 M CH_3COOH spiked with 0.10 mg L^{-1} Se(IV): (a) atomic absorption obtained with H_2 added; (b) atomic absorption obtained without added H_2; (c) blank.

For a fixed sample flow rate, the residence time of the analyte in the irradiation field is dependent on the length of the PTFE tube wrapped around the UV lamp. Using a solution containing 0.1 mg L^{-1} Se(IV) and 0.7 mol L^{-1} formic acid, the optimum length of the photoreactor tubing was determined to be 3−6 m. This length ensured that the sample solution tested received 1.4−2.9-min irradiation. When longer tubing was used, possible losses of volatile analyte species could be induced via competitive photochemical decomposition. For most solutions tested, a tube length of 5 m was sufficient, providing an irradiation time of 2 min.

The effect of the length of the Tygon transfer tube line between the gas−liquid separator and the quartz tube on the signal intensity from a 0.1 mg L^{-1} solution of Se(IV) was examined. No significant decrease in intensity was observed as the transport distance increased (up to 1 m), suggesting that, once formed, the volatile species is very stable and does not suffer any losses during the transport process. For convenience, a tube length of 0.2 m was selected for this study.

Effects of Acidity. Formic acid was initially investigated for its effects on the photochemical generation of volatile selenium species, as it has the simplest structure among the organic acids studied. The UV generation efficiency was found to be dependent on the acidity under which the reaction is performed, as shown by the data in Figure 3. A plateau in the range of 0.4−1.0 M HCOOH is evident. Additional studies revealed that the optimum acidity range can be shifted to higher values (up to 2 M formic acid) by utilizing an increased irradiation time. In this work, 0.7 M formic acid was selected as the optimum acidity with an irradiation time of 2 min. Higher concentrations (more than 2 M) of $HCOO^-$, supplied either as formic acid or sodium formate, resulted in a decrease in signal response. By maintaining the pH at <5 with the use of H_3PO_4, a similar Se response could be obtained when HCOONa was used as the source of formate anion, as opposed to HCOOH. No signal was observed at pH values higher than 5. It should be noted that, in the presence of H_2O_2 (optimal concentration in the range 20−100 mM), the volatile selenium species can be formed even if the concentration of formic acid is very low (e.g., down to 20 mM). Although the role played by H_2O_2 is yet unclear, UV decomposition of H_2O_2 likely produces an increase in OH radicals, favoring increased attack of the formic acid, as compared to the case when a pure 0.7 M solution of formic acid alone is used. Addition of NaCl (in the range of 0−0.5 M), HCl (0−0.3 M), NH_4Cl (0−0.5 M), H_2SO_4 (0−0.1 M), or H_3PO_4 (0−0.5 M) had no noticeable effect on the generation efficiency. Most notably, nitric acid was found to give rise to a 3-fold enhancement in the generation efficiency of the selenium species. Further investigation indicated that the signal intensity is equally increased by the simple presence of the NO_3^- or NO_2^- anion, derived from either sodium nitrate or sodium nitrite, at a concentration of 10−30 mM.

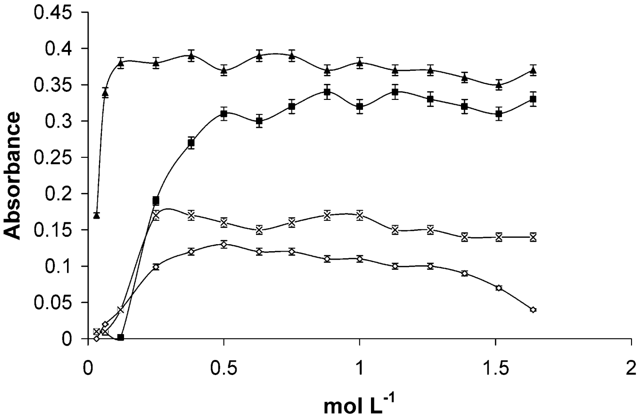

Figure 3. Effect of the concentration of low molecular weight organic acids on AAS signals arising from the continuous photochemical treatment of solutions containing 0.10 mg L^{-1} Se(IV): ◇, formic; ■, acetic; ▲, malonic; X, propionic.

Compared to the formic acid system, acetic acid can be more easily used to generate volatile selenium compounds under UV irradiation. The effects of acid concentration on the intensity of the AAS signal for a solution containing 0.1 mg L^{-1} Se(IV) are shown in Figure 3. Increasing the concentration of acetate ion (as sodium acetate or acetic acid), even to the point of saturation ($[Ac^-] > 30\%$ w/v), produced no notable negative effects on the Se signal intensity, provided the pH of the reaction solution was maintained slightly acidic (i.e., pH <5). Furthermore, enhancement effects on the Se signal intensity earlier obtained by the addition of H_2O_2 or $NaNO_3$ were no longer observed. In contrast to this, when the concentrations of these weak oxidizing reagents were higher than 0.1 M for H_2O_2 and 20 mM for $NaNO_3$, the selenium signal rapidly decreased to almost zero, despite increases in the concentration of acetic acid.

In addition to acetic acid, volatile selenium species could also be generated from both malonic and propionic acid solutions (cf. Figure 3). In a malonic acid medium, the UV irradiation time for production of volatile species could be as short as 17 s, and the entire reaction could be completed within 40 s, whereas at least 2 min was needed with the other systems.

Species Identification. As noted earlier, the volatile selenium species formed under UV irradiation appear to behave differently in the quartz tube atomizer compared to that obtained using a conventional borohydride reduction system. Several experiments were thus undertaken to elucidate the identity of these volatile species. Attempts to measure their IR spectra were unsuccessful, irrespective of the organic acid used for generation; no selenium-related compounds were detected due to the poor sensitivity. However, a significant molecular absorption spectrum of CO_2 and

H_2O was obtained, as expected for the decomposition of these simple organic acids. Khriachtchev et al.[13] reported that CO_2 and H_2 were produced during photolytic decomposition of *cis*-formic acid, and CO and H_2O were produced during photolytic decomposition of *trans*-formic acid. Hydrogen and carboxyl radicals generated by UV irradiation of formic acid can, theoretically, reduce selenite (Se^{4+}) to amorphous selenium Se^0 and ultimately to selenium hydride or selenium carbonyl (SeCO). When TiO_2 was present as a photocatalyst, H_2Se was presumed to be formed.[11] In an effort to distinguish whether selenium hydride or other carbon-bonded selenium compounds are generated in the photoreactor, the volatile species were swept from the gas−liquid separator and subsequently bubbled through a solution of NaOH (at concentrations of 0.1, 0.5, 2, or 4 M) prior to entering the quartz tube atomizer. It is known that H_2Se is easily decomposed and can be completely absorbed in such an alkaline solution,[14] whereas other carbon-bonded selenium compounds are generally regarded as sufficiently stable to pass unimpeded through such a trap. The resulting AAS signals revealed that, in all cases tested, about 60−70% of the volatile selenium species formed in formic acid solutions was absorbed by this alkaline solution. This implies that a fraction (about 60−70% v/v) of the volatile selenium species produced and absorbed by the NaOH solution is H_2Se. The remaining species (30−40% v/v) are likely Se−C bonded compound(s). More interesting was the observation that, in the presence of 10 mM $NaNO_3$, all of the photochemical reaction products passed completely through the alkaline-absorbing solution without loss, suggesting that H_2Se was no longer a product of the reaction. The volatile species resulting from subjecting a 1-L volume of sample containing 0.1 mg L^{-1} Se(IV), 10 mM $NaNO_3$, and 0.7 M HCOOH to UV irradiation were cryogenically trapped, as described earlier. Introduction of a subsample of the collected gas phase into the GC/ICPMS resulted in the detection of only one selenium-containing peak. Results from subsequent GC/MS measurements on this same sample were also obtained. Fragments containing Se were easily recognized in the mass spectra as a result of their characteristic isotopic pattern (^{74}Se (0.89%), ^{76}Se (9.37%), ^{77}Se (7.63%), ^{78}Se (23.77%), ^{80}Se (49.61%), ^{82}Se (8.73%)) arising from the six natural selenium isotopes present in the chromatographic peak. This isotope pattern was evident in fragments for Se^+ at m/z 80 and $SeCO^+$ at m/z 108. The resulting fragmentation pattern is consistent with the reported[15] mass spectrum of SeCO. Identical results (a retention time of 2 min for the chromatographic peak and for the SeCO mass spectral pattern) were obtained on treating a solution containing 0.1 mg L^{-1} Se(IV) and 0.7 M HCOOH without added nitrate anion, although the intensity was 3-fold lower in comparison with that arising from a solution containing nitrate anions. No peak corresponding to H_2Se, which was expected to appear as a reaction product, was obtained in these experiments, likely as a consequence of the instability of this molecule and its decomposition during transport through the chromatographic column. From the above, it is clear that about 60−70% (v/v) SeH_2 and 30−40% (v/v) SeCO are photochemically produced from irradiation of inorganic selenium in the formic acid solution. In the presence of nitrate anion, only SeCO is formed and the overall signal intensity is enhanced ~3-fold.

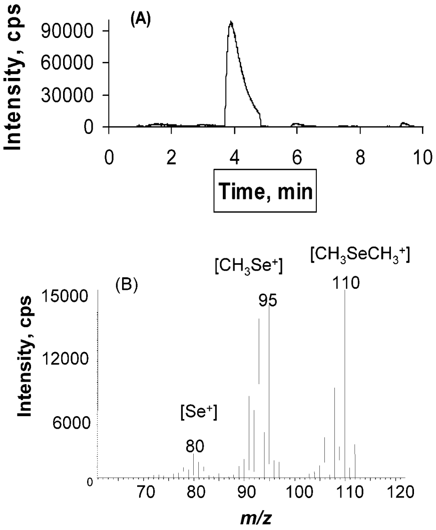

Figure 4. GC/MS spectra arising from sampling of cryogenically trapped volatile Se compounds produced by UV irradiation of solutions containing 0.10 mg L^{-1} Se(IV), 0.7 M CH_3COOH: (A) total ion chromatogram; (B) mass spectrum for ion peak at 3.96 min.

The NaOH trapping solution was not effective in absorbing any fraction of the volatile reaction products formed in an acetic acid system. Only one selenium- containing compound was detected by GC/ICPMS. Detailed information illustrating the structural identification of the cryogenically trapped compound by GC/MS is shown in Figure 4. The reason for the unexpected rapid drop in this total ion chromatogram at ~4.7 min is unknown but does not detract from the usefulness of the data for identification (not quantitation) purposes. Only one peak, at 3.7−4.6 min, contains Se. Mass spectra presented in Figure 4 show the molecular ion $[CH_3 - Se - CH_3]^+$ at m/z 110, as well as fragmentation peaks $[CH_3 - Se]^+$ at m/z 95 and at m/z 80 $[Se]^+$. This mass spectrum agrees well with previously published mass spectra of pure DMSe.[16] DMSe is produced from the trimethylselenonium ion during hydride generation[17] and from bacterial cultures.[18−20] It may be concluded that the volatile selenium-containing species produced by UV photolysis of selenite in acetic acid solution is dimethyl selenide, $(CH_3)_2Se$. In addition to acetic acid, the same mass spectrum could be obtained from malonic acid solutions, suggesting that dimethyl selenide could also be generated from a malonic acid solution. However, diethyl selenium ($(CH_3CH_2)_2Se$, DESe) was detected in the reaction products from UV irradiation of propionic acid solutions. A molecular ion at m/z

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138 $[CH_3CH_2-Se-CH_2CH_3]^+$ and several probable fragmentation peaks at m/z 123 $[CH_3CH_2-Se-CH_2]^+$, 110 $[CH_3CH_2-SeH]^+$, 95 $[CH_3-Se]^+$, 82 $[SeH_2]^+$, and 80 $[Se]^+$ were evident and are consistent with the reported mass spectrum of diethylselenium (DESe) $[(CH_3CH_2)_2Se]$.[21]

Proposed Mechanism. A proposed set of reactions, which may serve to account for these observations, is summarized below. Aliphatic organic acids may follow either of two different pathways during their anaerobic photolytic decomposition, which usually produces hydrocarbons, CO_2, and small amounts of CO and H_2,[13] i.e.:

$$\mathrm{R{-}COOH} \xrightarrow{h\nu} \mathrm{R^{\bullet}} + {}^{\bullet}\mathrm{COOH} \rightarrow \mathrm{RH} + \mathrm{CO_2}$$

$$(\mathrm{R} = \mathrm{C}_n\mathrm{H}_{2n+1},\quad n = 0, 1, 2) \tag{1}$$

$$\mathrm{RCO{-}OH} \xrightarrow{h\nu} \mathrm{RCO^{\bullet}} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{CO} + \mathrm{ROH}$$

$$(\mathrm{R} = \mathrm{C}_n\mathrm{H}_{2n+1},\quad n = 0, 1, 2) \tag{2}$$

Reaction 1 occurs more frequently than reaction 2. In the case of formic acid, reaction 1 occurs 6-fold more frequently than reaction 2. The resultant hydrogen and carboxyl radicals can, theoretically, reduce selenite (Se^{4+}) to amorphous selenium (Se^0) and likely further. Such reduced selenium species exist as H_2Se and various alkylated adducts of Se, i.e.:

$$2\mathrm{RCOOH} + \mathrm{Se^{4+}} \xrightarrow{h\nu} \mathrm{CO_2} + \mathrm{R_2Se}$$

$$(\mathrm{R} = \mathrm{C}_n\mathrm{H}_{2n+1},\quad n = 0, 1, 2) \tag{3}$$

$$\mathrm{RCOOH} + \mathrm{Se^{4+}} \xrightarrow{h\nu} \mathrm{SeCO} + \mathrm{ROH}$$

$$(\mathrm{R} = \mathrm{C}_n\mathrm{H}_{2n+1},\quad n = 0, 1, 2) \tag{4}$$

With increasing length of the carbon chain, it is likely that reaction 2 becomes less favorable, and with n equal to 1 or 2 (acetic and propionic acids), selenium carbonyl is the only detectable product in the formic acid photochemical system. In the case of malonic acid, acetic acid is formed by photolytic decomposition (reaction 5). This sequence explains the formation of $(CH_3)_2Se$; the same end product arises as when acetic acid is initially used.

$$\mathrm{HOOCCH_2COOH} \xrightarrow{h\nu} \mathrm{CH_3COOH} + \mathrm{CO_2} \tag{5}$$

If H_2O_2 or NO_3^- is present in the formic acid system, reactions 9 and 10 may occur, in which additional carbonyl radicals, $CO^{\bullet}$, are produced as a result of the formation of additional $HO^{\bullet}$ radicals arising from reactions 6–8. These $HO^{\bullet}$ radicals consume the hydrogen radical, $H^{\bullet}$, which is produced via reactions 1 and 3 and which is responsible for the formation of H_2Se. Consequently, the addition of either nitrate anion or H_2O_2 not only produces a 3-fold increase in the yield of SeCO but completely inhibits the formation of SeH_2. The relevant reactions are presented below:

$$\mathrm{H_2O_2} \xrightarrow{h\nu} 2\mathrm{HO^{\bullet}} \tag{6}$$

$$\mathrm{NO_3^-} \xrightarrow{h\nu} {}^{\bullet}\mathrm{NO_2} + {}^{\bullet}\mathrm{O^-} \tag{7}$$

$${}^{\bullet}\mathrm{O^-} + \mathrm{H^+} \xrightarrow{h\nu} \mathrm{HO^{\bullet}} \tag{8}$$

$$\mathrm{HCOOH} \xrightarrow{h\nu} \mathrm{HCO^{\bullet}} + {}^{\bullet}\mathrm{OH} \tag{9}$$

$$\mathrm{HCO^{\bullet}} + {}^{\bullet}\mathrm{OH} \xrightarrow{h\nu} \mathrm{CO^{\bullet}} + \mathrm{H_2O} \tag{10}$$

Generation Efficiency. In this study, the overall generation efficiency is defined as the convolution of the efficiency of species formation with those of its gas–liquid separation and transport to the detector. The overall efficiency was estimated from a comparison of the resulting AAS signals with those arising from conventional generation of H_2Se using a $NaBH_4$–HCl hydride generation system. In this latter system, the individual efficiencies for formation, gas–liquid separation, and analyte transport are known to be essentially quantitative and the response can thus be used as a relative benchmark for performance. In a formic acid medium, efficiency was estimated to be in the range 10–15% for conversion of Se(IV) to a volatile product, as measured by AAS response relative to an equal concentration of Se(IV) generated in the conventional hydride system. Efficiency increased to ~40% in the presence of 10–30 mM NO_3^-. In acetic and malonic acid systems, efficiency was determined to be 50 ± 10% using a 2-min UV irradiation. When propionic acid was used as the generation medium, efficiency was reduced to ~30%. It is believed that this rather low efficiency is related more to the likely low volatility of the diethylpropyl species that are produced in this reaction medium than to a reflection of the actual efficiency of product generation.

Interferences. One serious problem with the conventional hydride generation technique for the determination of selenium is the aforementioned interference caused by the transition metals of groups 8–11, mainly Co, Cu, and Ni. Pohl and Zyrnicki[22] reported that the presence of 10 mg L^{-1} Ni^{2+}, Co^{2+}, or Cu^{2+} seriously suppressed the selenium signal (by almost 30%). In the presence of 50 mg L^{-1} Ni^{2+}, only 19% recovery was obtained by Tao and Sturgeon.[23] With Co^{2+} or Cu^{2+} at a concentration of 20 mg L^{-1}, the recovery was ~50%. These transition metal ions are very easily reduced to their metallic state or to colloidal forms by $NaBH_4$ (or KBH_4) and scavenge or decompose the volatile analyte before phase separation can be accomplished. Other possible interferences include hydride-forming elements, which may cause gas-phase interference in the heated quartz tube. In the photochemical system, these effects would not be expected to be problematic because such metal ions are difficult to reduce by organic acid UV irradiation. In this study, the effects of 20 diverse ions on the generation of volatile species were tested, and as expected, no interference from Ni or Co was detected, even for concentrations as high as 500 mg L^{-1} for $Ni^{2+}$and 100 mg L^{-1} for Co^{2+}. This can be seen from the data in Figure 5. However, Cu^{2+}

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[21] Gómez-Ariza, J. L.; Pozas, J. A.; Giráldez, I.; Morales, E. *J. Chromatogr., A* **1998**, *823*, 259–277.

[22] Pohl, P.; Zyrnicki, W. *Anal. Chim. Acta* **2002**, *468*, 71–79.

[23] Tao, G.-H.; Sturgeon, R. E. *Spectrochim. Acta B* **1999**, *54*, 481–489.

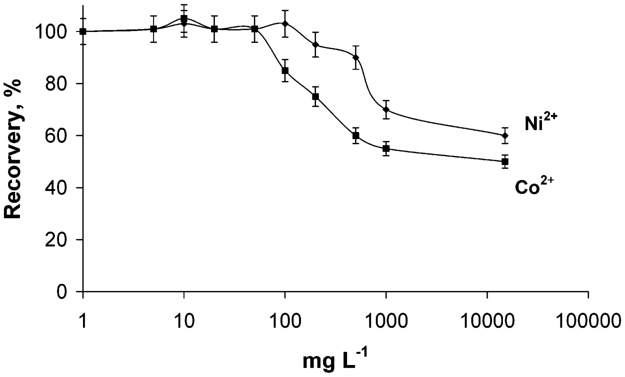

Figure 5. Influence of Ni^{2+} and Co^{2+} concentrations on the recovery of 0.10 mg L^{-1} Se^{4+}.

Table 2. Influence of Concommitant Ions on the Recovery of Selenium (0.1 mg L^{-1} Se (IV), 0.7 mol L^{-1} CH_3COOH)

interference	[M] (μg mL^{-1})	[M]/[Se^{4+}]	recovery (%)
Ag^+	2	20	102
As^{3+}	3	30	109
Au^{4+}	2	20	90
Br^-	3	30	85
	0.5	5	100
Cd^{2+}	20	200	120
Co^{2+}	100	1000	85
Co^{2+}	50	500	101
Cr^{3+}	10	100	107
Cu^{2+}	0.2	2	50
	0.02	0.2	97
Fe^{3+}	2	20	95
Fe^{2+}	3	30	80
	1	10	90
Hg^{2+}	0.1	1	80
	0.05	0.5	100
I^-	5	50	80
	1	10	100
La^{3+}	10	100	105
Mg^{2+}	50	100	98
Ni^{2+}	500	5000	90
Pb^{2+}	3	30	98
Pt^{4+}	0.05	0.5	60
Sb^{3+}	15	150	98
Sn^{4+}	10	100	105
Sn^{2+}	20	150	90
Te^{3+}	0.2	2	100
Zn^{2+}	400	4000	90

or Cu^+, and large amounts of Fe^{3+} or Fe^{2+} caused serious interference with the generation of 0.1 mg L^{-1} Se(IV). Various masking agents were tested in an effort to overcome the interference from copper, but without success. In addition to copper, bromine and iodine also caused interference. However, the interference caused by other hydride-forming elements is not as serious as reported in the borohydride reduction system. The maximum tolerated concentrations of the interfering elements are summarized in Table 2. Further investigation of these interferences and their elimination are necessary. To explain these effects, an ICP-AES system was used in an effort to determine whether volatile forms of any interfering elements were co-generated. It is interesting to note that signals for cobalt, nickel, arsenic, tellurium, iodine, and mercury were also observed, but at much lower intensity than that of selenium. These species may play a role in the suppression or enhancement effects, and a detailed description of their generation will be reported in the future.

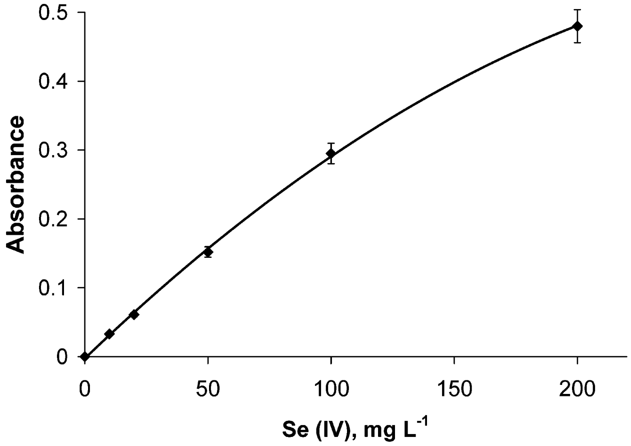

Figure 6. Typical calibration curve obtained using photochemical vapor generation with 0.7 M CH_3COOH solutions, 2-min irradiation, and steady-state absorbance measurements.

Figures of Merit. Among the organic acids tested, acetic acid was chosen for analytical vapor generation because its product, DMSe, offers the highest stability and is considered nontoxic to the analyst. Furthermore, despite an approximate 15% enhanced conversion efficiency when malonic acid is used, acetic is favored because of its widespread availability and ease of use in liquid form. The efficiency of photochemical methylation depends on the concentration of selenium and the time used for irradiation. The use of a lower selenium concentration permitted shorter irradiation times to be used. As an example, complete transformation of a solution of 0.020 mg L^{-1} Se(IV) to volatile product required a 20-s irradiation time, whereas for a Se(IV) concentration of 0.20 mg L^{-1}, at least 1.5 min was needed. At higher concentrations (100−1000 mg L^{-1}), no volatile product could be detected despite several minutes of irradiation. In such cases, a large amount of a red product (most likely amorphous Se^0) was deposited onto the inner surface of the reactor tubing. Such deposits have occasionally been noted in biological systems undergoing methlation.[24] At such concentrations, many hours of UV irradiation may be required, which may more efficiently be achieved using a batch reactor rather than a flow system. It is clear that optimal application of this technique will lie with the analysis of selenium at the trace level. Figure 6 illustrates a typical calibration curve obtained with this technique. With the instrumental setup and the analytical conditions optimized, a detection limit of 0.0025 mg L^{-1} and precision of 1.2% (RSD, $n = 11$ at a concentration of 0.050 mg L^{-1}) for selenium were obtained. A steady-state absorbance measurement sensitivity (corresponding to 0.0044 absorbance) of 0.0012 mg L^{-1} was obtained.

Table 3 summarizes data obtained detailing the recovery of Se(IV) spikes added to a sample of Ottawa River water, CASS-4 CRM seawater, and the North Atlantic seawater sample. It was necessary to spike all samples with analyte because their endogenous concentrations were far below the detection limit obtained for Se using this quartz tube AAS technique. It is noteworthy that no recovery of the spike is seen in the undiluted seawater matrixes. However, as the samples are diluted with DIW, reducing the salinity from its initial value of 30.7 parts per thousand (ppt) for CASS-4 and 34 ppt for the North Atlantic sample, the efficiency

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[24] Doran, J. W.; Alexander, M. *Soil Sci. Soc. Am. J.* **1977**, *41*, 70−73.

Table 3. Results for Determination of Se(IV) (0.7 M Acetic Acid)

sample	Se^{4+} (μg L^{-1}) native	added	found	recovery (%)
Ottawa River water	<2	50	44.1 ± 2.3	88
			52.1 ± 3.0[a]	104[a]
		100	85.6 ± 5.2	86
			98.9 ± 5.0[a]	99[a]
CASS-4 seawater	nd[d]	100	30.5 ± 0.9[a]	31[a]
			104.9 ± 5.0[b]	105[b]
MOOS-1 seawater	nd[d]	100	15.9 ± 3.0[a]	16[a]
			83.3 ± 4.0[c]	83[c]
NASS-5 seawater	0.018[e]	50	34.8 ± 5.0[a]	69[a]
			57.0 ± 5.2[c]	114[c]
		100	109.1 ± 4.2[c]	109[c]

[a] Twofold dilution. [b] Fourfold dilution. [c] Tenfold dilution. [d] nd, not detected. [e] Information value.

of generation rises. The increased efficiency is probably caused by bromine or iodine present in the seawater, as noted earlier.

CONCLUSIONS

This study has reported the first successful generation and identification of volatile selenium species formed in the presence of low weight molecular organic acids by the action of UV light. Identification by GC/MS revealed that the volatile species formed are SeCO, CH_3SeCH_3, and $CH_3CH_2SeCH_2CH_3$ in the presence of formic, acetic, and propionic acids, respectively. The proposed method is selective and simple in operation and can be used as an alternative to conventional hydride generation for the determination of trace amounts of selenium in some specific samples, the most noteworthy being those containing high concentrations of nickel and cobalt. UV light-induced vapor generation offers a number of other advantages, in that the only chemicals used in the alkylation process are the organic acids and the consumption of expensive, high-purity $NaBH_4$ and HCl can be avoided. This is therefore an extremely clean and safe means of production of metallic vapors used in the analytical chemistry laboratory. Clearly, the detection limit of the method might be improved further once an enhancement in vapor generation efficiency is achieved. It is also significant that other elements are apparently amenable to vapor generation by this route such that new, selective, and sensitive methods based on this same principle might be developed. This new area requires further investigation.

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