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A Cryotrap Membrane Introduction Mass Spectrometry System for Analysis of Volatile Organic Compounds in Water at the Low Parts-per-Trillion Level

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Detection of volatile organic compounds (VOCs) in aqueous solution at low parts-per-trillion (ppt) levels is accomplished using a very simple and efficient on-line preconcentration cryotrap membrane introduction mass spectrometry (CT-MIMS) system. The conventional MIMS probe is modified so that the membrane interface is placed about 15 cm away from the ion source. A U-shaped trap tube is then inserted between the membrane interface and the ion source. Cryotrapping is performed with liquid nitrogen for 15 min, followed by fast heating at ∼15 °C s^{-1}, which thermally releases the condensed VOCs almost at once into the ion source region of a quadrupole mass spectrometer. By applying electron ionization and a selective ion monitoring scan mode, a very sharp and intense peak is obtained. The performance of the CT-MIMS system was compared with that of conventional MIMS, and after reaching the best conditions for the trapping and heating cycles, an improvement factor in signal intensity of about 100 was observed for a series of VOCs. The extraordinary sensitivity of CT-MIMS system allows VOCs to be detected at very low concentrations, detection limits being typically on the order of 10−20 ppt. The results also show excellent linearity and reproducibility for the system.

Increasing consciousness of environmental issues has generated a fast-growing number of alternative techniques aimed at efficiently performing qualitative and quantitative analyses of chemical contaminants in water, air, and soil samples. Additionally, the increasing need for on-site monitoring and shorter sample holding times has created a great demand for the development of simple, rapid, and efficient analytical techniques to detect and quantify a large variety of chemicals in various environmental matrices.[1] These techniques have to deal with the often-difficult task of performing selective and efficient extraction of analytes from the sample matrices. Such a step is critical for the accuracy, precision, and sensitivity of the analytical process, because ideal extraction systems which display all the desirable features (such as simplicity, high speed, high selectivity, solvent-free methods, and performance independent of instrument design) are not available.[2] These difficulties are crucial when analyzing volatile organic compounds (VOCs), one of the most common and important classes of chemical contaminants.

Membrane introduction mass spectrometry (MIMS)[3] has emerged as a very efficient technique for the direct analysis of VOCs in water and air, showing outstanding speed and trace-level detection capabilities. Direct introduction of VOCs from a liquid or gas sample into a mass spectrometer is achieved in MIMS as the result of selective transport through a membrane, most often one made of silicone polymer. The membrane also works as the interface between the liquid or gaseous sample and the high-vacuum mass spectrometer. The hydrophobicity of the membrane and the permeability of the VOCs permit the extraction, concentration, and injection steps to be performed rapidly and simultaneously. The VOCs are adsorbed from the solution into the membrane, diffuse through the membrane, and evaporate from the membrane surface directly into the high-vacuum ion source region of the mass spectrometer.[3]

The capability to perform rapid and direct (without extraction or pretreatment) analysis of VOCs in aqueous solutions is one of the most attractive features of MIMS, besides its superior detection limits normally at the low parts-per-billion (ppb) levels, the best results being observed for the less polar and relatively light VOCs. A series of interesting trapping strategies[4−10] have been recently applied in conjunction with MIMS to lower the detection limits of various VOCs. By trapping the *analyte ions* in a highly sensitive ion-trap mass spectrometer fitted with a capillary

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membrane probe,[4] parts-per-trillion (ppt) detection limits for a variety of VOCs have been attained. Even lower parts-per-quadrillion (ppq) detection limits for toluene and *trans*-1,2-dichloroethene in water have been recently reported,[5] also obtained by using ion-trap MIMS analysis and by additionally applying the stored wave form inverse Fourier transform (SWIFT)[6] method. Trapping was performed in the course of ionization at relatively long periods of time via selective ejection of all but the analyte ions.[5]

Trapping the *VOCs*, not the analyte ions, after membrane separation has also been tested and showed improved detection limits for MIMS. Sequential placement exactly between the membrane and the ion source of the mass spectrometer of two cells filled with selective sorbent materials (Zeolit KA and a mixture of Al_2O_3 and SiO_2), followed by thermal desorption of the VOCs, was shown to improve sensitivity and broaden the range of substances that can be efficiently analyzed by MIMS.[7] Another trapping method was accomplished by connecting a helium-purge membrane inlet to a trap GC/MS system.[8] In these experiments, relatively polar VOCs passing the membrane were swept by the helium carrier gas onto the top of a Tenax trap before they were thermally desorbed into the GC/MS system. An interesting "chemical trapping" experiment has also been efficiently performed recently by using a chemically modified membrane that selectively traps aldehydes.[9] A fully integrated trap MIMS system has also attained preconcentration of semivolatile organic compounds (SVOCs) inside the MIMS membrane itself before they were thermally released into the ion source of the mass spectrometer, thus expanding the application of MIMS for the detection of SVOCs at low ppb levels.[10]

Although it shows considerably improved detection limits, the use of trapping materials has also its own limitations. Background signals produced by thermal decomposition during the heating cycle or inefficient, slow, or inconstant release of the adsorbed chemicals compromises reproducibility and limits the sensitivity and applicability of these trapping techniques. In the present work,[11] we describe a very simple and efficient on-line preconcentration MIMS system, i.e., a cryotrap MIMS system (CT-MIMS), that allows the detection of VOCs in aqueous solution at very low ppt levels using a simple quadrupole mass analyzer. The trapping uses no trapping material but is performed by "external" liquid nitrogen cooling, followed by fast heating, which thermally releases almost at once the trapped VOCs into the mass spectrometer. This leads to extraordinarily lower detection limits, typically on the order of 10−20 ppt. Excellent linearity and reproducibility are observed.

EXPERIMENTAL SECTION

Figure 1 shows a diagram of the cryotrap membrane introduction mass spectrometry (CT-MIMS) system and the setup used for comparing its performance with that of the conventional MIMS system. The conventional MIMS probe (A)[12] is modified so that the membrane interface (B) connected by $^1/_4$ in. o.d. stainless-steel tubing is placed about 15 cm away from the ion source (C) of the mass spectrometer. Not being limited by the diameter of the inlet system (D), a relatively large circular membrane sheet (Silastic 500-3 from Dow Corning Co., 0.010 in. thickness, 10 mm diameter) was used to enhance the contact surface area and consequently the permeation of the analyte. The analyte solution is pumped through the membrane interface by an eight-roll peristaltic pump (E) at the rate of 3 mL/min via two 10 cm long stainless-steel tubes that are silver-soldered into the base of the membrane interface. A U-shaped trap tube (stainless-steel, $^1/_4$ in. o.d., F) was inserted between the membrane interface and the ion source. The trap is cooled with liquid nitrogen for a certain period of time, followed by fast heating, which thermally releases the trapped VOCs directly into the ion source. The heating system (G) uses a low-voltage (0.7 V), high-current (82 A) transformer with the ends directly connected to the trapping tube. The electrical resistance of the trapping tube, which dissipates ~60 W, is exploited for heating. The heating system is also fitted with a timer that precisely controls the duration of the heating cycle.

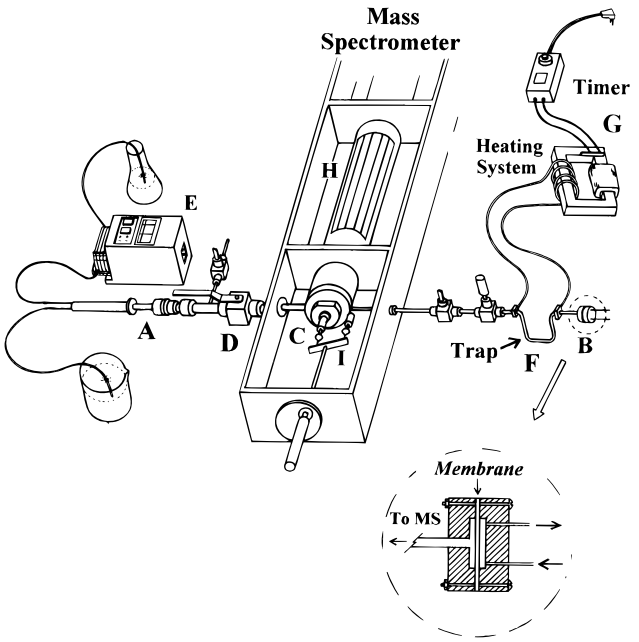

Figure 1. Diagram of the CT-MIMS system and the setup used for comparing its performance with that of the conventional MIMS system. The highlighted items are as follows: (A) the conventional MIMS probe, (B) the membrane interface, (C) the ion source of the mass spectrometer, (D) the second inlet system, (E) the peristaltic pump, (F) the U-shaped trap tube, (G) the heating system, (H) the high-transmission $^3/_4$ in. Extrel quadrupole, and (I) the interchangeable EI and CI ion volumes.

An Extrel (Pittsburgh, PA) pentaquadrupole mass spectrometer[13] fitted with high-transmission $^3/_4$ in. quadrupoles (H) was used. The instrument in its simple MS mode of operation shows ion transmission similar to that of most single-quadrupole mass spectrometers, as evidenced by the observation of similar detection limits when applying conventional MIMS for a series of VOCs.[14] The mass spectrometer is also equipped with interchangeable (I) EI and CI ion volumes and a second inlet system (D), from which the conventional MIMS probe (A) was introduced. This allows simultaneous comparison of the performance of both the conventional and CT-MIMS systems.

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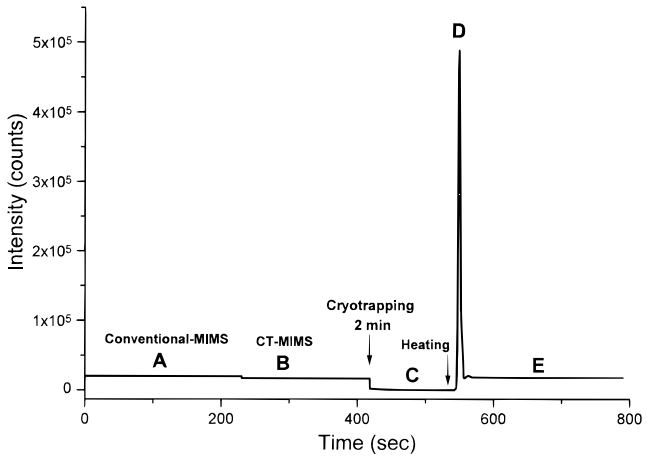

Figure 2. Signal profile observed in the various cycles of MIMS (A) and CT-MIMS analyses (B–E). The continuous flow of the permeated analyte (B) is stopped by liquid nitrogen cryotrapping (C), while a very sharp and intense signal (D) is produced when liquid nitrogen is removed and fast heating of the trap tube is performed, after which the continuous flow of the analyte returns (E).

Aqueous standard solutions were prepared by serial dilutions with doubly distilled water of stock solutions (typically 10 ppm), which were prepared by directly dissolving neat chemicals into pure methanol (Aldrich).

RESULTS AND DISCUSSION

Signal Profile of the CT-MIMS System. Figure 2 exemplifies the profile observed for analyte signal intensity in the various cycles of the CT-MIMS analyses. To allow a better visualization of signal improvement, a relatively short trapping period of 2 min was employed in this experiment. Continuous flow of the permeate through the CT-MIMS system produces a constant signal (B). Placing the U-trap tube in liquid nitrogen (C) immediately blocks the analyte by condensation, and signal intensity drops to zero (a signal with intensity less than 3 times the noise is filtered by the pentaquadrupole software[13]). A very sharp and intense signal (D) is produced when liquid nitrogen is removed and fast heating of the trap tube is performed, after which the continuous flow of the analyte is again observed (E). The gain of the CT-MIMS system can therefore by defined as the ratio between the intensity in B (or E) and that of the maximum of peak D. Figure 2 also shows the signal intensity (A) obtained under the same experimental conditions (solutions in both systems were run at room temperature) by applying the conventional MIMS probe (A in Figure 1).

The results show that the CT-MIMS sensitivity in normal operation conditions (B, no cryotrapping) is quite similar to that of conventional MIMS (A); hence, the CT-MIMS performance can be directly compared to that of conventional MIMS. It is interesting to note that both systems show similar performance in normal operation conditions, although they differ considerably from the position of the membrane interface relative to the ion source. This is probably compensated by the approximately 4 times larger membrane that is used in the CT-MIMS interface.

Effect of the Cryotrapping Period. To determine the best cryotrapping period, a series of experiments were performed, and the results are given in Figure 3 for toluene at 1 ppm in water. In these experiments, the $C_7H_7^+$ fragment of toluene of m/z 91 was monitored using the selective ion monitoring (SIM) scan mode.

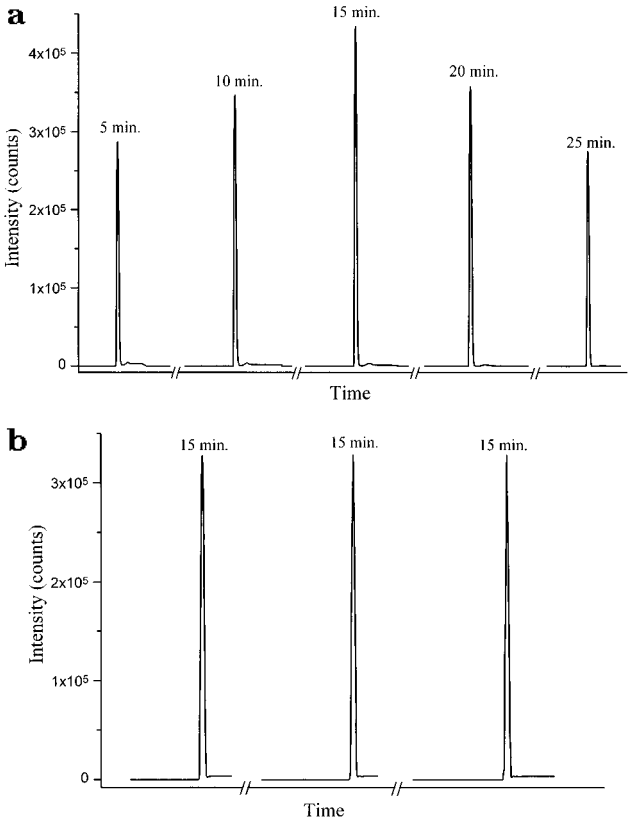

Figure 3. (a) Effect of the cryotrapping period for a 1 ppm solution of toluene in water. (b) Signal reproducibility after repeated cycles of 15 min of liquid nitrogen trapping.

Since fast heating is performed (see below), a narrow and relatively concentrated "package" of trapped VOCs as well as water[15] is released and reaches the ion source in a very narrow time window. Very sharp peaks are produced, with increasing intensities up to 15 min of trapping (Figure 3a). Signal intensity starts to drop, however, after 15 min of trapping, most likely due to both saturation of the ionization capability of the EI ion source and the occurrence of ion–molecule reactions in high-pressure conditions that favor competitive chemical ionization. Trapping periods greater than 25 min lead to overpressure conditions and the consequent shut down of the mass spectrometer. Given that the same trapping period is used, a great signal reproducibility is observed after repeated cycles, as shown in Figure 3b.

For less concentrated solutions, one could suppose that greater trapping periods could be applied since small quantities of VOCs permeate the membrane and are trapped and released upon heating. However, most likely due to approximately constant water permeation,[15] similar results in trapping time efficiencies were observed for solutions at a broad range of concentrations.

Effect of Heating Time. The voltage applied to the ends of the trapping tube, and consequently the heating power dissipated, were varied so that fast heating could produce the narrowest as well as the most intense peak possible. Although it is desirable that heating should be as fast as possible, too rapid a heating rate was shown to produce very narrow but not so intense or reproducible peaks. The best conditions were determined with a dissipation of ~60 W. Once these values are set, heating times

(15) Although much less efficiently, water also permeates the membrane; see, for instance: LaPack, M. A.; Tou J. C.; Enke, C. G. *Anal. Chem.* **1990**, *62*, 1265.

Table 1. CT-MIMS Gains and Detection Limits for a Series of VOCs

VOC	monitored ion (m/z)	MIMS signal (kcounts)	CT-MIMS signal (kcounts)	CT-MIMS gain	MIMS detection limit[14] (ppb)	CT-MIMS detection limit (ppt)
benzene	78	11.4	1099	96	1	10
toluene	91	11.0	1139	103	1	10
xylene	106	10.4	987	95	1	10
chlorobenzene	112	14.5	1419	98	1	10
benzaldehyde	106	1.8	170	95	15	150
acetone	58	3.4	321	95	10	100
2-butanone	43	7.9	836	106	5	50
ethyl ether	59	10.9	1136	104	1	10
tetrahydrofuran	72	0.4	35	96	50	500
carbon tetrachloride	117	3.4	311	92	5	50
chloroform	83	6.0	583	98	2	20
dichloromethane	49	1.6	193	118	20	200
1,1,2,2-tetrachloroethane	83	3.0	275	93	5	50
chlorodibromomethane	127	5.3	579	110	2	20

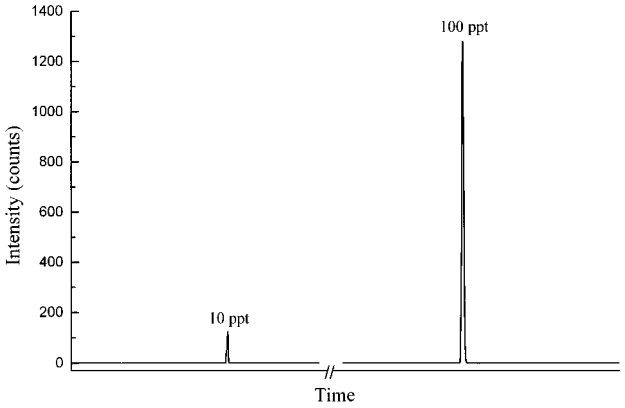

Figure 4. CT-MIMS signal for 100 and 10 ppt chloroform solutions. Note that no signal is observed under normal operating conditions, whereas intense and narrow peaks are observed after the cryotrapping/heating cycle.

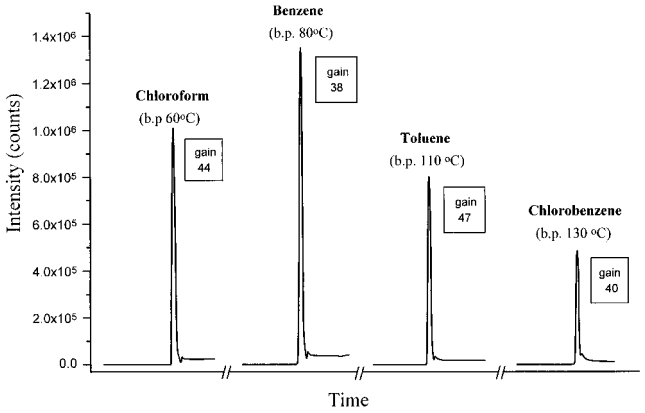

Figure 5. Gain in signal intensity obtained by the CT-MIMS system for chloroform (44), benzene (38), toluene (47), and chlorobenzene (40) with 5 min of cryotrapping.

greater than 15 s practically do not affect the sharpness and intensity of the signal, and therefore very reproducible peaks are obtained. At these conditions, the CT-MIMS peak is observed after ~7 s of heating and has an average duration of 5−6 s. This corresponds to a heating rate of ~15 °C s^{-1}.

Gain of the CT-MIMS System. A variety of VOCs (Table 1) were tested, and similar CT-MIMS gains (D/B ratios, see Figure 2) around 100 were obtained after 15 min of trapping, followed by 30 s of heating. To minimize memory/carryover effects caused by the membrane interface and its considerable distance from the ion source, pure water was run between each measurement in ~5 min intervals. The great sensitivity of the CT-MIMS system is demonstrated in Figure 4, which shows the signal observed for both 100 and 10 ppt chloroform solutions. Note that, because solutions with concentrations far below the detection limit of conventional MIMS are being analyzed, no signal is observed under normal operation conditions. However, intense and narrow peaks are observed right after the cryotrapping/heating CT-MIMS cycle. The improved sensitivity led to much lower detection limits, as shown in Table 1. Also noteworthy in Table 1 are the results for the VOCs that display relatively high detection limits with conventional MIMS, such as benzaldehyde, acetone, dichloromethane, and particularly tetrahydrofuran. Using the CT-MIMS system, they can be detected at ppt levels.

The results presented in Table 1 show that the sensitivity of CT-MIMS is practically unaffected by the differences in volatility of the VOCs. Figure 5 also demonstrates that VOCs display similar CT-MIMS gains independent of the duration of the cryotrapping period. With 5 min of cooling, for instance, chloroform (bp 60 °C, gain = 44), benzene (80 °C, 38), toluene (110 °C, 47), and chlorobenzene (130 °C, 40) all show approximately the same gain.

Linearity and Recording of Full Mass Spectra. By applying the optimized conditions for the CT-MIMS system, a great linearity was observed for all the VOCs investigated in a broad range of concentrations ranging from low ppt to low ppm. Correlation factors typically in the range of 0.998−0.999 were obtained. Additionally, although a quite sharp peak is obtained by the cooling/heating process, its broadness of 5−6 s and the rapid scanning characteristic of quadrupole mass analyzers permit that a full mass spectrum of the VOCs be obtained in all cases studied in the full range of concentrations employed. This is particularly useful for mixture analysis.

CONCLUSIONS

The cryotrap membrane introduction mass spectrometry (CT-MIMS) system described in this study is a very simple and efficient technique that allows the detection of VOCs in aqueous solution at very low ppt levels using a simple quadrupole mass analyzer. The experiments show that trapping VOGs that had permeated a relatively large silicone membrane with liquid nitrogen for a period of 15 min, followed by fast heating, produces linear, reproducible, and ~100 times more intense signals when compared with the performance of a conventional MIMS system.

This leads to much lower detection limits for the CT-MIMS system, which typically drops from low ppb to low ppt levels. One very practicable increment of the CT-MIMS system is therefore the detection at ppt levels of VOCs that normally display poor detection limits with conventional MIMS, as demonstrated in the present study for benzaldehyde, acetone, dichloromethane, and particularly tetrahydrofuran.

It is also clear from the great signal improvement obtained that application of the CT-MIMS system, together with the very sensible ion traps mass spectrometers[4−6] or high-transmission MIMS-dedicated single-quadrupole mass spectrometers,[16] or in combination with modified membrane inlets such as that of the "helium-purge" type,[17] can lead, in principle, to detection limits even lower than the low ppt or even the extraordinary low ppq limits[5] that have already been obtained with conventional MIMS.

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