

Short communication

Determination of dimethylselenide and dimethyldiselenide by gas chromatography–photoionization detection

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Abstract

A simple method for the determination of volatile selenium compounds employing a gas chromatograph equipped with a photoionization detector is described. The method involves the direct injection of dimethylselenide (DMS) or dimethyldiselenide (DMDS) into the gas chromatograph; no derivatization of the sample was required. The photoionization detector was capable of detecting 60 pg (0.55 pmol) of DMS and 150 pg (0.80 pmol) DMDS. Sensitivity was 10–50 times greater with DMS and 4–20 times greater with DMDS when the photoionization detector was employed than when the flame ionization detector was employed.

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1. Introduction

Selenium is a common environmental element whose presence in soils and groundwaters may be due to either natural or anthropogenic activities. In small amounts, inorganic selenium is an essential element; however, in large amounts, selenium toxicity can cause fatigue, irritability, and damage to the nervous system [1]. Many plants and microorganisms can transform inorganic selenium species into volatile organic species. This biological activity is important in the global cycling of selenium and is an important step in reducing the toxicity of inorganic selenium in soils. Volatile organic species escape from the soil and are far less toxic than are inorganic selenium species [2]. Dimethylselenide is the most common volatile organic selenium species produced by microorganisms [3,4].

There have been a number of reviews on the analysis of selenium and selenium-containing compounds and a number of analytical procedures are available [5–10]. Atomic absorption spectrometry (AAS) is perhaps the most commonly used method for total selenium analysis [10] with hydride

generation AAS being the most sensitive of the AAS procedures. For dimethylselenide (DMS) and dimethyldiselenide (DMDS), detection limits of 5–25 pg have been reported [5]. For the AAS analysis of gaseous selenides, the vapors must first be trapped and then oxidized to selenite for analysis.

Gas chromatography (GC) has been used to identify and determine the amount of volatile organic selenium species in samples. Flame ionization detection (FID) has been employed as a method for the detection of DMS and DMDS. FID analysis is simple, requiring no sample derivatization or other sample preparation, and is cost effective, in that FID detectors are inexpensive. In addition, FID systems are probably the most common detectors available on gas chromatographs. However, FID is not as sensitive as many alternative approaches. Also, flame ionization detectors, because they detect hydrocarbons and because there are so many different hydrocarbon compounds, have poor selectivity. Electron-capture detection (ECD) has also been employed to measure organoselenium compounds. This approach offers good selectivity and detection limits in the picogram range but requires that the selenium species be derivatized to a form that can be detected by ECD [11–13]. Mass spectrometry and hydride generation AAS can be coupled to GCs and used to detect DMS and DMDS [5]. Mass spectrometry offers very high assurance of sample identity

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and detection limits that are in the picogram range for many organoselenium compounds [13,14] though the cost of mass spectrometry can be a problem for some laboratories.

Colorimetric approaches are also available but are tedious and offer very low sample throughput. These approaches involve trapping of the volatile selenium species and conversion to selenite for colorimetric measurement [10]. With any procedure involving the chemical alteration of the volatile selenium species, be it derivatization for ECD measurement or conversion to selenite for chemical or AAS measurement, losses caused by incomplete transformation during the process can be a problem.

The objective of this study was to evaluate the use of photoionization detection (PID) as a simple procedure for the direct measurement of DMS and DMDS and to compare this procedure with the direct measurement of these compounds with FID.

2. Experimental

2.1. Instrumentation

Gas chromatography was carried out using a Hewlett-Packard 5790 instrument equipped with a Hewlett-Packard FID system and with a HNU Systems (Newton, MA, USA) model PI 52-02A photoionization detector. Liquid injections were 1 μl and headspace injections were 500 μl in volume. Injection was into a split–splitless injector operated in the splitless mode. Port temperature was 235 $^{\circ}\text{C}$. Peak separation was achieved on a GS-Q 30 m \times 0.540 mm column supplied by J&W Scientific (Folsom, CA, USA). The carrier gas was helium at 37 ml min^{-1} . Oven temperature varied from study to study. The FID system was operated at 235 $^{\circ}\text{C}$ with hydrogen supplied at 30 ml min^{-1} and air supplied at 240 ml min^{-1} . The PID system was operated with a 10.2 eV bulb at 235 $^{\circ}\text{C}$. Peak area was estimated using a Shimadzu Class VP electronic integrator.

2.2. Materials

DMS and DMDS were obtained from Sigma–Aldrich (Milwaukee, WI, USA). Stock solutions containing 1000 $\text{ng } \mu\text{l}^{-1}$ were prepared by diluting 7.1 μl of DMS or

5.0 μl DMDS into 10.0 ml methanol. Standard solutions in methanol containing 100, 10, 1 and 0.1 $\text{ng } \mu\text{l}^{-1}$ were prepared by serial dilution of the stock solution.

2.3. Soil columns

Columns were 2.6 cm \times 30 cm glass tubes filled with a support matrix of 30 grit (0.35 mm sieve size) washed quartz sand coated with 2.5 g of soybean oil and packed to a bulk density of 1.49 g ml^{-1} . Reconstituted water [15] supplemented with 10 mg l^{-1} selenite-Se was pumped upwardly through the columns at 1.8 ml h^{-1} throughout the study. Columns were inoculated with a soil wash [16] and incubated in the dark at 15 $^{\circ}\text{C}$ for 5 weeks. Gases forming in the columns were collected in an all glass and stainless steel effluent line gas trap equipped with a Teflon-lined rubber septum. A syringe equipped with a valve was used to transfer 0.5 ml of “effluent gas” to the GC inlet.

2.4. Statistical comparisons

Statistical comparisons and linear regression analysis were made using the InStat computer program (GraphPad Software).

3. Results and discussion

3.1. PID analysis

The GC system was capable of resolving and detecting picogram amounts of DMS when the PID was used. This was demonstrated by injecting a sample containing 100 pg DMS into a 140 $^{\circ}\text{C}$ isothermal GC. Under the conditions used for this study, the limit of detection (LOD), using the three times noise criterion, was about 60 pg (0.55 pmol) for DMS. The LOD was higher with the DMDS analysis. No peak was detected when a 100 pg sample of DMDS was injected into a 220 $^{\circ}\text{C}$ isothermal GC, but a peak of about 10 times noise was detected when a 500 pg sample of DMDS was injected. Thus, the minimum amount detectable would be about 150 pg (0.80 pmol). Detector response was linear over the range evaluated with both compounds (Table 1).

Table 1
Figures of merit

Detector	Compound	Reproducibility with DMS or DMDS (R.S.D., %; $n = 3$)					Calibration ($y = kx + d$) ^a		
		0.1 ng	1.0 ng	10 ng	100 ng	1000 ng	k	d	r^2
FID	DMS	ND ^b	ND	20.1	5.9	1.7	530	282	0.9997
	DMDS	ND	ND	19.4	3.7	3.0	364	2	0.9991
PID	DMS	6.8	0.5	1.4	2.8	4.3	461	127	0.9984
	DMDS	ND	10.6	6.9	4.2	5.6	−1479	746	0.9972

^a y = peak area (counts s^{-1}); x = concentration of DMS or DMDS in nanograms.

^b Not detected.

3.2. FID analysis

When the GC system was operated in the isothermal mode at 140 °C and the FID employed as the detector the LOD was between 1 and 5 ng of DMS. This was in part due to the large peak formed by the methanol solvent. DMS appeared as a tangent peak on the tail of the methanol peak and the methanol tail interfered with the integration of the DMS peak. This was less of a problem with the PID system as methanol does not produce a large peak with this detector. Reducing the temperature of the oven to 110 °C isothermal reduced the interference caused by the methanol tail but did not lower the detection limit. With DMDS, the LOD was between 10 and 100 ng when the GC was operated in the isothermal mode at 220 °C (data not presented), and, as was the case with DMS, the tail of the methanol solvent peak interfered with the integration of the peak. Reducing the temperature of the oven to 180 °C isothermal, lowered the detection limit to about 5 ng. Detector response was linear over the range evaluated with both DMS and DMDS (Table 1).

3.3. Soil column gas analysis

The analysis of DMS and DMDS standards in gas samples worked well and achieved detection limits that were similar to those observed with liquid samples containing DMS and DMDS (data not presented). Based on these results with gas samples, headspace analysis of samples collected weekly was used to monitor the formation of DMS and DMDS in the gaseous effluent of three soil columns over a period of 6 weeks. In the first 3 weeks of operation, no DMS was detected in the effluents from these columns but in week 4, 3 ± 1 ml of gas containing 0.68 ng ml⁻¹ DMS (0.338 ±

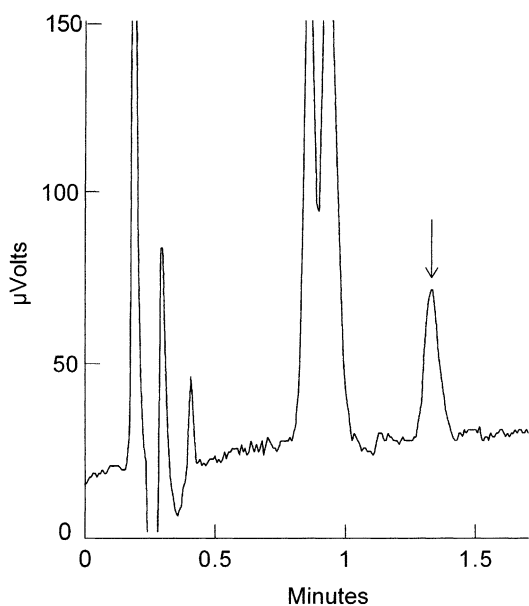


Fig. 1. DMS, 470 pg in a 0.5 ml headspace sample, collected in a gas trap placed in the effluent line from a 4-week-old soil column fed selenite in the influent buffer.

0.092 ng per 0.5 ml injection) was detected (Fig. 1). In week 5, 3 ± 0.4 ml of gas containing 0.99 ng ml⁻¹ DMS (0.494 ± 0.124 ng per 0.5 ml injection) was detected in the “effluent gas” from the columns. No DMDS was detected.

4. Conclusions

The PID was found to provide a simple and sensitive method for the determination of DMS and DMDS in both liquid and headspace samples. With DMS, the PID was 10–50 times more sensitive than FID; with DMDS, PID was 4–20 times more sensitive than FID. Detection limits when the PID was employed were about 60 pg (0.55 pmol) with DMS and 150 pg (0.80 pmol) with DMDS. Similar detection limits were observed when gas samples were injected and PID proved to be a useful detection method for analyzing DMS vapors evolving from soil columns.

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