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Selective Detection of Selenium in Water Utilizing Chemical Reaction Interface Mass Spectrometry†

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Gas chromatography/chemical reaction interface mass spectrometry (GC/CRIMS) is shown to be a successful selective method for the detection of selenium-containing compounds. Two reaction gases, sulfur dioxide (SO_2) and hydrogen chloride (HCl), were examined in order to optimize selectivity and sensitivity. A high degree of selectivity was obtained with SO_2 as a reaction gas; however, the detection limit of $^{80}SeO_3^+$ at m/z 128 (the most sensitive ion for the SO_2-containing plasma) was only 3 ng μl^{-1}. HCl gas, which had been shown to be a good reaction gas for sulfur-containing compounds, was also shown to be an excellent reaction gas for selenium-containing compounds. In the HCl-containing plasma, $^{80}SeCl^+$ at m/z 115 was the most sensitive and selective ion for the detection of selenium-containing compounds. Selectivity was demonstrated by using mixtures of selenium-containing and non-selenium-containing compounds. The utility of GC/CRIMS as a method for the selective detection of selenium-containing compounds was demonstrated with a variety of selenium complexes that were formed by the addition of selective selenium complexing agents to selenium-containing water. The detection limit of selenium in water was ~62 pg and the linear dynamic range spanned at least two orders of magnitude (620 pg μl^{-1}–308 ng μl^{-1}).

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INTRODUCTION

Selenium-containing compounds play an important role in the environment and in human health. The element is recognized as an essential dietary mineral, with the recommended daily intake for humans set at 55 μg for females and 70 μg for males.[1] Zhang *et al.*[2] have determined that there is a significant difference in the selenium content of hair taken from healthy males compared with that of males with cancers of the digestive tract. Cardiomyopathies and muscular discomfort have also been linked to low selenium levels, often as a result of selenium deficiencies in the diet.[3,4] The necessity for determining the role of selenium in human nutrition, its sources and the relationship between its intake and requirements[5] make selenium detection studies increasingly important.

Variations in the amounts of selenium in the environment have made its detection in complex mixtures exceedingly difficult. For instance, in animal feed crops in the USA, the concentration of selenium can range from 0–80 mg per kilogram of whole plants.[6] The selenium content of US foods ranges from 120 μg kg^{-1} in poultry, eggs and dairy products to 29 600 μg kg^{-1} in Brazil nuts.[7] Since the 1980s, selenium levels in water have been a focal point for researchers in various disciplines.[8] In drinking and waste waters and in air, the Se concentration ranges from 0.200–15 pg ml^{-1} and from 0.47–0.84 pg ml^{-1}.[9] These important findings have led to an interest in developing techniques tailored to determine selenium concentrations in water.

Gas chromatography/mass spectrometry (GC/MS) is one of the most popular techniques in many areas of environmental analysis. However, owing to the complexity of selenium matrices and low concentrations of analytes, GC-MS often fails to afford the selectivity required for trace analysis. Inductively coupled plasma mass spectrometry (ICP-MS) and numerous non-mass spectrometric techniques have been developed in order to detect and quantify selenium.[10–13] Approximately 70–80% of all Se analyses have been performed using fluorimetry and atomic absorption spectrometry.[14] These techniques, although sensitive, suffer from background interferences and are unable to provide the necessary compound identification. Herold and coworkers[15] used isotope dilution GC-MS for determination of Se in urine. Although adequate precision in the determination of various isotope ratios was obtained by using 10 ng of Se, this technique required enriched ^{76}Se (>96% enrichment). Electron capture detection (ECD) has been used extensively in the determination of total selenium content. This has been accomplished through derivatization of selenium with 4-(trifluoromethyl)-1,2-phenylenediamine (TFPD) and 4-nitro-1,2-phenylenediamine (NPD) followed by GC.[15–18] Because ECD cannot identify unknown compounds directly, it requires that a standard be obtained. Since pure TFPD selenide (Se-TFPD) and pure NPD selenide (Se-NPD) are not commercially available, obtaining a standard requires much effort. Thus, a method of selective detection that combines compound independence, sensitivity and selectivity of atom and/or isotope-specific detection with compound character-

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ization is highly desirable.

Chemical reaction interface mass spectrometry (CRIMS) has been successful as a selective detection method for both elements and stable isotopes.[19–21] This technique involves a post-column reaction (a reaction interface) in which a reaction gas is added to a low-pressure microwave-induced helium plasma (MIP). As the effluent from a chromatographic column enters the reaction interface, it is converted into small, stable, neutral molecules. The mass spectra of these neutrals are used to identify and quantify the elements of interest. Once the retention time of the element of interest has been identified, the full mass spectrum of the element-containing compound can be acquired by repeating the experiment with the microwave plasma turned off. The CRIMS method combines the sensitivity of a selective GC detector with the compound identification ability of a mass spectrometer.

Recently, the CRIMS method of detection has been reviewed.[20] Abramson utilized GC/CRIMS in biological applications.[20] The major focus of this laboratory has been the application of GC/CRIMS in environmental studies.[22] This paper presents an extension of GC/CRIMS by demonstrating its application to the selective detection and characterization of selenium-containing compounds. Two reaction gases were studied with regard to their selectivity for selenium compounds in mixtures. The detection limits and quantitation of the selenium-containing compounds are also presented.

EXPERIMENTAL

The experimental details were reported previously.[22] A 30 m × 0.25 mm i.d. DB-5 capillary column (J & W Scientific, Folsom, CA, USA) was used to introduce samples into the plasma. A variable-leak valve (Granville-Phillips, Boulder, CO, USA) controlled the flow of the reaction gas into the plasma. A Varian (Fernando, CA, USA) Model 3400 gas chromatograph was interfaced to a Finnigan (San Jose, CA, USA) Model 4023 mass spectrometer by means of a heated transfer line. Electron impact ionization with an electron energy of 70 eV was used for ionization. Graphite Vespel ferrules (SGE, Austin, TX, USA) were used for the column, transfer line and ceramic tube connections. The microwave chamber was powered by a 100 W, 2450 MHz power supply (Opthos, Rockville, MD, USA) operated at 70 W forward power and 6 W reflected power. The instrumental set-up is shown in Fig. 1.

In the initial stages of experimentation, HCl (with an unspecified purity) was used as a reaction gas. However, it was found to contain trace amounts of HBr. The HBr contamination presented a barrier to selective detection because of the formation of $ClBr^+$ at m/z 114 and 116 within the plasma. The intensities of these signals were too high for any sensitive detection of $^{80}SeCl^+$ at m/z 115. This complication was overcome by utilizing research-grade HCl gas. For the selective detection of Se-containing compounds with SO_2 as a reaction gas, a stock solution containing 832.5 ng μl^{-1} diphenyl selenide in hexane was used to make a serial dilution down

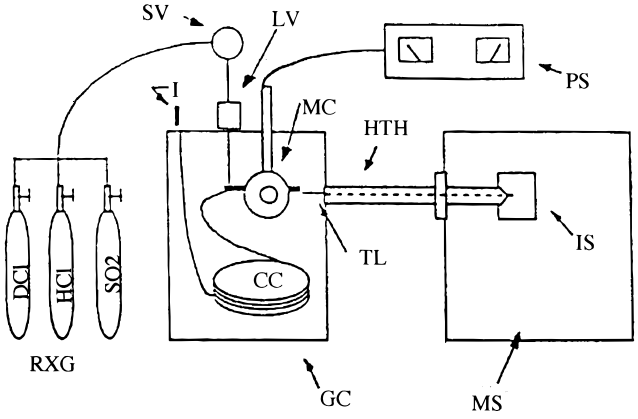

Figure 1. Schematic diagram of the GC/CRIMS instrumental set-up. GC, Varian Model 3400 gas chromatograph; MS, Finnigan Model 4023 mass spectrometer; IS, Finnigan Model 4500 ion source; CC, 30 m DB-5 capillary column; TL, SGE megabore transfer line; HTH, TSQ-70 heated transfer line housing; MC, microwave cavity; LV, Granville-Phillips Series 203 variable-leak valve; SV, Predyne solenoid valve; PS, Kiva 24.5 MHz microwave power supply; I, Varian Model 3400 split/splitless injector; RXG, reaction gas supply tank.

to 8.3 pg μl^{-1} in hexane. Each solution contained constant amounts of *p*-dichlorobenzene (85 ng μl^{-1}) and dodecane (83 ng μl^{-1}) that acted as an internal standard for the dynamic range study.

Two complexing agents, TFPD and NPD, are commonly used for selenium trace analysis involving GC. The chemical procedure used to prepare the selenium complexes from selenious acid (H_2SeO_3) was similar to the protocol used by Reamer and Veillon.[5,23]

The CRIMS method of analysis, with HCl as the reaction gas, was applied to the quantitation of selenium in water. Selenium(IV) was formed by dissolving selenious acid in pure water. The selenium in water was derivatized by TFPD and NPD to form Se-TFPD and Se-NPD according the following procedure.

A 1% (w/v) NPD solution was prepared by dissolving 0.500 g of NPD in 5.0 ml of absolute ethanol and diluting to 50 ml. The selenium solution was prepared by mixing 2.0 ml of the NPD solution, 2.0 ml of 2.5 M formic acid, and 5.0 ml of 500 ppm selenious acid. This solution was then diluted to 25 ml with deionized water and heated to 50 °C in a water-bath. After cooling to room temperature, the selenium complex was extracted using 10 ml of toluene. The samples were dried under a stream of nitrogen and the residue was dissolved in 1 ml of toluene. A serial dilution was made from this stock solution. Each serial solution was then spiked with phenyl sulfide as the internal standard. The final concentration of the internal standard in each solution was 100 ng $\mu l.^{-1}$ A blank solution of NPD was also prepared by the above procedure. The same procedure was followed for derivatization with TFPD. A 1 µl volume of each solution was then injected into the GC system in the splitless mode. The mean of the three injections for each dilution was used to establish the linear dynamic range.

All chemicals used were of reagent grade from Aldrich (Milwaukee, WI, USA), except as follows: anisole (Kodak, Rochester, NY, USA), nitrobenzene (Malinckrodt, Paris, KY, USA), diphenyl selenide (Alfa, Danvers, MA, USA), TFPD (Lancaster, Windham, NH,

USA), HCl gas, reagent grade (99.999%), and SO_2 gas, reagent grade (99.98%) (Matheson, Amarillo, TX, USA) and 500 ppm selenious acid (H_2SeO_3) in water (Multielement Mix B-1 Spectrometric Standard Solution, Reference Material 3172a, National Institute of Standards and Technology, Gaithersburg, MD, USA).

The GC temperature program for the SO_2 experiment was: initial temperature 80 °C held for 2 min, increased from 80–230 °C at 50 °C min^{-1}, held at 230 °C for 20 min. The GC programming conditions for the HCl experiments were: initial temperature 80 °C held for 1 min, increased from 80–250 °C at 30 °C min^{-1} held at 250 °C for 10 min.

RESULTS AND DISCUSSION

Chemistry

Two reaction gases, SO_2 and HCl, were examined. The idea was to use SO_2 as a source of excess oxygen to produce selenium oxides when selenium-containing compounds are introduced into the SO_2-containing helium plasma. In addition, SO_2 has previously been shown to be effective as a reaction gas for the selective detection of chlorine- and bromine-containing compounds when using GC/CRIMS.[23] When SO_2 was used as the reaction gas, $^{80}SeO_3^+$ at *m/z* 128 and HCl^+ at *m/z* 36 were the most sensitive ions for the selective detection of selenium- and chlorine-containing compounds, respectively; CO_2^+ at *m/z* 44 was the most sensitive ion for the non-selective detection of all carbon-containing compounds. These three ion chromatograms were used to study the selectivity and quantitation of GC/CRIMS. Figure 2 shows the ion chromatograms for *m/z* 44 and 128, and also for *m/z* 112 ($^{80}SeO_2^+$) and 36 (HCl^+). SeO_2^+ at *m/z* 112 was also completely selective for selenium-containing compounds [Fig. 2(C)], but the sensitivity of this ion was only one tenth of that of *m/z* 128.

It is important to note that when the SO_2-containing helium plasma was used, $S_2O_4^+$ at *m/z* 128 was also detected. This compound interferes with $^{80}SeO_3^+$ at *m/z* 128, the most sensitive selenium ion. This is shown in Fig. 2(D), in which the $S_2O_4^+$ creates a broad peak between 4:10 and 6:15 min. When SO_2 was used as a reaction gas, the limit of detection for *m/z* 128 ($^{80}SeO_3^+$) was ~3 ng for a 1 µl injection of diphenyl selenide solution. At high SO_2 flow rates, the spectrum of $S_2O_4^+$ was stable and the peak for it did not obscure that of $^{80}SeO_3^+$ at *m/z* 128; on the other hand, the high SO_2 concentration complicated plasma ignition.

In summary, SO_2 was useful as a reaction gas for the detection of selenium-containing compounds. In addition to selenium, chlorine- and bromine-containing compounds could also be selectively detected. However, the limit of detection of selenium-containing compounds was only 3 ng μl^{-1}, and the presence of $S_2O_4^+$ background chemical noise interfered with $^{80}SeO_3^+$. These complications made it necessary to study an alternative reaction gas.

Hydrogen chloride has proved to be an effective reaction gas for selective detection of sulfur-containing compounds in complex mixtures.[24] Since selenium is in the same group of the Periodic Table as sulfur and exhibits many similar chemical properties, HCl was examined with regard to selenium detection. In the HCl-containing helium plasma, selenium-containing compounds are produced in the ion source of the mass spectrometer as $^{80}SeCl^+$ at *m/z* 115, the most selective selenium ion, and HCN^+ at *m/z* 27, the non-selective carbon ion,[24] which is used to detect all organic compounds. The complete selectivity of the *m/z* 115 ion was demonstrated by using a mixture containing anisole, 1,3-dichlorobenzene, nitrobenzene, dodecane, phenyl sulfide and diphenyl selenide (Fig. 3). As shown, *m/z* 115 is completely selective for the selenium-containing compound. For these reasons $^{80}SeCl^+$ was chosen to be studied with regard to the selectivity and quantitation of selenium-containing compounds.

Detection and quantitation of selenium in water

The application of GC/CRIMS for the selective detec-

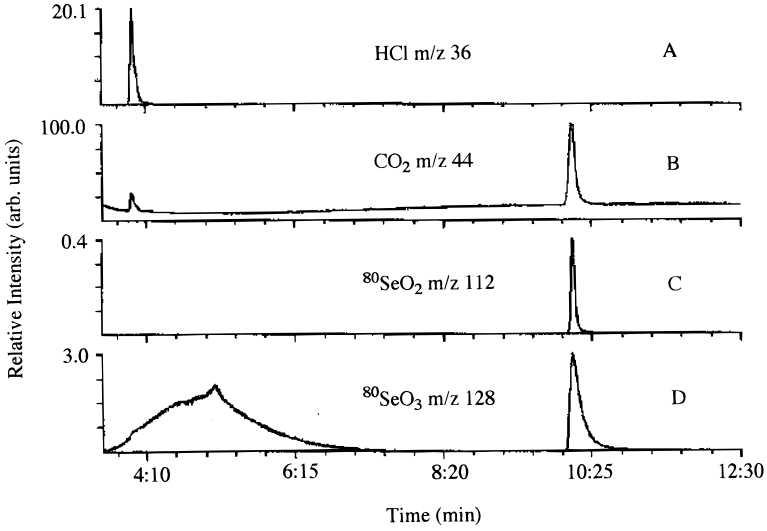

Figure 2. Single ion chromatograms for (A) *m/z* 36 (HCl^+), (B) *m/z* 44 (CO_2^+), (C) *m/z* 112 ($^{80}SeO^+$) and (D) *m/z* 128 ($^{80}SeO_2^+$) using SO_2 as a reaction gas. A 1 µl volume of 832.5 ng μl^{-1} diphenyl selenide in hexane which contained 85 ng μl^{-1} of *p*-dichlorobenzene as internal standard was injected using the splitless mode.

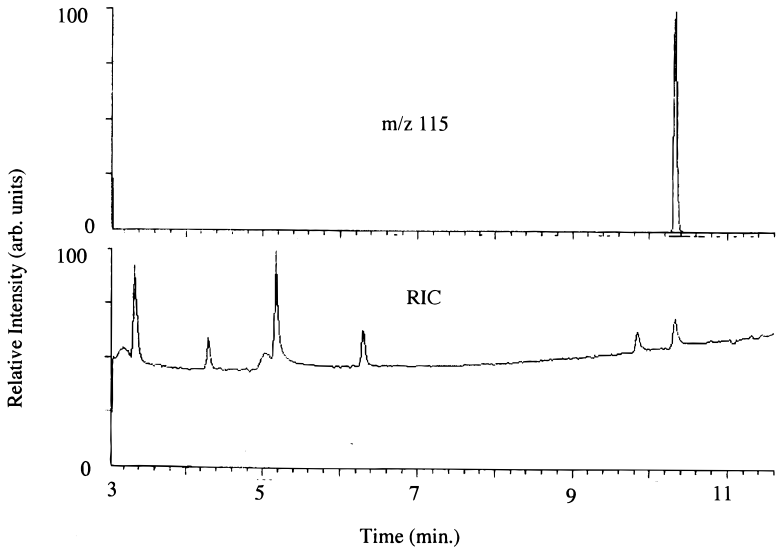

Figure 3. Reconstructed ion chromatogram/single-ion chromatogram showing selective detection of a diphenyl selenide mixture of six compounds, anisole, 1,3-dichlorobenzene, nitrobenzene, dodecane, phenyl sulfide and diphenyl selenide (in order of elution time), using HCl as reaction gas.

tion of Se-TFPD is shown in Fig. 4. A 1 μl volume of toluene solution that contained 7 ng μl^{-1} Se-TFPD and 100 ng μl^{-1} phenyl sulfide was injected into the GC system with the injector in the splitless mode. Two masses, *m/z* 115 ($^{80}SeCl^+$) and *m/z* 67 (SCl^+), were monitored using the single-ion monitoring mode with an integration time of 100 ms per ion. Phenyl sulfide was used in this experiment as the internal standard because sulfur-containing compounds are known to be selective when HCl is the reaction gas.[24] As shown in Fig. 4, an excellent signal-to-noise ratio (S/N) is achieved for 7 ng of Se-TFPD injected. This amount represents the detection of ~3 ppm of selenium(IV) in the original water solution. A detection limit (S/N = 3) of ~61 ppb of selenium(IV) was achieved with Se-TFPB as the selenium-containing compound; however, the limit of quantitation (the lowest point on the linear dynamic range curve) was ~600 pg.

To demonstrate the applicability of CRIMS for the selective detection of Se-NPD, a solution containing this compound and diphenyl selenide (internal standard) was injected into the GC system with the injector in the splitless mode. The resulting data were used to construct the linear dynamic range of the Se-NPD complex (Fig. 5). Single-ion monitoring at *m/z* 115 was used with a 200 ms integration time. As shown, the linear span is at least 2.5 orders of magnitude [600 pg–308 ng of selenium(IV)]. If the identity of the selenium- or sulfur-containing compounds was necessary, the experiment could be repeated, and the mass spectrum could be obtained using the full-scan mode with the microwave plasma off.

In order for CRIMS to be useful for the trace determination of selenium in real samples, the detection limits must be enhanced by one to two orders of magnitude. Many protocols for the analysis of environmental samples, however, require concentration prior to qualitative and subsequent quantitative analysis. These manipulations often result in one to two orders of mag-

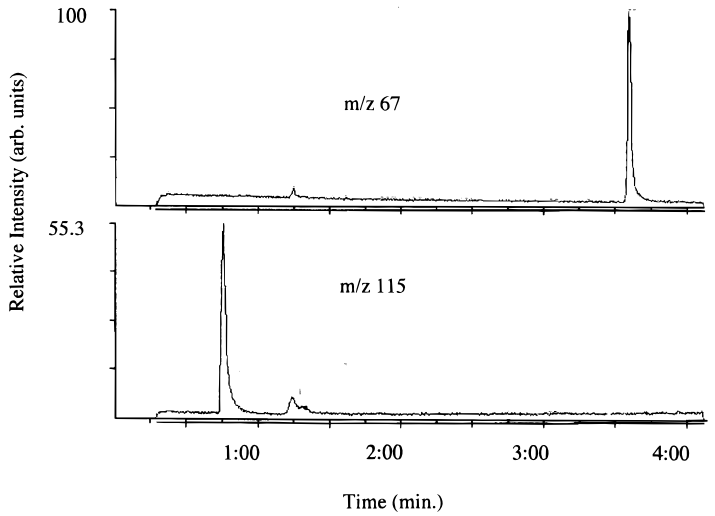

Figure 4. Single-ion chromatogram for a 1 μl injection of a solution containing 7 ng μl^{-1} trifluorophenyldiamine selenide ($SeCl^+$ at *m/z* 115 and SCl^+ at *m/z* 67) and 100 ng μl^{-1} phenyl sulfide as an internal standard using HCl as reaction gas.

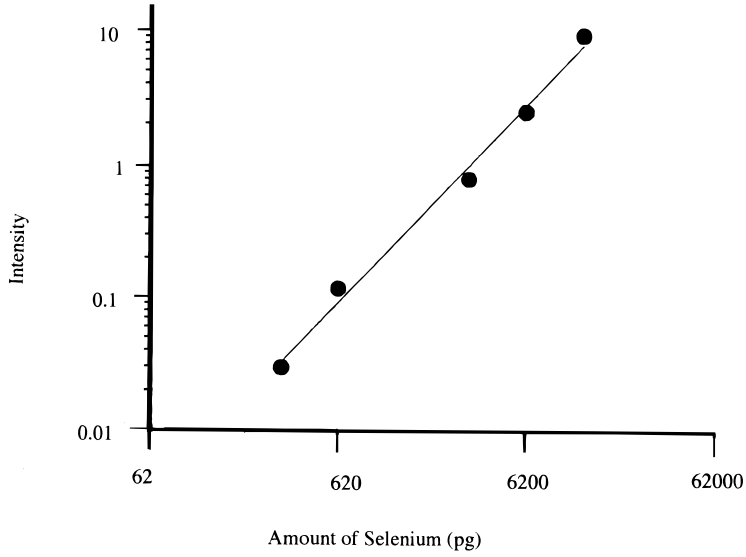

Figure 5. Linear dynamic range for 4-nitropiazselenol with diphenyl selenide as an internal standard using HCl as reaction gas.

nitude increases in the sample's concentration. In such cases, GC/CRIMS may be used to detect trace amounts of selenium in real samples.

CONCLUSIONS

GC/CRIMS was applied to the selective detection of selenium-containing compounds in mixtures. SO_2 and HCl were examined as reaction gases. A detection limit of 7 ng was achieved for diphenyl selenide using SO_2 as the reaction gas. A lower detection limit for selenium(IV) in water (60 pg) was achieved when HCl was used as the reaction gas. A linear dynamic range of 2.5 orders of magnitude (600 pg–308 ng) was obtained. It was found that HCl is a better reaction gas than SO_2 for the selective detection and quantitation of selenium-containing compounds. Moreover, both selenium- and sulfur-containing compounds can be detected very selectively at the same time. Selective detection of selenium in water by complexation reactions that are common to GC analysis demonstrates the utility of CRIMS for detection of selenium-containing compounds in mixtures.

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