

Technical Notes

Headspace Membrane Introduction Mass Spectrometry for Trace Level Analysis of VOCs in Soil and Other Solid Matrixes

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A new MIMS-derived technique, headspace membrane introduction mass spectrometry (HS-MIMS), is described for direct trace level analysis of volatile organic compounds (VOCs) in soil and other dry or wet solid matrixes. A silicone membrane interface is placed about 15 cm from the ion source, and a closed airspace (headspace) is created by connecting a toggle valve to the 1/4 in. tubing that connects the membrane interface to the ion source. For the VOC analysis, the headspace is evacuated and the solid sample vessel is heated to 90 °C. The VOCs are rapidly desorbed from the sample, pervaporated through the membrane, and preconcentrated for 4 min in the evacuated headspace. Then, the toggle valve is opened and the trapped VOCs are released into the ion source region of a quadrupole mass spectrometer. By electron ionization and selected-ion monitoring, a relatively sharp and intense peak is obtained and used for quantification. The HS-MIMS analysis shows excellent linearity and reproducibility and detection limits for many VOCs typically of 50–100 ng/kg (ppt).

Soil, though only a tissue-thin layer compared to Earth's total diameter, is the most important part of the geosphere; it is vital to life on earth, to humans, and to most terrestrial organisms.¹ Soil is the major medium in which the food required by most living organisms is produced; and soil is in direct contact with the sources of drinking water. It is mandatory, therefore, to efficiently monitor, control, and remediate any type of soil contamination. Poisonous chemicals are major soil contaminants, and leaking storage tanks, improper disposal of spent solvents, and inadequately designed landfills are major sources of soil contamination by a variety of organic compounds.

Volatile organic compounds (VOCs) are major soil contaminants, and VOCs easily diffuse from the point of emission over wide areas, finding their way into groundwater.² Therefore, methods to collect and analyze soils contaminated by VOCs have been actively researched and debated.³ A conventional method

for VOC analysis in soil and other solid samples uses collection of the sample into a headspace vial followed by static or dynamic headspace gas chromatography or gas chromatography/mass spectrometry analysis.⁴ The static headspace method is relatively simple and requires little sample preparation, but sensitivity is limited; hence, the method has been restricted to soils with relatively high VOC concentrations. Higher sensitivity for VOC analysis in soil is often achieved by more demanding dynamic headspace methods.³

The increasing demand for efficient on-site monitoring and shorter sample holding and processing times has stimulated the development of simpler, more rapid, more sensitive, and more selective analytical techniques to detect and quantitate various chemical contaminants in the diversity of environmental matrixes.⁵ Driven mainly by this demand, membrane introduction mass spectrometry (MIMS)⁶ and several MIMS-derived techniques such as purge-and-membrane mass spectrometry (PAM-MS),⁷ cryotrapping-MIMS (CT-MIMS),⁸ trap and release-MIMS (T&R-MIMS),⁹ and laser desorption-MIMS (LD-MIMS)¹⁰ have emerged as highly efficient methods for the direct, rapid, selective, and very sensitive analysis of VOCs^{6–8} and semi-VOCs^{9,10} in various matrixes,¹¹ particularly in aqueous matrixes. Owing to selective transport through the hydrophobic silicone polymer membrane, MIMS concentrates and introduces VOCs from gaseous or aqueous matrixes *directly* into a mass spectrometer. The silicone membrane

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also functions as an efficient interface between the liquid or gaseous sample and the high vacuum of the mass spectrometer. The hydrophobicity of the silicone membrane and the permeability of the VOCs permit extraction, concentration, and injection to be performed rapidly and simultaneously. On-line preconcentration procedures can also be applied,^{8-10,12} thus further improving the already low MIMS detection limits for VOCs or reducing the not so low conventional MIMS detection limits for semi-VOCs.

For the direct soil analysis of VOCs by MIMS, a purge-and-membrane mass spectrometry technique (PAM-MS)⁷ was recently developed. In the PAM-MS technique, VOCs are purged from the soil matrix (ideally dry or low humidity soil samples) with an inert gas and the stream is directed through a sheet membrane module. Then, the VOCs pervaporate through the membrane directly into the ion source of a mass spectrometer. Excellent linearity, reproducibility, and VOC detection limits in the low-ppb range (1–20 $\mu\text{g}/\text{kg}$) normally obtained by conventional MIMS are achieved.⁷

Herein we describe an alternative, simple, relatively rapid, specially more sensitive (low ppt's) headspace-MIMS (HS-MIMS) technique¹³ for the analysis of VOCs in both dry and wet soil and other solid matrixes. The HS-MIMS technique combines the major advantages of MIMS for VOC analyses, solvent-free direct analysis with superior VOC enrichment, selectivity, and sensitivity for dry and specially for wet solid samples, with the great signal enhancement provided by headspace preconcentration.

EXPERIMENTAL SECTION

Figure 1 shows a diagram of the headspace membrane introduction mass spectrometry (HS-MIMS) system. The polymethylsilicone membrane (C, Silastic 500-3 from Dow Corning Co., 0.010 in. thickness, 20 mm diameter) is firmly connected by six screws to a stainless steel membrane holder (D, 35 mm o.d., 19 mm i.d.) placed about 15 cm from the ion source. A $1/4$ in. o.d. stainless steel tube with a toggle valve (F) connects the membrane holder to the ion source of a quadrupole mass spectrometer (ABB-Extrel, Pittsburgh, PA) fitted with a high-transmission $3/4$ in. mass analyzer quadrupole. A stainless steel sample vessel (I, 40 mm o.d., 32 mm i.d., 100 mm height) is screwed into the membrane holder and inserted into an aluminum oven (A, 65 mm o.d., 42 mm i.d., 110 mm height) heated by four electrical resistances (B, 15 Ω) that dissipate ~ 200 W. An electronic unit (G) with a thermocouple (E) controls the final oven temperature and speed of heating. To reduce memory effects, the transfer lines were constantly heated to 120 $^{\circ}\text{C}$; this heating avoids condensation and speeds transfer of the trapped analytes into the mass spectrometer.

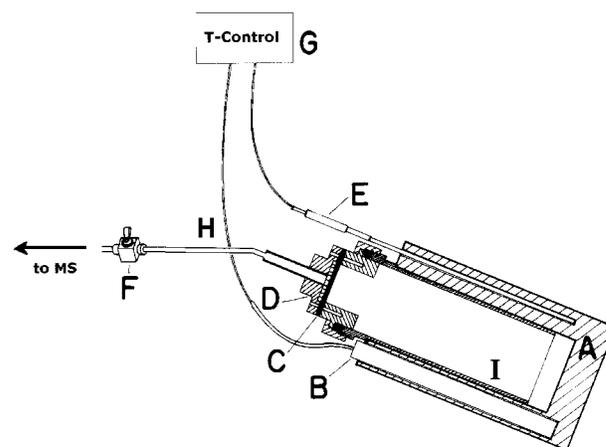


Figure 1. Diagram of the HS-MIMS system: (A) aluminum oven; (B) electrical resistances; (C) membrane interface; (D) membrane holder; (E) thermocouple; (F) toggle valve; (G) heating and oven temperature control; (H) headspace; (I) sample vessel.

For the HS-MIMS analysis, the solid sample is placed into the sample vessel, which is then screwed into the membrane holder. The oven is connected to the sample vessel, and the toggle valve is opened to evacuate the headspace (H). Then, the toggle valve is closed and the oven is rapidly heated to 90 $^{\circ}\text{C}$ for 4 min; during heating, the VOCs (as well as water vapor and air) permeate the membrane (pervaporation) and are preconcentrated in the headspace. Finally, the toggle valve is opened, and the trapped VOCs are rapidly transferred from the headspace to the ion-source region of the mass spectrometer, where they are analyzed. To test the system, the concentrations of the VOC contaminants were adjusted to 500 $\mu\text{g}/\text{kg}$ and the humidity set to near 25%, unless otherwise noted.

Deuterated benzene was used as the internal standard¹⁴ for initial instrument calibration, to determine response factors (RFs) and reproducibility for VOC quantitations and to verify instrument operation and calibration on a daily basis.¹⁵ Calibration standards for each analyte were prepared at five different concentrations, and the standard and internal standard (benzene- d_6) solutions were spiked (without aging) into a known and constant amount of the solid sample. After the determination of the peak height responses for each standard and internal standard, the response factors for each analyte were calculated. Five replicates were performed for all measurements.

RESULTS AND DISCUSSION

HS-MIMS Signal Profile. Figure 2 exemplifies the signal profile using selected-ion monitoring (SIM) (of the major m/z 91 fragment ion) for HS-MIMS analysis of a solid sample (powered silica, grade 60, 70–230 mesh, Merck) contaminated with toluene. After the toggle valve is closed, and during the 4 min of sample heating, no signal is observed, since the VOCs are being preconcentrated in the headspace. The toggle valve is then opened, and the m/z 91 signal increases sharply as the trapped VOCs are rapidly transferred from the headspace to the ion-source region of the mass spectrometer. The signal then starts to vanish, fading away nearly completely after 15 min. During analysis,

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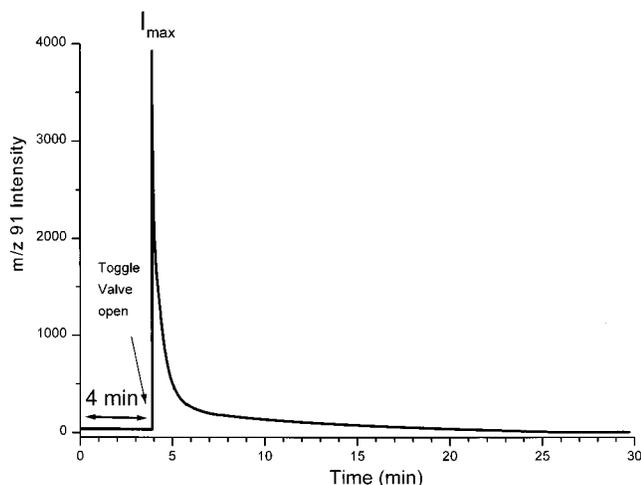


Figure 2. HS-MIMS signal profile for powered silica spiked with toluene.

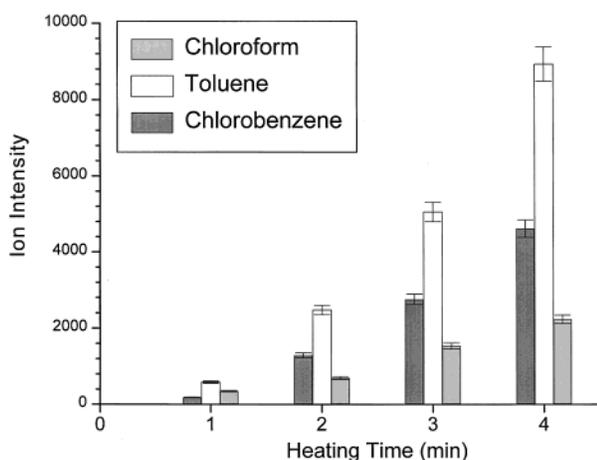


Figure 3. HS-MIMS signal intensity (I_{\max}) at different heating and trapping times for SIM of powered silica spiked with toluene, chloroform, and chlorobenzene.

however, complete purging of the headspace is not necessary; to shorten the analysis time, the sample is removed just after the signal maximizes (typically after 1 min) while purging of the headspace is completed during preparation of the next sample. The maximum HS-MIMS peak intensity (I_{\max}) is then used for calibration and for calculating the concentration of purgable VOCs in the samples.

Operating parameters. (a) Heating and Trapping Time.

To determine the best heating and trapping time, during which a sample is heated and the VOC analytes permeate the membrane and are trapped in the headspace, a series of experiments were performed for toluene, dichlorobenzene, and chloroform in powered silica (used as a standard solid sample). In these experiments, SIM was applied to the major 70 eV EI fragment of each analyte: $C_7H_7^+$ of m/z 91 for toluene, $CHCl_2^+$ of m/z 83 for chloroform, and $C_6H_5Cl^+$ of m/z 112 for chlorobenzene. The results are summarized in Figure 3. Signal profiles similar to that shown in Figure 2 were observed with increasing intensities from 1 min up to 4 min of oven heating. For heating and trapping periods beyond 4 min, however, opening of the toggle valve caused overpressure (owing mainly to VOC but also to water and air permeation), which resulted in a shutdown of the mass spectrom-

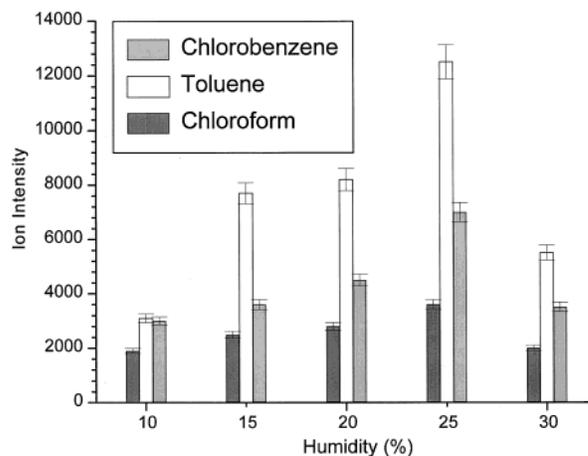


Figure 4. HS-MIMS signal intensity (I_{\max}) at different humidities for SIM of powered silica spiked with toluene, chloroform, and chlorobenzene.

eter. The heating and trapping time for the HS-MIMS analysis was then defined as 4 min.

(b) Humidity. Soils contaminated with VOCs are often humid, and sorption of VOCs in soil has been shown to depend on humidity, since these two constituents often compete for the same sites.^{4b} The HS-MIMS system seems particularly suitable for the analysis of wet soil and other wet solid samples; hence, experiments were performed for a solid sample with variable humidity. Powered silica was contaminated with toluene, chloroform, and chlorobenzene, and the humidity was varied from 10 to 30%.

Figure 4 shows that the HS-MIMS system works adequately for wet solid samples and that humidity significantly influences the HS-MIMS responses; the three compounds behave similarly, and the highest signal intensity was observed for 25% humidity. Since humidity helps in the heat transmission through the sample, for up to the limit of 25% humidity, the higher the humidity of the solid sample, likely the more rapid and uniform the heating of the sample, likely the more efficient the VOC desorption owing to water vapor transport, and thus the greater the VOC responses. However, as indicated by responses at 30% humidity, too high humidity reduces sensitivity.

As maximum HS-MIMS sensitivity occurs for soils with ~25% humidity, it is therefore desirable for trace-level analysis to adjust the humidity of dry soil samples or of those with low humidity levels. For this purpose, diluted aqueous solutions of the selected internal standard can be added to the soil samples, so that humidity adjustment to a value close to 25% is attained and fluctuations in signal response owing to possible variations in the final humidity can be compensated when the responses of the internal standard are determined for each sample.

(c) Oven Temperature. Experiments using powered silica of 25% humidity contaminated with toluene, chlorobenzene, and chloroform were also performed to determine the best oven temperature. For all three analytes, 90 °C was found to be the best oven temperature, resulting in the highest HS-MIMS responses.

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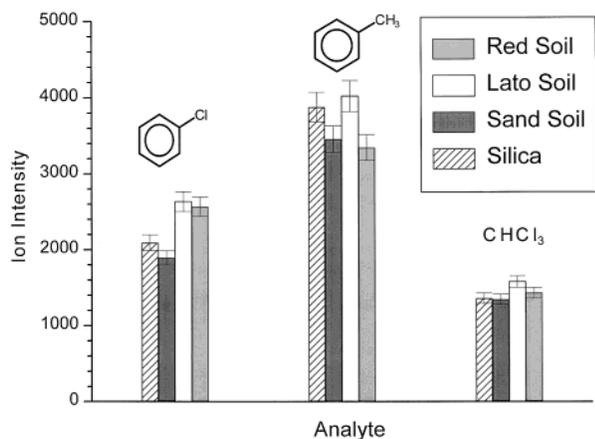


Figure 5. HS-MIMS signal intensity (I_{\max}) for SIM of powered silica and three samples of different soil types spiked with chlorobenzene, toluene, and chloroform.

Higher temperatures favor analyte permeation through the membrane,¹⁶ but for temperatures higher than 90 °C, as the temperature approaches the water boiling point, too much water likely permeates the membrane. This excessive water permeation then causes VOC dilution in the headspace and water–analyte competition during ionization, as well as undesirable (for EI monitoring) competitive water chemical ionization.¹⁷

(d) Type of Soil. Applying the optimized conditions for the HS-MIMS system (4 min of heating and trapping, 90 °C oven temperature, and 25% humidity), we tested HS-MIMS responses for soils of three different types: a sand soil, a red soil, and a lato soil. Powered silica was used as a reference for comparison. The HS-MIMS responses were expected to vary owing to different properties of the soils such as (i) their VOC sorption properties, (ii) the porosity of their mineral grains, and (iii) their content of organic matter. As Figure 5 shows, however, the responses varied little. This finding indicates that the type of soil (after humidity adjustment) does not significantly affect HS-MIMS responses; as is the case for the humidity level, this reduced effect is compensated when an appropriate internal standard is used.

(e) Matrix. Figure 6 compares the HS-MIMS responses for 10 g samples of four different types of matrixes: powered silica, sawdust, mineral oil, and cotton, spiked with 2.5 mL of an aqueous solution of chloroform, toluene, and chlorobenzene to a final 500 $\mu\text{g}/\text{kg}$ concentration of each analyte. For the three analytes, the results are similar, showing greater VOC adsorption by silica and mineral oil than by sawdust and cotton. These significant differences in HS-MIMS responses likely result from differences in VOC sorption properties, porosity, and thermal conductivity of the matrixes.

Linearity, Reproducibility, Detection Limits, and Full Mass Spectrum Acquisition. As Figure 7 exemplifies, good linearity (correlation factors in the range 0.998–0.999) in HS-MIMS responses was observed for all VOCs investigated in a broad range of concentrations ranging from 100 ng/kg to 50 $\mu\text{g}/\text{kg}$. Also, as Table 1 summarizes, with benzene- d_6 used as the internal standard, relatively high recoveries, good reproducibility

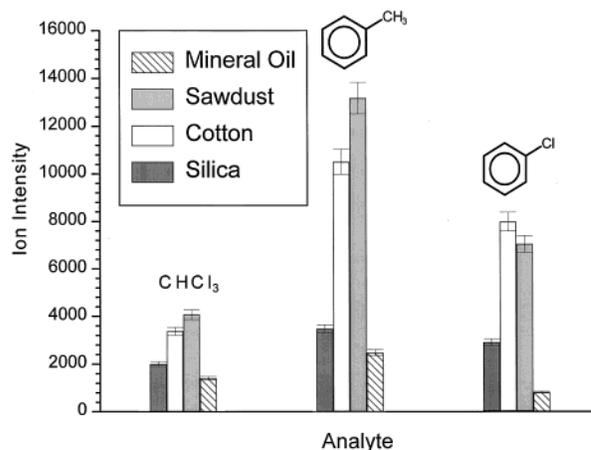


Figure 6. HS-MIMS signal intensity (I_{\max}) for SIM of four different types of matrixes: mineral oil, sawdust, cotton, and powered silica spiked with chlorobenzene, toluene, and chloroform.

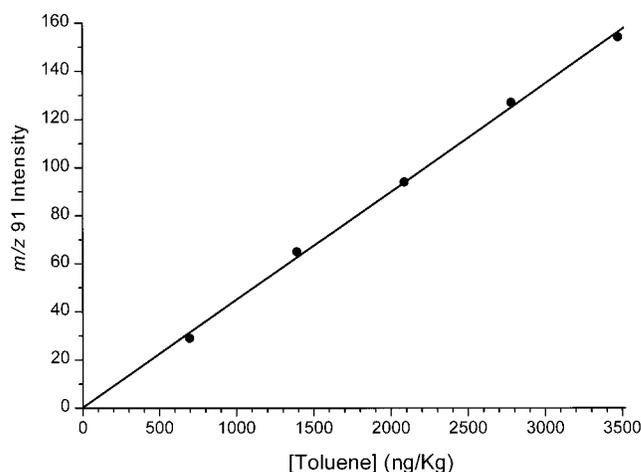


Figure 7. Typical HS-MIMS (SIM, I_{\max}) analytical curve for powered silica spiked with toluene.

Table 1. Monitored Ions, Recoveries, Relative Standard Deviations (RSDs), and Detection Limits (DLs) for HS-MIMS Analysis of VOCs in Soil Samples

compd	m/z	recovery (%)	RSD (%)	DL ^a (ng/kg)
benzene	78	97	4.5	50
chlorobenzene	112	95	5.6	50
chloroform	83	96	3.2	50
dichlorobenzene	146	85	9.3	100
dichloroethane	62	94	5.1	50
dichloromethane	49	93	6.5	50
toluene	91	98	4.6	50
trichloroethane	97	94	5.4	50
trichloroethylene	95	91	6.2	100
xylene	91	94	4.6	50

^a A signal-to-noise ratio of 3:1 was used to define the detection limits.

as demonstrated by the relative standard deviations (RSDs), and very low detection limits (DL) in the low ng/kg (ppt) range were commonly obtained for most VOCs.

The rapid scanning characteristic of quadrupoles (and of most mass analyzers) and the relatively long duration of the HS-MIMS peak (Figure 2) also permit several full mass spectra to be obtained when total ion monitoring (TIM) is performed. Full mass scan acquisition in HS-MIMS is certainly beneficial for mixture

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analysis and correct MS identification and for sample screening before more sensitive SIM monitoring.

Real-Sample Analysis. Having determined the best operating parameters for the HS-MIMS system, we successfully applied it in our laboratory to the analysis of many real-soil samples. For maximum sensitivity, the humidities of the soil samples were always adjusted to ~25% by adding diluted aqueous solutions of the internal standard (benzene-*d*₆). The use of the internal standard is necessary and highly beneficial for accuracy, since it compensates for fluctuations in responses owing to different types of soils and humidity levels and for small variations in experimental parameters such as oven temperature (adjusted to 90 °C) and heating and trapping time (4 min). First, a full mass spectrum with long dwell times for maximum sensitivity was acquired for sample screening; then, SIM of the detected VOCs was applied for maximum sensitivity and quantitation.

EI was always applied, since the real samples analyzed were often found to be contaminated with just a few VOCs having characteristic EI fragments, whereas the membrane selectively blocked contaminants other than the VOCs. However, and as already widely demonstrated for MIMS,⁶ chemical ionization was advantageous for samples contaminated with complex VOC mixtures.

CONCLUSIONS

Headspace membrane introduction mass spectrometry (HS-MIMS) combines the major advantages of MIMS and headspace preconcentration and offers a solvent-free, simple, relatively rapid, selective, and specially highly sensitive (low ng/kg (ppt)) technique for the direct analysis of VOCs in both dry and wet soils and in other solid or highly viscous liquid matrixes.

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