
16 Remote Monitoring of Volatile Organic Compounds in Water by Membrane Inlet Mass Spectrometry

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16.1 INTRODUCTION

European Union Directive 98/83 underlines the importance of determining the quality of drinking water in order to protect human health. In particular, a number of chemical compounds are listed, such as benzene, 1,2-dichloroethane, tetrachloroethylene, chloroform, and trihalomethanes, whose concentration in drinking water must be kept under well-defined thresholds. In Italy, laws DL 31/01, DM 152/99, and DM 471/99 set the norms for the concentrations of these, and of many other compounds in drinking water, wastewater, and contaminated sites, respectively.

Volatile Organic Compounds (VOCs) constitute a very important class of water pollutants because of their persistence; in addition, many of them are suspected of being carcinogenic. There are about 60 VOCs, including benzene, toluene, ethylbenzene, and xylenes ('BTEX compounds'), halomethanes, and haloethanes. The presence of some of them in water is due to anthropic activities, for example, the use of chlorinated solvents in industries and laundries, and the formation of halomethanes as by-products of water disinfectants. With respect to Italian law DL 31/01, the maximum allowable concentration (threshold) for the sum of trichloroethylene and tetrachloroethylene concentrations in drinking water is 10 ppb, whereas the minimum account for the sum of a set of four halogenated compounds, namely chloroform, bromoform, bromodichloromethane, and chlorodibromomethane must be as low as possible and must not exceed 30 ppb. Note that 30 ppb is equivalent to 30 $\mu\text{g L}^{-1}$.

A real-time, on-line, continuous monitoring system for such compounds would allow either prompt actions to be taken in order to avoid the diffusion of pollutants into the water system or to take appropriate countermeasures, thus restoring safe conditions in the case of accidental contamination. In general, only the conventional chemical-physical parameters, such as dissolved oxygen temperature, pH, conductivity, and turbidity, are monitored continuously in water [1]. VOCs are usually analysed in the laboratory by means of Purge and Trap/Gas Chromatography/Mass Spectrometry (P&T/GC/MS) using the U.S. Environmental Protection Agency (USEPA) Method No. 8260B which sets the standard for the analysis of VOCs in water. Although the method is state-of-the-art in terms of sensitivity, reproducibility, validation of the overall procedure and has been adopted worldwide by water laboratories, it can by no means be considered an alarm tool giving rapid warning of concentration increases. For an analytical procedure to be considered a warning device, it should be rapid, simple, and able to work unattended 24-hours-a-day for several days in unmanned sites and to send remotely analytical reports. As appropriately stated by Mikkelsen and coworkers, reporting upon a robust and sensitive on-line remote monitoring system for heavy metals in natural waters, "it is a great distance from developing a method (...) for continuous outdoor measurements" [2]. To our knowledge, little research has been made on the use of the ion trap for continuous, on-line monitoring of environmental parameters. Masuyoshi Yamada *et al.* studied a continuous monitoring system for the determination of polychlorinated biphenyls in air; the system employed direct sampling atmospheric pressure chemical ionization (APCI)/ion trap mass spectrometry (ITMS) [3]. Direct sampling ion trap mass spectrometers with two direct sampling interfaces, developed at Oak Ridge National Laboratory, TN, USA,

have been tested in field studies to determine VOCs in the effluents from hazardous-waste incinerators [4]. Kurten *et al.* developed an ion trap mass spectrometer for the on-line chemical analysis of atmospheric aerosol particles [5].

16.2 MEMBRANE INLET MASS SPECTROMETRY (MIMS)

Riter *et al.* applied Membrane Inlet Mass Spectrometry (MIMS) coupled to a miniature mass spectrometer equipped with a cylindrical ion trap (CIT) analyzer to monitor the flavor components directly from human breath [6]. Johnson *et al.* measured ethanol concentrations on-line in fermentation broths from a 9000-L fermentation reactor for a period of four days [7]. However, data reported in the above papers referred to experiments lasting no more than a few days.

MIMS has been extensively studied for the determination of VOCs in various environmental matrices, especially water and air samples [8–16]. Ketola and coworkers published a review that listed 172 references of MIMS applications to water and air [17]. MIMS allows the introduction of VOCs to the mass spectrometer through a thin (some tenths of a millimeter) hollow-fiber polymeric membrane, which is selective toward organic compounds. When the membrane is in contact with the sample and an ion trap mass spectrometer is used as the detector, such as in the case here, VOCs are extracted into the membrane, concentrated in its small volume, and swept into the mass spectrometer by a gentle stream of helium carrier gas. The whole process is called pervaporation and is divided into three steps: (a) phase-partitioning equilibrium of the organic compound between the sample (water or air) and the membrane; (b) diffusion of the compound by a concentration gradient from the outer side of the membrane (in contact with the sample) to the inner side (connected to the mass spectrometer); and (c) evaporation of the compound from the inner side of the membrane [18]. Diffusion is the rate-determining step, whereas partitioning and evaporation can be considered to be instantaneous. When the membrane is exposed to a sample containing the target compounds and the ions characteristic of each target compound are detected by mass spectrometry, the inherent ion current increases up to a plateau showing that the analyte's pervaporation rate and transport flow to the detector are equal.

The pervaporation process can be described by the Fick's equations of diffusion [18], that is,

$$I_m(x,t) = -AD \left\{ \frac{\partial C_m(x,t)}{\partial x} \right\} \quad (16.1),$$

$$\left\{ \frac{\partial C_m(x,t)}{\partial t} \right\} = D \left\{ \frac{\partial^2 C_m(x,t)}{\partial x^2} \right\} \quad (16.2)$$

where:

I_m = analyte flow through the membrane (mol s^{-1});

C_m = concentration of the analyte in the membrane wall (mol cm^{-3});

A = membrane surface (cm^2);

D = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$);

x = membrane thickness (cm);

t = time (s).

The characteristic ions are the qualitative information which allows identification of the analytes, while plateau height ($I_{ss} = ADC_m/L$, where I_{ss} is the analyte flow and L is the membrane thickness) is the quantitative information, with sensitivity in the sub-ppb levels and dynamic range of up to four decades for many VOCs [17,19].

16.3 MEMBRANE INLET MASS SPECTROMETRY (MIMS) INSTRUMENTATION FOR PROLONGED MONITORING

Although the many papers cited above have demonstrated that MIMS is a potentially excellent technique for continuous VOC monitoring given its simplicity and sensitivity, to our knowledge no account has been published of experimental attempts to demonstrate that MIMS can really be implemented in a device able to work unattended for months. Following our previous paper on MIMS upgrades [19], this present work reports on laboratory and field tests of hardware and software for MIMS instruments built in our laboratory.

Four instruments were deployed in unmanned sites, where they monitored VOCs in natural waters and wastewater during a period exceeding one year for each instrument. The instruments were equipped with software that facilitated the automatic operation of each analysis, the identification and quantitation of VOCs from the raw mass spectra, and the transmission of the results to a remote control room *via* internet connection. In the remote control room, a personal computer with dedicated software displayed the results as bar graphs and was programmed to activate alarms when set concentration thresholds were exceeded. Laboratory performance in terms of sensitivity, reproducibility, linearity tests, and comparison with P&T/GC/MS together with field performance in terms of data output, most frequent maintenance operations and technical failures, and overall stability of the four remotely-controlled instruments are discussed.

16.3.1 EXPERIMENTAL

Table 16.1 lists the VOCs used in the present study together with their respective characteristic ions. All compounds were purchased from Sigma-Aldrich (St Louis, MO, USA). The MIMS system (Analytical Research Systems, Bologna, Italy) was equipped with a helium carrier gas cylinder (chromatography grade, SIAD, Milan, Italy), pressure regulator and a 30 m column with no stationary phase to provide a constant gas flow (1 mL min^{-1}), sample cell, and hollow fiber membrane connected to a quadrupole ion trap mass spectrometer (Varian Inc., Walnut Creek, USA) through a fused silica column (0.32 mm ID, 5 m, Supelco) without a stationary phase. All mass spectra were acquired (5 min) from m/z 50 to 200 at a rate of 1 spectrum/5 s. The trap temperature was 170°C . The sample was kept under magnetic stirring at room temperature during the analysis. Each instrument had five sample inlets so that up to five different water streams could be analyzed. During normal operating conditions, two inlets were dedicated to blank water and calibration solutions, respectively. The device was operated by means of proprietary software able to set: (a) sampling, analytical, and data-transmission functions; (b) identification and

TABLE 16.1
Characteristic Ions (m/z); MIMS and P&T/GC/MS Limit of Detection (LOD, ppb), Standard Deviation (SD %), and R²; USEPA Method 8260B LODs (ppb).

	Compound	MIMS				P&T/GC/MS			USEPA 8260B	
		Characteristic Ions (m/z)	LOD	SD%	R ²	LOD	SD%	R ²	LOD	LOD
1	Benzene	78	0.05	7	0.9996	0.25	3	0.9989	0.25	0.2
2	Toluene	91	0.3	9	0.9998	0.25	5	0.9949	0.25	0.55
3	Ethylbenzene	91 + 106	0.1	9	0.9998	0.1	6	0.996	0.1	0.3
4	Cumene	77 + 105 + 120	9	9	0.9087	0.25	6	0.9975	0.25	0.75
5	Styrene	78 + 104	0.2	6	0.9922	0.5	6	0.9981	0.5	0.2
6	1,4-dichlorobenzene	146 + 148 + 150	0.2	5	0.9986	0.5	6	0.9878	0.5	0.15
7	1,2-dichlorobenzene	146 + 148 + 150	0.2	5	0.9986	0.5	6	0.9878	0.5	0.15
8	Chloroform	83	0.03	6	0.9977	0.13	4	0.998	0.13	0.15
9	Trichloroethylene	130 + 132	0.03	4	0.9984	0.5	4	0.9966	0.5	0.95
10	Tetrachloroethylene	164 + 166	0.08	8	0.9994	0.5	7	0.9951	0.5	0.7
11	Carbon tetrachloride	117 + 119	0.1	16	0.9965	1	5	0.9917	1	1.05
12	Bromoform	173	0.20	19	0.9927	0.5	8	0.9969	0.5	0.6
13	Dibromochloromethane	129	0.1	9	0.9986	0.5	5	0.9979	0.5	0.25
14	Dichlorobromomethane	83	0.1	6	0.9964	0.5	7	0.9977	0.5	0.4
15	1,1,1-Trichloroethane	96 + 97	0.09	10	0.9982	0.5	7	0.9967	0.5	0.4
16	Acrylonitrile	52	40	11	1.0000	/	/	/	/	/

quantification functions; and (c) display and archiving of the results in the remote station. Verification of the status of the device, simple operations related to the control of the mass spectrometer, and checking of the raw results (for example, air/water checks, tuning, view of the total ion current and mass spectra, etc.) were performed remotely by means of a commercial software package (Laplank Software Inc., Bellevue, WA, USA).

16.3.2 LABORATORY TESTS

Limits of Detection (LOD) were determined by subsequent dilutions of standard solutions down to a signal-to-noise ratio, S/N , of ≥ 3 . Signal reproducibility was determined by six replicates of analyte solutions with concentrations ten times larger than the LOD. Finally, linearity was calculated over a concentration range extending from the LOD to 20–100 times the LOD values. All analyses were performed with solutions freshly prepared immediately before use by appropriate dilution of mother solutions with organic-free triply-distilled water. In turn, mother solutions were prepared daily by dilutions of concentrated solutions of the analytes in methanol stored in a refrigerator except during the daily preparation of solutions.

MIMS results were compared to those obtained by USEPA Method 8260B based on P&T/GC/MS. A Tekmar Velocity XPT Purge and Trap (Teledyne Tekmar, Mason, OH, USA) coupled to a Varian Star 3400X Saturn 2000 GC/MS (Varian, Palo Alto, CA, USA) was used under the following conditions:

P&T

Sample volume: 5 mL;
Trap: Supelco Trap E (SP 2100/Tenax/Silica gel/Charcoal);
Purge temperature: 30°C;
Purge time: 11 min; Purge flow: 40 mL min⁻¹;
Desorbing temperature: 180°C;
Desorbing time: 4 min; Desorbing flow: 300 mL min⁻¹;
Bake temperature: 180°C;
Bake time: 10 min; Bake flow: 400 mL min⁻¹;
Transfer-line temperature: 150°C.

GC/MS

Column: Supelco SPB 624, 60 m x 0.32 mm ID, 1.8 μm film thickness;
Injector temperature: 125°C;
Oven temperature: from 35 to 50°C at 4°C min⁻¹ holding the initial temperature for 2 min; then to 220°C at 10°C min⁻¹ holding the final temperature for 10 min;
Mass spectra: m/z 25–300 at 1 scan min⁻¹.

16.3.3 FIELD TESTS

Four MIMS instruments were deployed for field tests in plants that produced water: one instrument was deployed in each of two plants that produced drinking water from

TABLE 16.2
MIMS Performance in Field Experiments.

Field Test Site	Application	Days On	Days Off	% Off	Analyses /day	Total Analyses
A	Ground Water Potabilization	323	11	3	24	7752
B	Ground Water Potabilization	492	24	5	48	23,616
C	Surface Water Potabilization	510	37	7	24	12,240
D	Industrial Wastewater Treatment	526	20	4	3	1587
Total		1,851	92	5 (aver.)	23 (aver.)	45,195

Note: A Tabulation of the Operational Performance of the MIMS Instruments with Respect to Functional Days, Non-Functional Days, the Percentage of Non-Functional Days, Analyses/Day, and Total Number of Analyses for Each of Four Sites

ground water; one instrument was deployed in a plant that produced drinking water from surface water; and the fourth instrument was deployed in a plant for the treatment of industrial waters. All the plants were located in the area near Bologna. The instruments were programed to sample and to analyze water (analysis duration: 5 min; 1 scan/5 s; full scan of the mass range: m/z 50–200) with the frequency of analysis ranging from three analyses per day to two analyses per hour. Instrument performances were checked over a period ranging from 323 to 526 days (Table 16.2).

16.4 RESULTS AND DISCUSSION

16.4.1 LABORATORY TESTS

The compounds used for the present study were chosen on the basis of the following criteria: halomethanes and haloethanes (compounds 8–15 in Table 16.1) are solvents and disinfection by-products; for compounds 8 and 2–4, the sum of the concentrations in drinking water must be less than $30 \mu\text{g L}^{-1}$ whereas for compounds 9 and 10, the threshold is $10 \mu\text{g L}^{-1}$; the remaining compounds (compounds 1–7 and acrylonitrile, Table 16.1) are of interest because they are often found in industrial wastewaters such as were used for the present study.

16.4.1.1 Detection Limits (LOD)

MIMS detection limits (LOD, $S/N \geq 3$) were determined by analysis of reference solutions and were compared with (a) LODs obtained by P&T/GC/MS operated as described in the previous section, and (b) LODs reported by USEPA Method 8260B (Table 16.1). MIMS LODs were (a) smaller than those obtained by P&T/GC/MS for the organohalogen compounds and for benzene by about, in some cases, one order of magnitude; (b) comparable to the other technique for toluene, ethylbenzene, styrene,

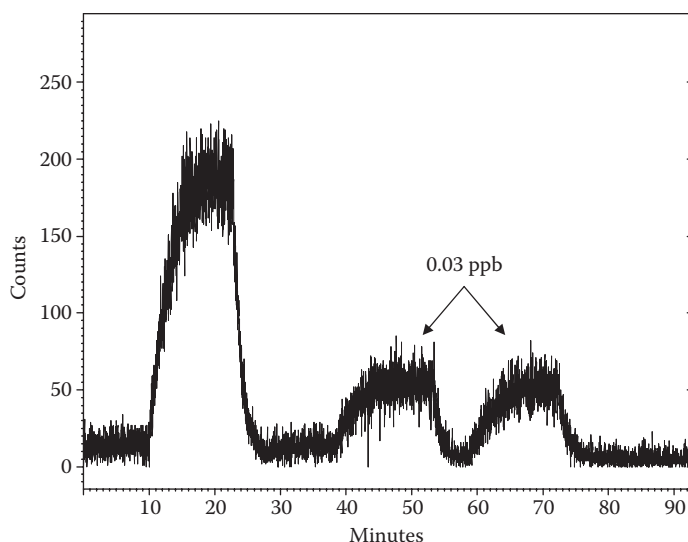


FIGURE 16.1 A typical example of a temporal trace of the ion current for m/z 130–132 from trichloroethylene at a concentration of 0.03 ppb, showing the signal intensity and S/N ratio at the detection limit.

and for the two dichlorobenzene isomers (compounds 6 and 7); and (c) markedly higher for cumene. Acrylonitrile showed a high LOD probably due to its poor partitioning equilibrium in the membrane that, in turn, can be ascribed to its relatively high polarity. USEPA Method 603 reports 0.5 ppb as the detection limit for acrylonitrile, using Purge and Trap and gas chromatography with either a Poropak or a Chromosorb 101 packed column. Figure 16.1 shows the ion current (m/z 130–132) of a 0.03 ppb solution of trichloroethylene as a typical example of the signal intensity and S/N ratio at the detection limit.

16.4.1.2 Reproducibility

The reproducibility (six replicates) of MIMS' responses was compared to that obtained by the reference method. The results (expressed as standard deviation percentage, $SD\%$, Table 16.1) were comparable for the two methods, with the exception of carbon tetrachloride and bromoform, whose MIMS standard deviations were greater than those obtained by P&T/GC/MS. The standard deviation percentage for compounds of relatively high polarity and/or low volatility (such as toluene, ethylbenzene, cumene, bromoform, and carbon tetrachloride) was relatively higher than that obtained by P&T/GC/MS; these results probably indicate an unfavorable partitioning equilibrium for these particular compounds in the membrane.

16.4.1.3 Linearity

With respect to linearity (Table 16.1), MIMS and P&T/GC/MS were comparable ($R^2 > 0.99$), with the exception of cumene, whose MIMS R^2 was 0.9087, probably

due to the previously-mentioned lower partitioning equilibrium of this compound in the membrane; this observation was consistent with the high detection limit of this compound. Acrylonitrile (Figure 16.2) showed perfect linearity over the 50–750 ppb concentration range.

16.4.1.4 Matrix Effects

Standard additions of BTEXs to industrial wastewaters showed no matrix effect. The angular coefficient of the straight line obtained by four additions in the 0.1–2 ppm range was practically identical to that of a similar calibration plot using triply-distilled water (18,954 vs 18,883), the two lines being parallel (Figure 16.3).

16.4.2 CASE STUDIES

16.4.2.1 Acrylonitrile

Acrylonitrile, a compound that is not included in the family of the VOCs, could be determined at high concentration levels (4.78 ppm) in industrial waters containing

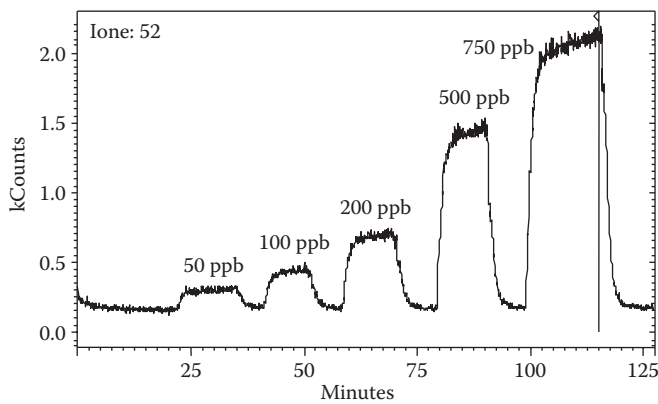


FIGURE 16.2 The m/z 52 ion current for acrylonitrile showed perfect linearity over the 50–750 ppb concentration range.

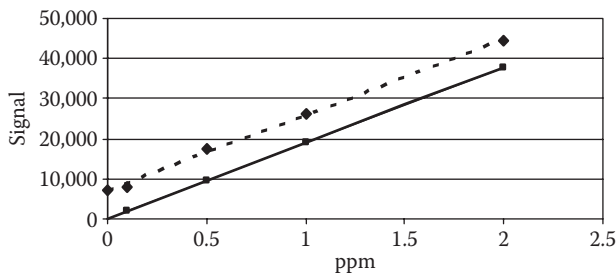


FIGURE 16.3 Calibration of BTEXs in triply-distilled (continuous line, $y = 18,883x + 115.59$, $R^2 = 1$) and industrial water (dotted line, $y = 18,954x + 7002.1$, $R^2 = 0.9977$).

a wide range of aromatic hydrocarbons. Figure 16.4 shows a MIMS full scan mass spectrum with ions at m/z 78, 104, 91, 120, 121 and 118 (typical of such aromatic substances as styrene, ethylbenzene, xylene, cumene, cumene hydroperoxide, α -methylstyrene) along with an ion at m/z 52 (acrylonitrile) of much lower ion signal intensity, whose ion currents for duplicate analyses are shown in Figure 16.5.

16.4.2.2 Comparison of Membrane Inlet Mass Spectrometry (MIMS) with Purge-and-Trap/Gas Chromatography (GC)/Mass Chromatography (MS)

A series of experiments was performed in order to compare MIMS and Head-Space Purge and Trap /GC/MS by analyzing a total of 20 industrial wastewater samples from seven different sampling points. In Figure 16.6 is shown the MIMS mass spectrum of one of the wastewater samples; in this example, seven compounds that

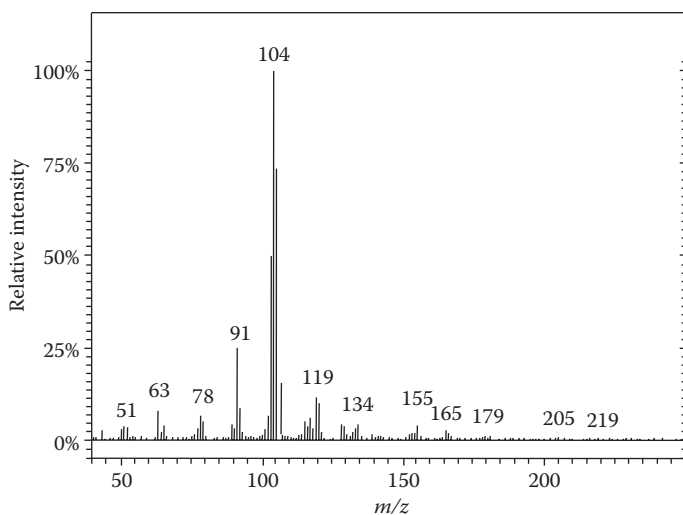


FIGURE 16.4 Full scan mass spectrum of a sample of industrial waters containing acrylonitrile (m/z 52) along with aromatic substances such as styrene, ethylbenzene, xylene, cumene, cumene hydroperoxide, and α -methylstyrene.

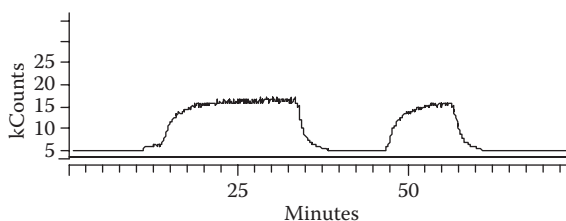


FIGURE 16.5 Ion current of m/z 52, acrylonitrile at 4.78 ppm, duplicate analysis of the same sample of industrial waters as was used for Figure 16.4.

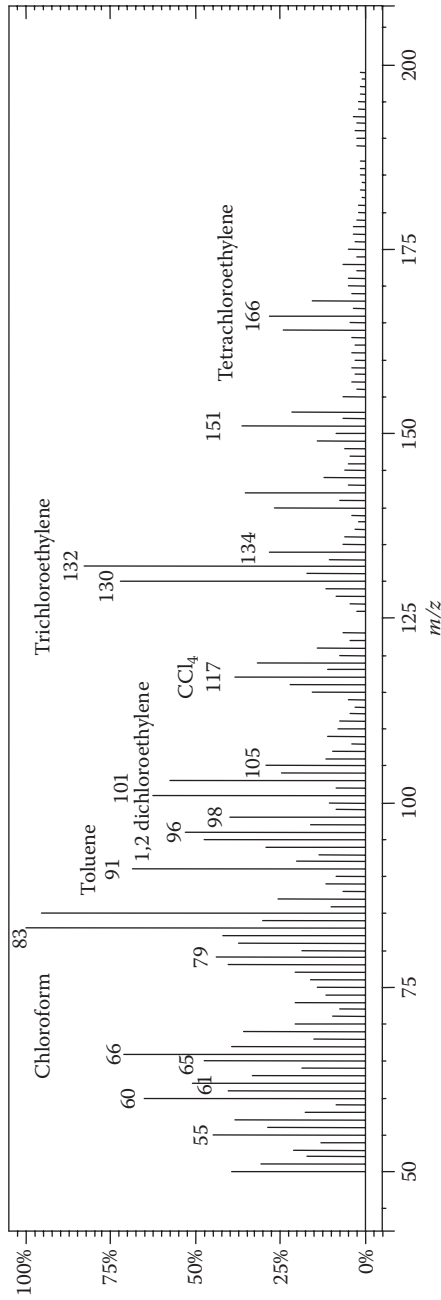


FIGURE 16.6 Mass spectrum of industrial water used to compare MIMS and Purge-and-Trap/GC/MS. Identified compounds and ions used for quantification are reported.

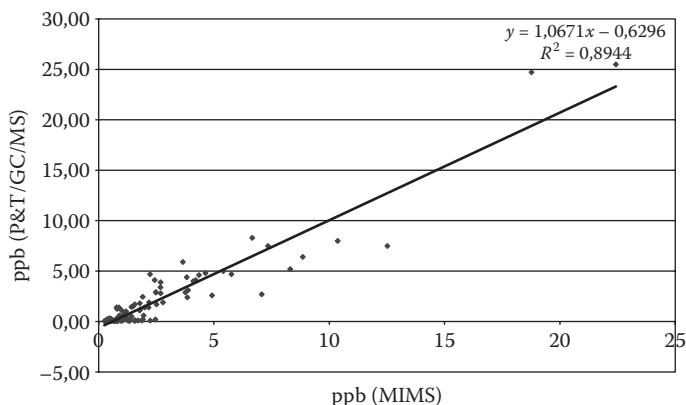


FIGURE 16.7 Comparison of data obtained by analyzing samples with Purge-and-Trap/GC/MS and MIMS. The concentration (in ppb) of each of toluene (m/z 91), benzene (m/z 78), 1,2-dichloroethylene (m/z 98), trichloroethylene (m/z 130 + 132), chloroform (m/z 83), and vinyl chloride and dichloroethane (m/z 62 for both compounds) in each of 20 wastewater samples determined by MIMS is plotted against that determined by Purge-and-Trap/GC/MS.

have been identified by their characteristic ions are indicated on the mass spectrum. Toluene (m/z 91), benzene (m/z 78), 1,2-dichloroethylene (m/z 98), trichloroethylene (m/z 130 + 132), chloroform (m/z 83), and vinyl chloride and dichloroethane (m/z 62 for both compounds) were detected and quantified in all 20 samples with both techniques. The concentration (in ppb) of each of the above seven compounds in each of 20 wastewater samples determined by MIMS is plotted against that determined by P&T/GC/MS as shown in Figure 16.7. The equation of the regression line calculated from these data (Figure 16.7) is $y = 1.0671x - 0.6296$, $R^2 = 0.8944$. The slight differences between the actual and the ideal coefficients (slope = 1, intercept = 0 and $R^2 = 1$) are probably due to the contributions of other compounds to the abundances of the ions used for quantitation.

16.4.3 FIELD TESTS

Four instruments were deployed in different plants representative of typical cases of water treatment, namely two plants for the potabilization of ground water (A and B), the third plant for surface water potabilization (C), and, finally, a plant for industrial water treatments (D) (Table 16.2). In field test A, the instrument was deployed in a plant for the production of drinking water from ground water using chlorine dioxide as a disinfection agent. Due to past industrial activity in that area, the ground water was heavily contaminated by chloroform and trichloroethylene. Charcoal filters were used to abate the organohalogen concentration in drinking water down to 1–10 ppb levels. The instrument was located in a 2×3 m container maintained at room temperature. The instrument was able to identify and to quantify drinking water pollutants by means of a mass spectrum in which the ions characteristic of the individual compounds were recorded clearly, showing their

respective diagnostic isotopic patterns (Figure 16.8a). Hourly analyses were carried out in order to check that pollutant concentrations did not exceed the legal thresholds. The position was unmanned and the results were transmitted to the remote control room by e-mail at the conclusion of each analysis. The instrument was monitored over a period of 334 days during which it functioned for 323 days; failures and maintenance resulted in the loss of 11 days (that is, 3% of the time monitored) (Table 16.2). Almost 8000 determinations were performed corresponding to 646 hours of analysis.

In plant B, both ground water and drinking water were monitored every hour, corresponding to a total frequency of 1 analysis/30 min. Here, the contaminant was trichloroethylene. The plant was not equipped with charcoal filters, consequently the pollutant concentration was kept within the regulation limit (10 ppb) by shifting water uptake from one well to another. Figure 16.8b shows a typical full-scan mass spectrum recorded from the ground water of this location, with the characteristic trichloroethylene molecular ion isotopic quartet at m/z 130, 132, 134, and 136. As for the previous field study in plant A, the location was unmanned and the results were transmitted by e-mail. The percentage of inactivity in plant B (5%) was comparable with that of plant A (3%), despite the fact that the working period for plant B (almost 500 days) was longer than that for plant A, and the number of analyses carried out at plant B (23,626) was more than three times higher than those carried out in plant A (7,752); see Table 16.2.

Field test C was an example of application to surface waters used for human consumption. Such waters were essentially uncontaminated by chemicals and needed only a conventional disinfection. Nevertheless, this plant was monitored in consideration of the fact that accidental pollution by gasoline and oil had been recorded in the past due to the proximity of an adjacent highway with heavy traffic. Figure 16.8c shows a typical mass spectrum of this instance, with no significant ions. This instrument was monitored over 547 days (12,240 analyses, 1020 hours) during which the days off were 37, that is 7% of the period (Table 16.2).

Finally, industrial wastewaters (plant D) were analyzed from the outlet of a pipe connected into a municipal sewage treatment plant. In such a case, the concern was that organohalogenated compounds from industrial wastes may affect the biological treatment of urban wastewaters. The instrument recorded 3 analyses per day on those days when the industrial wastewaters were discharged. Figure 16.8d shows the typical mass spectrum of such samples. Ions characteristic of chloroform (m/z 83, 0.3 ppb), trichloroethylene (m/z 130, 23 ppb), and toluene (m/z 91, 31 ppb) were found in the mass spectrum reported in Figure 16.8d. The complex matrix of such wastes did not affect the MIMS determinations (see previous discussion, Figure 16.3). The instrument was monitored during more than 500 days (about 1600 analyses or 130 functioning hours) with a 4% of non-functioning time (Table 16.2).

For all types of mass spectrometers, particularly those operated in remote locations, it is of interest to consider the frequency of mass calibration and, for those instruments that employ electron impact ionization, the frequency with which the filament must be replaced. It was found for the MIMS instruments that mass calibrations were carried out on 24 occasions and filaments were replaced on 16 occasions.

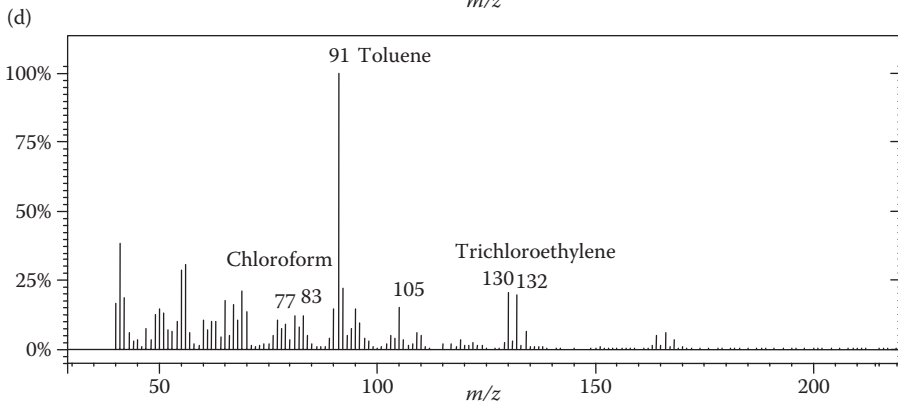
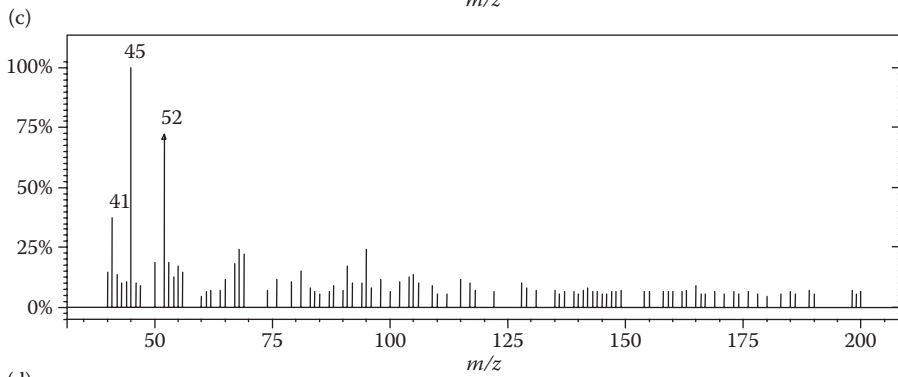
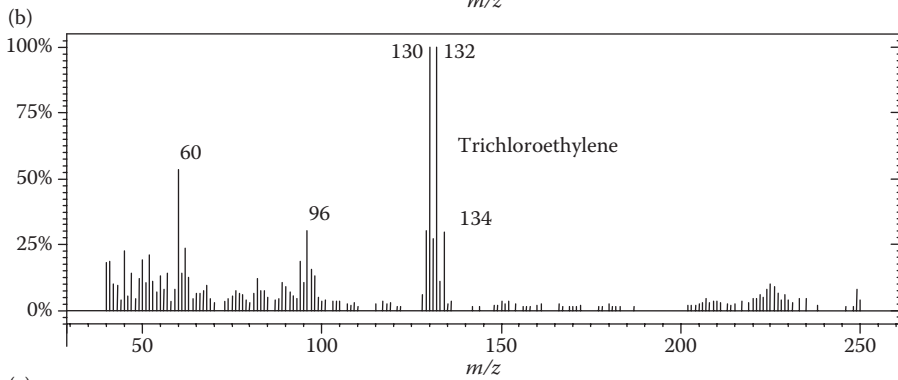
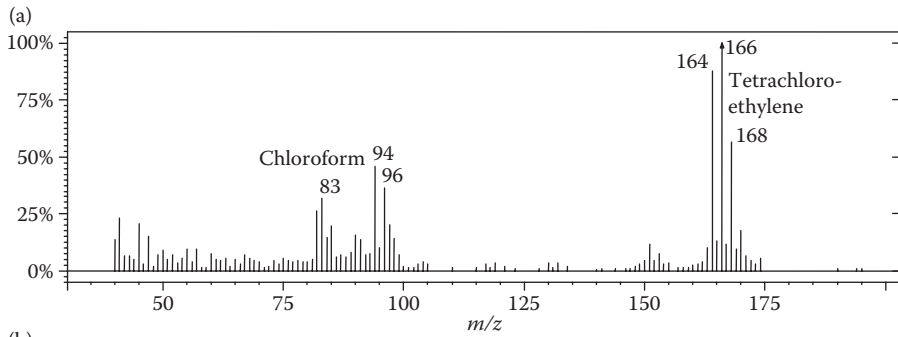


FIGURE 16.8 (Opposite) (a) Field test A. Mass spectrum of a water sample from a plant for the production of drinking water from ground water. Chlorine dioxide had been used as a disinfection agent. Ground water was contaminated heavily by chloroform and trichloroethylene due to past industrial activity; charcoal filters had been used to abate the organohalogen concentration in drinking water down to 1–10 ppb levels. (b) Field test B. Mass spectrum recorded from the ground water of this location. At this site, the contaminant was trichloroethylene and the mass spectrum shows the characteristic trichloroethylene molecular ion isotopic quartet at m/z 130, 132, 134, and 136. The plant was not equipped with charcoal filters, consequently pollutant concentration was kept within the regulation limit (10 ppb) by shifting water uptake from one well to another. (c) Field test C. Mass spectrum of surficial water used for human consumption. Such waters were essentially uncontaminated by chemicals and needed only a conventional disinfection. No significant ions were observed. (d) Field test D. Mass spectrum of a sample of industrial wastewaters taken from the outlet of a pipe connected into a municipal sewage treatment plant. In this case, the concern was that organohalogenated compounds from industrial wastes may affect the biological treatment of urban wastewaters. This typical mass spectrum shows ions characteristic of chloroform (m/z 83, 0.3 ppb), trichloroethylene (m/z 130, 23 ppb), and toluene (m/z 91, 31 ppb).

From the data shown in Table 16.2 concerning the numbers of operating days and the number of analyses carried out each day at each of the four sites, it is found that averages of 2825 analyses were carried out with each filament and 1883 analyses were carried out between successive calibrations. Comparing these data with those of a GC/MS instrument used presently in our laboratory and which has shown good instrumental stability and reliability, it was found that the GC/MS instrument performed 305 analyses per filament and 78 analyses per calibration. When it is borne in mind that the duration of a GC/MS analysis was 50 min while that of a MIMS analysis was 5 min, it is clear that both systems performed comparably in terms of operation time per filament.

16.5 CONCLUSION

A number of laboratory tests to determine LOD, linearity and repeatability of MIMS instruments applied to the analysis of VOCs in water were performed. Data were comparable with those obtained by the classical method of VOC analysis in water (P&T/GC/MS and USEPA Method 8260B). Four MIMS instruments were tested over an extensive period of time to evaluate their on-site performance in unmanned locations. Results were remarkable: the instruments worked unchecked for long periods producing a total of more than 45,000 analyses and VOC amounts were quantified automatically and sent to a remote control room where non-expert personnel could understand the results readily.

In conclusion, MIMS instruments proved to have great potential for utilization in continuous VOC-monitoring stations. These instruments are reliable, cost-effective and simple to use; they have no environmental impact because no solvent is used for the extraction of organics from water, and they can be located on-site, unattended, providing a continuous flow of data on water quality and pollution.

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