Experimental Upgrades of Membrane Introduction Mass Spectrometry for Water and Air Analysis

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Some improvements to the membrane introduction mass spectrometry (MIMS) technique, resulting in low-ppt detection limits for volatile organohalogen compounds (CX) in water (namely, chloroform, bromoform, bromo-dichloromethane, chlorodibromomethane, tetrachloro-ethylene, trichloroethylene, 1,1,1-trichloroethane, and carbon tetrachloride) and low-microgram per cubic meter detection limits for benzene, toluene, ethylbenzene, and xylenes (BTEX) in gaseous samples, are shown. A static MIMS configuration was compared to a dynamic one, the former requiring longer time to obtain the analytical response. A cryotrapping preconcentration step is introduced and linearity of response, mixture effects, and detection limits are presented. The instrumental setup consists of a hollow fiber silicone membrane, a water or air container, a cryofocusing trap based on Tenax adsorbent, a Peltier cell, and a Varian ion trap benchtop mass spectrometer is described. This instrumental setup, which we named membrane extraction trap focusing mass spectrometry, allowed the detection of CX in water at a concentration as low as 8 ppt and of benzene in air at 0.1 μg/m^3. The whole assembly shows great potential for on-site routine monitoring of drinking water resources and urban and indoor air under current EU and Italian regulations.

Membrane inlet mass spectrometry (MIMS) has long been used for the rapid determination of volatile organic compounds (VOCs) at trace level in water and air samples.[1−13] In the attempt to further improve detection limits, MIMS advances have com-bined membrane and, respectively, liquid nitrogen trap,[16] jet separator,[14,15] sorbent trap,[17,18] and purge and trap.[19] In some cases, a gas chromatographic step has been included between the sampling device and the mass spectrometer. In general, MIMS improvements are impressive from the standpoint of skillfulness of instrumental solutions, number and diversity of applications, and very low detection limits.

Compared to other sampling and concentration techniques, MIMS shows great potential for on-line, on-site, and continuous monitoring of drinking water resources, wastewater outlets, or urban air pollution. For such applications, a rugged, simple-to-operate, sensitive, and cost-effective instrument is crucial. Consequently, MIMS should maintain an optimum compromise between simplicity of the instrumentation, rapidity of the analysis, and analytical performance.

In this paper, in the frame of a research program aimed at developing a device for routine on-site monitoring of CX (chloroform, bromoform, bromodichloromethane, chlorodibromomethane, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride) in drinking water and BTEX (benzene, toluene, ethylbenzene, xylenes) in air under current European (upper limit of the total amount of CX in potable water: 30 μg/L, regulation 80/778) and Italian (maximum benzene concentration in air: 10 μg/m^3, DM 25/11/1994) limits, we studied introduced and tested a few instrumental upgrades, including a cryotrapping step, of the MIMS technique. The experimental conditions were optimized, and the performance of the technique as applied to water and gaseous samples, detection limits, and response linearity was evaluated.

EXPERIMENTAL SECTION

MIMS. A Varian 3400 gas chromatograph (Varian, Walnut Creek, CA) connected to a Varian Saturn 2000 ion trap mass

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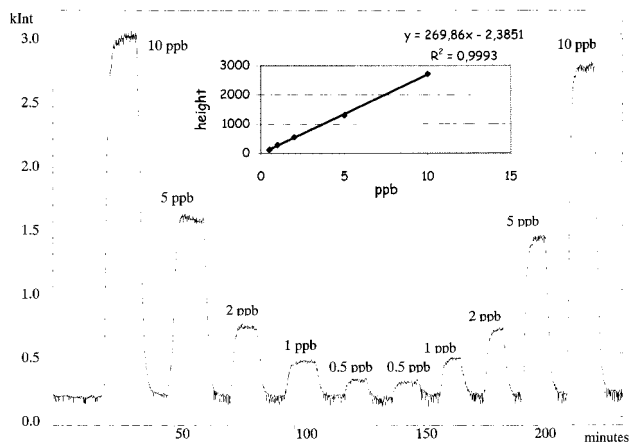(19) Shoemaker, J. A.; Bellar, T. A.; Eichelberger, J. W.; Budde, W. L. *J. Chromatogr. Sci.* **1993**, *31*, 279−284.

Figure 1. MIMS analysis of chloroform solutions (0.5, 1, 2, 5, and 10 ppb, duplicate) and calibration curve. The single-ion monitoring for m/z 83 is shown. (Kint = ionic intensity/1000).
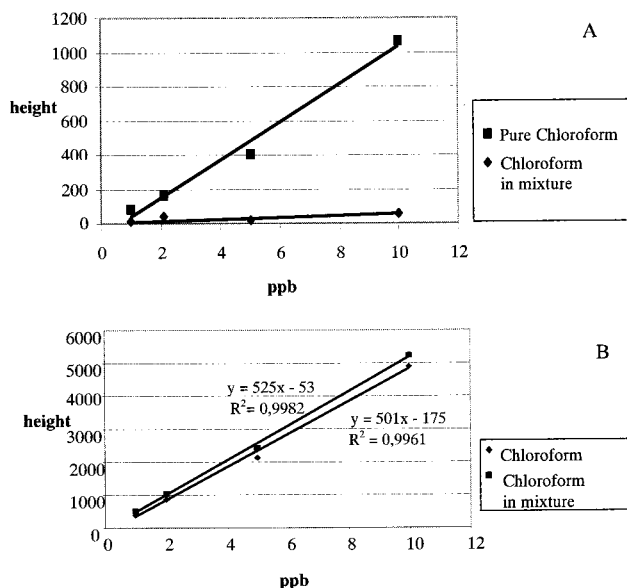

Figure 2. Calibration curves obtained analyzing solutions of chloroform both alone and in mixture with the other seven organohalogenated compounds with (A) A 4-cm-long hollow fiber membrane and (B) a 12-cm-long membrane. The ionic intensity for ion m/z 83 was measured.
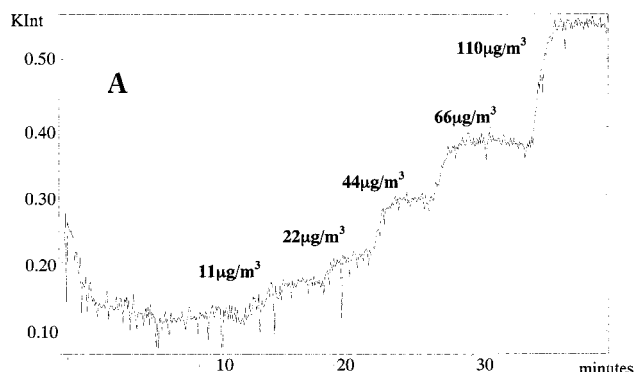

Figure 3. MIMS analysis of increasing amount of benzene in gaseous samples (11−110 μg/m³) obtained by sequential injections. The single-ion monitoring for ions at m/z 78 is shown.

spectrometer was used. A deactivated fused-silica capillary column, with no stationary phase (30 m × 0.32 mm i.d, Supelco, Bellefonte, PA) was connected to the GC injector to supply the optimum helium pressure inside the mass spectrometer. Ahead of the mass spectrometer, the column was cut and the two segments were joined by a hollow fiber membrane. The membrane, a silicone rubber tube (Silastic Dow Chemical, Midland, MI), was 4−12 cm long (i.d. 0.51 mm, 0.23 mm in thickness) and was set inside a glass vial. The aqueous sample was stirred by means of a magnetic stirrer. When aqueous samples were analyzed, no headspace was present in the vial in order to avoid losses of analytes due to evaporation of the volatile compounds. When gaseous reference samples were analyzed, the glass vial was substituted by a 2-L glass bottle which was repeatedly flushed with nitrogen before use. The experiments were performed in a controlled-temperature laboratory. The temperature was set at 23 °C. Mass spectra were acquired in the mass range 50−200 m/z, 1 scan/5 s. Quantitative data were obtained by measuring the intensity of the ions characteristic of the single compounds. The signal for quantitative analysis was the height of the plateau after subtraction of the baseline value.

Membrane Extraction Trap Focusing Mass Spectrometry (MTF-MS). A chemical trap, which could be heated or cooled, was placed between the hollow fiber membrane and the mass spectrometer. The trap was made of a segment of an uncoated capillary column, a few centimeters long, filled with Tenax (60−80 mesh, Supelco). The trap was set inside a copper manifold which, in turn, was carefully attached to a Peltier cell (Peltier effect heat pump 18.8 W, Catalog No. 618724, RS Components SpA, Milan, Italy). The signal was measured as the area of the peak subtracted from the blank value. All the other experimental conditions were identical to those described for MIMS analysis.

RESULTS AND DISCUSSION

In a previous paper,[10] we described the MIMS determination of 8 CX compounds, namely, chloroform, bromoform, bromodichloromethane, chlorodibromomethane, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, and carbone tetrachloride, in water samples at low-ppb concentrations. In the used configuration (which we named "dynamic"), the hollow fiber membrane

was set inside a glass chamber and the aqueous sample solution flowed around the membrane by means of a peristaltic pump.[10] In the present paper, a different instrumental setup of the membrane sampling device was tested. The membrane was set inside a glass vial containing the aqueous sample, which was kept tightly capped and under constant stirring. The stirring allowed the compounds to reach the membrane surface without formation of any concentration gradient in the sample solution. We named this configuration "stationary". The stationary experiments required longer time to achieve the plateau but led to a significantly higher response than the dynamic one for each of the eight analyzed compounds, and consequently, it was used in each of the following experiments.

Results obtained with the stationary configuration were comparable to those previously published and obtained by using the dynamic configuration,[10] and the reproducibility and linearity of the method were confirmed. In Figure 1, the analysis of chloroform solutions at different concentrations (0.5−10 ppb, replicate measurements) and the relative calibration curve are shown.
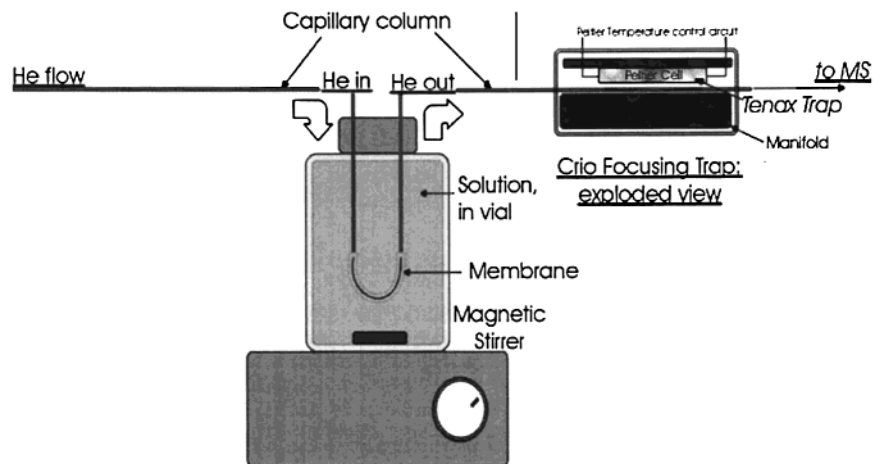
Figure 4. Schematic representation of the MTF-MS device.

Solutions containing either single compounds or all eight CXs were analyzed in order to verify possible differences in the quantitative results. A difference in response was observed, as probably due to a competition between the different organic components of the mixture to partition in the polymeric membrane. The calibration curves of reference solutions (1–10 ppb) showed very different slopes (Figure 2A), depending on whether the solution contained one or all CXs, the latter having the smaller one. Appropriate reference solutions, depending on real sample composition, should therefore be prepared in order to avoid systematic errors. This could clearly be a major drawback in the method.

To solve this problem, the length of the membrane was increased from 4 to 12 cm in order to provide a larger surface to the partitioning equilibrium. The slopes of the calibration curves obtained using a 12-cm membrane showed similar values (Figure 2B) both for mixtures and for single compound solutions.

For the analysis of gas samples, the polymeric membrane was set inside a gastight glass bottle having a volume of 2 L. Increasing amounts of the analyzed standard compound were sequentially injected by means of a gastight syringe in order to obtain the desired concentration ($\mu g/m^3$) inside the bottle. After each injection, the system was allowed to equilibrate and the signal reached a plateau whose height was related to the concentration of the compound inside the bottle. When a series of such injections was made, a typical step-shaped diagram was obtained, in which the plateau heights were proportional to the concentration resulting by the sum of all previous injections. No memory effect due to the adsorption of analytes on glass surface was noticed.

MIMS determinations of benzene, toluene, ethylbenzene, and *p*-xylene in gaseous samples in the 10–150 $\mu g/m^3$ concentration range were carried out. Quantitative data were obtained by measuring the height of the signal at the plateau after subtraction of the baseline. No depletion of amount of analyte in the gas phase due to the sampling membrane was noticed in the time frame of our measures.

In Figure 3, the analysis of increasing concentration of benzene (11–110 $\mu g/m^3$) as obtained by MIMS is shown. The linearity of the method was high with a R^2 value of 0.9999 and a detection limit for benzene, measured as 3 times the standard deviation of the noise signal, of 3 $\mu g/m^3$. Similar results were obtained for each of the tested compounds (Table 1).

Table 1. Detection Limits (LOD, S/N ≥ 3) for BTEX in Gas Phase Determined by MIMS Technique

compound	LOD ($\mu g/m^3$)
benzene	3
toluene	3
ethylbenzene	4
p-xylene	12

Quantitation limits are usually defined as 10 times the standard deviation of the noise signal; therefore, the results obtained by MIMS analysis of benzene, although quite impressive considering that no sample preparation is required by this analytical method, were not sufficient to meet the requirements (maximum concentration allowed 10 $\mu g/m^3$) of Italian regulations for urban air.

In Figure 4, the setup of a MTF-MS device is shown. In this approach, a chemical trap, fitted to a Peltier cell, was placed between the sampling hollow fiber membrane and the mass spectrometer in order to concentrate the organic compounds and allow their MS determination as a narrow band of molecules. In this instrumental configuration, the organic molecules permeate through the membrane and are carried, by the helium flow, to the adsorption medium where they are concentrated. The chemical trap, during the sampling and concentration step, is kept cooled (3–15 min, temperature in the range −15/−30 °C). The adsorbed molecules are then thermally desorbed by inverting the electrical polarity of the Peltier cell. This causes the rapid (less than 1 min) heating of the trap (temperature in the range 100–130 °C) and the consequent release of the organic molecules trapped in the Tenax layer. The trap temperature is monitored by means of a thermocouple inserted in the copper manifold. The carrier gas sweeps the desorbed molecules to the MS where they are detected.

In Figure 5, the different shape of the signal after MIMS and MTF-MS analysis of a 5-ppb solution of chloroform is shown. The higher signal-to-noise value obtained by MTF-MS experiments is due to the higher number of molecules per time unit that are sent, in a single band, to the MS.

The analysis of chloroform solutions with different sampling time (3, 5, 7, 10, 12, and 15 min) reflected an increase of peak areas. The area values reached a plateau from 10 min on. No significant increase in the peak areas was observed by further
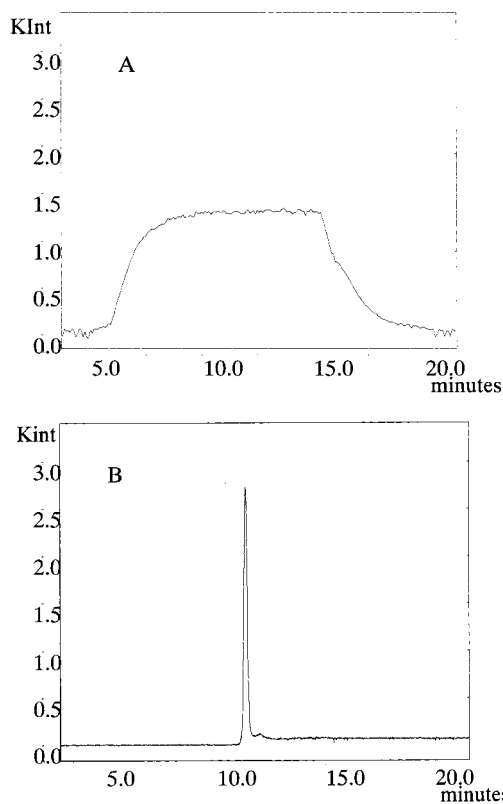
Figure 5. Difference in the signal shape as obtained by MIMS and MTF-MF analysis of a solution of chloroform of 5 ppb (traces are relative to ions at m/z 83).

Figure 6. MTF-MS analysis of increasing amounts of (A) benzene (traces relative to ions at m/z 78) and (B) toluene (traces relative to ions at m/z 91) in air samples.

increasing the sampling time. A sampling time of 10 min was considered the best compromise between the rapidity of the MIMS technique and the sensitivity of MTF-MS.

As a consequence of the concentration step introduced in the technique, MTF-MS detection limits for the determination of CX in aqueous samples were drastically improved and amounts of chloroform as low as 8 ppt could be detected. The linearity of response, obtained by this technique in the $0.4-2$ ppb range, was quite good ($R^2 = 0.98$).

MTF-MS was tentatively applied to the analysis of gaseous samples too. Concentrations as low as 0.1 $\mu g/m^3$ of aromatic compounds were analyzed. The signal obtained was significantly higher than the blank signal. In Figure 6, the analysis by MTF-MS of gaseous samples having different benzene (Figure 6A) and toluene (Figure 6B) concentrations is shown. Similar results were obtained with ethylbenzene and *p*-xylene. These preliminary results concerning limits of detection and linearity (R^2 values for the calibration curves in the range $0.9903-0.9999$) prove the potential of MTF-MS for the analysis of air samples.

CONCLUSIONS

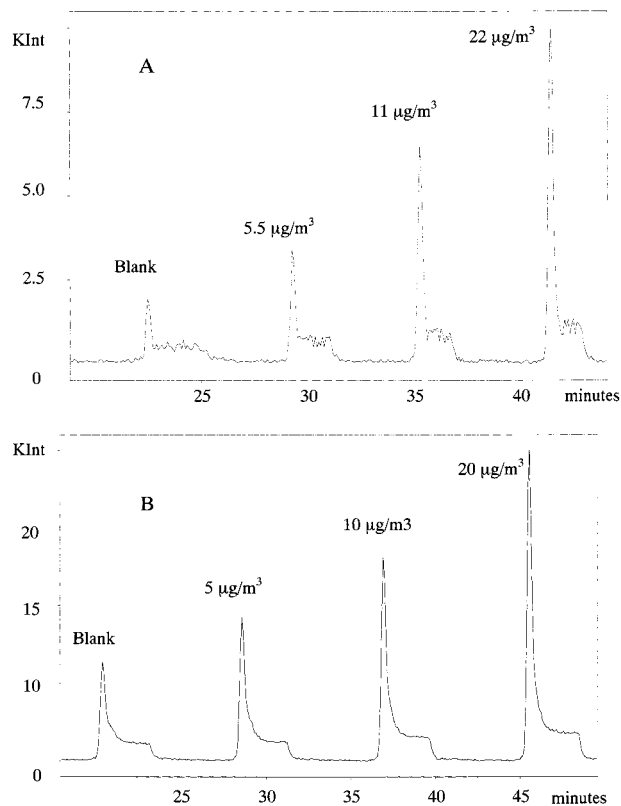In this work, some experimental upgrades of the MIMS technique were tested and applied to the analysis of both water

and air samples. For instance, the trapping step allowed the detection of trace amounts of organohalogen compounds in water (8 ppt) and of aromatics in air (0.1 $\mu g/m^3$). The use of a Peltier cell instead of a liquid nitrogen trap to obtain the trapping and desorption of analytes is more suited to a possible in-field application of the method. A great advantage of the described technique is that, just like MIMS, it does not require any preparation step. These characteristics are of particular interest when the analytical devices are to be used on site. The obtained detection limits and linearity are good, and the results obtained ensure interesting developments in the field of trace pollution analysis.