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# Novel membrane inlet mass spectrometric methods for analysis of organic compounds in aqueous and solid samples




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Marja Ojala

VTT Chemical Technology

Laboratory of Analytical Chemistry
Department of Chemistry
Faculty of Science
University of Helsinki

*ACADEMIC DISSERTATION*

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puh. vaihde (09) 4561, faksi (09) 456 4374

Statens tekniska forskningscentral (VTT), Bergsmansvägen 5, PB 2000, 02044 VTT
tel. växel (09) 4561, fax (09) 456 4374

Technical Research Centre of Finland (VTT), Vuorimiehentie 5, P.O.Box 2000, FIN–02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 4374

VTT Kemiantekniikka, Prosessit ja Ympäristö, Biologinkuja 7, PL 1401, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 7026, (09) 456 7021

VTT Kemiteknik, Processer och miljö, Biologgränden 7, PB 1401, 02044 VTT
tel. växel (09) 4561, fax (09) 456 7026, (09) 456 7021

VTT Chemical Technology, Processes and Environment,
Biologinkuja 7, P.O.Box 1401, FIN–02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 7026, + 358 9 456 7021

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# Abstract

Different volatile organic compounds (VOCs) are widely used in industry and due to accidents and fuel emissions the compounds can be discharged into the environment, causing contamination of soil and groundwater. Because of their toxicity the analysis of VOCs is very important. The traditional analytical methods for VOCs, such as static and dynamic headspace gas chromatography-mass spectrometry, are time consuming and difficult to apply in on-line analysis or even on-site analysis. For this reason, a purge-and-membrane mass spectrometric (PAM) method was developed for analysis of VOCs in solid samples. Two versions of PAM-devices are introduced in this study. The characteristics of the method, such as linear dynamic ranges (at least five orders of magnitude), detection limits and repeatability, are presented. The detection limits varied between 5 and 150 µg/kg depending on compounds and soil type, and the repeatability was good when an internal standard was used (RSD < 14%). The effects of soil parameters such as humidity and the content of organics on desorption were studied. Both soil type and moisture content had an effect on peak areas. In addition, moisture content had an inversely proportional effect on desorption times in the case of garden soil. Furthermore, the effects of PAM-parameters such as the preheating time and temperature are presented in detail. Even a preheating time of only ten minutes was suitable for analysis. The use of different purge gases was studied. In addition, an application of the analysis of VOCs in pharmaceuticals is presented. Some preliminary tests for water analysis with PAM were carried out. The results obtained with the PAM-method for soil samples were compared with those of static headspace gas chromatography. Both spiked and authentic soil samples were used in analysis and two different laboratories took part in the testing. The agreement between testing methods and laboratories was good. The results show that the new PAM-MS method is very promising for the determination of volatile organic

compounds in solid samples. Other advantages of the method are short analysis times (only a few minutes per sample), the non-requirement for pretreatment of samples, and for environmental and health risk reasons the fact that solvents are not used.

A membrane inlet mass spectrometry (MIMS) method was developed for testing volatile organic sulphur compounds, terpenes and phenolic compounds in water samples. Different conventional chromatographic methods were used to compare results. Detection limits obtained were at the low ppb level. Analysis times are short, only a few minutes, and no pretreatment of the samples is needed. Phenolic compounds were analysed both directly from water and after acetylation in aqueous phase. The detection limits obtained after acetylation increased from 5-fold for di- and trichlorophenols to 100 fold for 4-nitrophenol. The MIMS-method combined with the Solver program made it possible to calculate the amounts of monoterpenes and sesquiterpenes in water samples. It is worthy of notice that MIMS-Solver was the only reliable method (of four) to measure low concentrations of sulphur compounds in water samples.

# Preface

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I Kostiainen, R., Kotiaho, T., Mattila, I., Mansikka, T., Ojala, M., Ketola, R.A. Analysis of volatile organic compounds in water and soil samples by purge-and-membrane mass spectrometry. Analytical Chemistry 70 (1998), pp. 3028–3032.

II Ojala, M., Mattila, I., Särme, T., Ketola, R.A., Kotiaho, T. A New purge-and-membrane mass spectrometric (PAM-MS) instrument for analysis of volatile organic compounds in soil samples. Analyst 124 (1999), pp. 1421–1424.

III Ojala, M., Poutanen, M., Mattila, I., Ketola, R.A., Kotiaho, T., Kostiainen, R. Analysis of residual solvents in pharmaceuticals with purge-and-membrane mass spectrometry. Rapid Commun. Mass Spectrom. 14 (2000), pp. 994–998.

IV Ojala, M., Mattila, I., Tarkiainen, V., Särme, T., Ketola, R.A., Määttänen, A., Kostiainen, R., Kotiaho, T. Purge-and-membrane mass spectrometry, a rapid screening method for analysis of VOCs from soil samples. Analytical Chemistry 73 (2001), pp. 3624–3631.

V Ojala, M., Ketola, R., Mansikka, T., Kotiaho, T., Kostiainen, R. Detection of volatile organic sulphur compounds in water by headspace gas chromatography and membrane inlet mass spectrometry. J. High Resol. Chromatogr. 20 ( 1997), pp. 165–169.

VI Ojala, M., Ketola, R.A., Mansikka T., Kotiaho, T., Kostiainen R. Determination of mono- and sesquiterpenes in water samples by membrane inlet mass spectrometry and static headspace gas chromatography. Talanta 49 (1999), pp. 179–188.

VII Ojala, M., Ketola, R.A., Virkki, V., Sorsa, H., Kotiaho, T. Determination of phenolic compounds in water using membrane inlet mass spectrometry. Talanta 44 (1997), pp. 1253–1259.

# Contents

***Appendices of this publication are not included in the PDF version. Please order the printed version to get the complete publication (http://otatrip.hut.fi/vtt/jure/index.html)***

# Abbreviations

| | |
|---|---|
| A | Membrane surface area, $cm^2$ |
| amu | Atomic mass unit |
| $C_m(x,t)$ | Concentration inside the membrane, $mol/cm^3$ |
| D | Diffusion constant, $cm^2/s$ |
| EFNi | Electro-formed nickel |
| EI | Electron impact |
| ELCD | Electrolytic conductivity detector |
| EPA | Environmental Protection Agency |
| FID | Flame ionised detector or flame ionised detection |
| GC | Gas chromatography |
| HP | Hewlett Packard |
| HPLC | High performance liquid chromatograph(y) |
| HSGC | Headspace gas chromatograph(y) |
| ICH | International Conference on Harmonisation |
| I.D. | Inner diameter |
| $I_m(x,t)$ | Analyte flow inside the membrane, mol/s |
| LRD | Linear dynamic range |
| m/z | mass/charge |
| MIMS | Membrane inlet mass spectrometry |
| MS | Mass spectrometry or mass spectrometer |
| MTBE | 2-Methoxy-2-methyl propane, *tert.* butyl methyl ether |
| nd | Not detected |
| nm | Not measured |
| O.D. | Outer diameter |

| | |
|---|---|
| ODS | Octadecyl silane |
| P&T | Purge and trap |
| PAM | Purge and membrane |
| PAM-MS | Purge and membrane mass spectrometry or mass spectometer |
| PID | Photoionisation detector |
| r | Coefficient of regression |
| RA | Relative abundance |
| RSD | Relative standard deviation |
| S/N | Signal to noise ratio |
| SIM | Selected ion monitoring |
| SPME | Solid-phase microextraction |
| std | Standard deviation |
| t | time, s |
| $t_{(50)}$ | 50% steady state permeation |
| $T_0$ | Initial temperature |
| TAME | 1,1-Dimethylpropyl methyl ether, t-amyl methyl ether |
| VOC | Volatile organic compound |
| VOSC | Volatile organic sulphur compound |
| x | Depth in the membrane, cm |

# 1. Introduction

## 1.1 Overview of membrane inlet mass spectrometry

Membrane inlet mass spectrometry (MIMS) is an analytical method in which a membrane is used as an interface between fluid of gas and the vacuum of a mass spectrometer [1] (Figure 1.1). The compounds to be measured transfer from the liquid phase to vapour phase by pervaporation, which consists of three separate steps: 1) selective partitioning of the analyte into the membrane, 2) selective diffusion of the analyte through the membrane and 3) desorption of the analyte from the membrane to the vacuum. As the flow of water or the major constituents of air (nitrogen and oxygen) through the membrane is smaller than the flow of organic compounds, 10–100-fold enrichment of the organic compounds compared to water or air may be obtained. The main reason for this is the greater solubility of organic compounds in the typically used polydimethylsiloxane membrane compared to the solubility of water or gases. A schematic diagram of MIMS is presented in Figure 1.1. The water or air sample is circulated over the membrane and the analytes pass through the membrane into the ionisation chamber of the mass spectrometer.

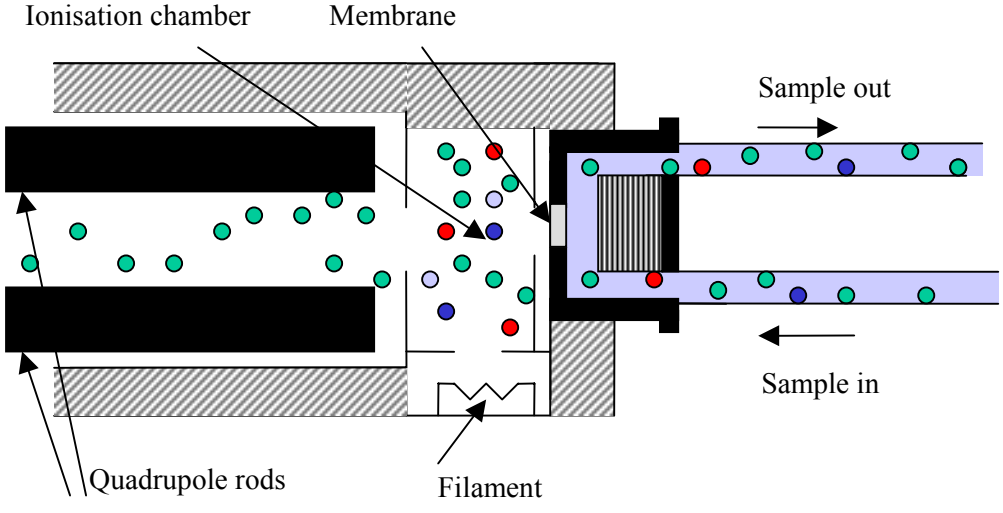



*Figure 1.1. Schematic diagram of a membrane inlet mass spectrometer.*

## 1.2 Theory of membrane inlet mass spectrometry

Fick´s first (1) and second (2) laws describe the permeation process, the basis of MIMS. Assuming that the constants for solvation and diffusion are independent of partial pressure, the equations can be written as

$$I_m(x,t) = -AD\frac{\partial C_m(x,t)}{\partial x} \quad (1)$$

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

Where $I_m(x, t)$ is analyte flow inside the membrane (mol/s), A is the membrane surface area ($cm^2$), D is a diffusion constant ($cm^2/s$) and $C_m(x,t)$ is the concentration inside the membrane ($mol/cm^3$), x is the depth in the membrane (cm) and t is time (s). Equation (1) describes the rate of molecular flow inside the membrane and equation (2) the rate at which the concentration changes as a function of time [2]. Membrane thickness is the most important parameter for MIMS of those presented in Fick´s equations, because response times and detection limits are highly dependent on this parameter. According to LaPack et al. [2], when the membrane thickness is doubled the response time will be quadrupled. This has also been shown to be true in practice [3]. Sensitivity of the MIMS method is proportional to the membrane area. The type of membrane has a major effect on the selectivity.

## 1.3 Applications and techniques of membrane inlet mass spectrometry

Hoch and Kok [4] first introduced membrane inlet mass spectrometry in 1963, when they used a planar membrane interface for measuring dissolved compounds in a biochemical system. Since its introduction the MIMS method has become very popular because it is solvent-free, simple, fast, well suitable for on-line and on-site analysis and there is no need for preconcentration. The main areas for MIMS methods are biochemistry, fermentation monitoring and environmental applications. Reuss et al. [5] reported the first application for fermentation monitoring in 1975 followed by numerous others, which have been

thoroughly, reviewed [6–8]. MIMS has been used both in on-line process monitoring and off-line analytics of reaction products [8].

Environmental applications are the most expanding area of MIMS. Collins and Utley presented the first application to direct air analysis with MIMS in 1972 [9]. They detected 0.1 ppm of Freon 113 in air. Since then some applications of air analysis have been published [10–15], mainly for the analysis of volatile organic compounds in air. The use of hollow fibre membrane for monitoring of organic compounds in water and air by Westover et al. [16] in 1974 is one of the first environmental applications of membrane inlet mass spectrometry. They tested different membrane materials in the analysis of different organic compounds in water and nitrogen atmospheres. Polydimethylsiloxane was found to be the most useful membrane material. Detection limits obtained for chloroform and methanol were 1 ppb and 1 ppm, respectively. The introduction of direct insertion membrane probes by Cooks et al. [17, 18] was an important development step of MIMS. This device allowed the transportation of analyte solution over a sheet membrane, through which compounds pervaporate directly into the heated ion source of a mass spectrometer. A similar type of membrane inlet utilising a sheet polydimethylsiloxane membrane built on a standard 70-mm Conflat flange was reported by Lauritsen 1990 [19] and this type was applied in our studies [3]. In 1991 Slivon et al. introduced a helium purge inlet [20] utilising a silicone capillary membrane.

Membrane inlet mass spectrometry is a widely used technique for monitoring organic compounds directly from aqueous solutions. Applications for water samples are numerous and they have been reviewed by many authors [1, 6, 7, 21–24], including on-line and on-site applications [8, 25, 26]. Most of the published applications are for the analysis of VOCs in water [27–40]. Low detection limits for several compounds were obtained. For example, Bauer and Solyom [27] reported detection limits in parts per trillion ranges for 59 volatile compounds, mainly for aromatic and halogenated hydrocarbons, listed in EPA method 524.2. Kana et al. developed a MIMS method for rapid determination of dissolved gases in water [28]. Headspace membrane introduction mass spectrometry has been used to analyse VOCs in soil samples [41]. In this technique the solid sample is placed into the sample vessel, which is connected to the membrane holder. When the oven is heated rapidly the VOCs permeate the membrane and are preconcentrated in the headspace. After a predetermined

time the valve is opened and the VOCs are transferred into the ion source of the mass spectrometer. Headspace membrane introduction mass spectrometry has also been used in water analysis [42]. The results obtained with the MIMS-method have been compared to those obtained with other analytical methods. For example, Creaser et al. compared the MIMS method with solid phase microextraction and purge-and- trap GC-MS for benzene analysis [40] and the results were satisfactory. The analysis of VOCs from water samples with MIMS compared to traditional analysis methods has been presented earlier [31, 43, 44].

Different preconcentration techniques have been developed which are specific to MIMS. In trap-and-release MIMS [37] the preconcentration occurs in the membrane, followed by thermal release. In order to allow the simultaneous analysis of VOCs and semivolatile organic compounds, the trap-and-release technique [37] was modified and used with a direct insertion membrane probe [38]. This method has also been used in the analysis of phenols in water [45]. These semivolatile organic compounds were preconcentrated inside the membrane before they were thermally desorbed into the ion source. Cryotrap MIMS [46] preconcentrates permeate in a cold trap, and thermal desorption is also used in this method. In laser desorption MIMS [47] a laser is used to release analyte from the mass spectrometer side of the membrane. Polycyclic aromatic hydrocarbons for example naphthalene, crysene and benz(b)fluoranthene, have been analysed at ppb concentrations using laser desorption MIMS [47]. A jet separator, which separates much of the purge gas, has been used in connection with MIMS to obtain lower detection limits [34, 35]. In traditional MIMS there is no separation of compounds and in order to improve selectivity gas chromatography has been used in connection with MIMS [48]. A similar effect can be obtained by using temperature programmed desorption MIMS [14]. An alternative way to achieve detection of different compounds at the same time is to use calculation programs. A program using a non-linear deconvolution algorithm has been published [49] for resolving a multicomponent mass spectrum.

The most often-used membrane type is a silicone polymer, but other polymeric membranes such as polyvinyl chloride, Teflon, polyurethane, polyimide and polyethene have been introduced. The use of alternative polymer membranes was reviewed recently [6].

Different mass analysers and ionisation techniques have been used in combination with the membrane inlets. For example, quadrupoles, ion traps [50, 51] and time-of-flight [15, 52] instruments have been used in different MIMS-applications. As alternatives to electron impact ionisation (EI) technique, many other techniques such as charge exchange ionisation [53] and glow discharge ionisation [54] have been used to increase selectivity and sensitivity. Desorption chemical ionisation sources have been used with a microporous membrane for the analysis of semivolatiles [55]. They have also been used in the detection of high molecular weight fat-soluble biomolecules [56]. Selective ionisation has been used in conjunction with ion trap MIMS to achieve parts-per-quadrillion level detection limits [33].

## 1.4 Analysis of volatile organic compounds in solid samples

### 1.4.1 Volatile organic compounds in soil samples

Different volatile organic compounds (VOCs) are widely used in industry for example as degreasing agents for metallic machinery and in the integrated circuit industry and as solvents for dry cleaning. Due to accidents and fuel emissions, the compounds may be discharged from such plants into the environment, which leads to contamination of soil and groundwater. Due to their toxicity and possible carcinogeneity the analysis of these compounds at low concentrations is extremely important. It is worthy of notice that the limit for remediation of contaminated soil in Finland is for example 25 mg/kg for benzene [57]. Due to the high volatility of VOCs, their analysis in soil samples is very difficult and special care must be taken in the sampling and storing of samples before analysis. The pretreatment of the samples should be as simple as possible to avoid loss of volatile analytes. Different analytical methods [58] have been used to analyse VOCs in contaminated soils. The most frequently used methods are headspace and purge-and-trap technique connected either to a gas chromatograph [59–62] or a mass spectrometer [63]. Multiple headspace extraction [64] and headspace solid phase microextraction [65, 66] have also been used. In order to avoid transportation of samples, different portable on-site analysis systems [67, 68] have been developed. On-site and on-line analytical methods [26] have also been applied for VOCs in water and soil samples. In

headspace analysis special care must be taken because quantitative results are strongly dependent on the partitioning of the VOCs between gas, liquid and solid phases [68]. Hewitt et al. [69, 70] compared laboratory purge-and-trap gas chromatography/mass spectrometry and on-site aqueous extraction headspace/gas chromatography in the analysis of VOCs in soils. Usually the agreement was good, but significant differences in the results were also observed.

Recently, static headspace-MIMS has been introduced for VOC analysis in soil samples [41]. The purge-and-membrane technique was first introduced with electron capture detection in an application for chlorinated hydrocarbons in water samples [71]. In this technique VOCs are purged from the samples with inert gas and the gas stream is directed through a membrane into the analyser.

### 1.4.2 Volatile organic compounds in pharmaceuticals

Both European Pharmacopoeia [72] and the International Conference on Harmonisation (ICH) draft guidelines [73] require the determination of residual solvents as an essential element in the quality control of pharmaceutical products. Residual solvents are defined as volatile organic compounds (VOCs) which may remain in active substances, excipients and medical products after processing [74]. Residual solvents are adsorbed on the drug material with varying strengths depending on the chemical and physical properties of the solvent and of the drug material [74]. Because of their possible health risks and toxicity, all solvents should be removed as completely as possible in order to meet product specifications and quality-based requirements. ICH has adopted "Impurities: Guideline for Residual Solvents", which prescribes limits for the contents of solvents in pharmaceuticals. Residual solvents are divided into three classes: solvents to be avoided (for example benzene and some chlorinated compounds), solvents to be limited (for example acetonitrile, toluene and methanol) and solvents with low toxic potential (for example acetic acid, ethanol and tetrahydrofuran) [73].

Analysis of residual solvents is necessary only for those compounds, which are used or produced in the manufacturing or purification of active substances, excipients or medical products. Residual solvents are typically determined using

chromatographic techniques [74–81]. If feasible, harmonised procedures described in the pharmacopoeias should be used for determining levels of residual solvents. Otherwise, manufacturers are free to select the most appropriate validated analytical procedure for a particular application [72].

Different analytical methods have been used to determine residual solvents in pharmaceutical products [75]. If only solvents with low toxic potential are used in a manufacturing process, a non-specific method such as weight loss during drying may be used. However, if solvents to be limited or solvents to be avoided are used, more specific and sensitive analytical methods are required. The most frequently used technique is static headspace gas chromatography (HS-GC) [74–79], which is relatively simple since extensive sample preparation is not required. However, the sensitivity of static headspace methods is limited and the method is thus restricted to samples with relatively high concentrations (ng/ml) of VOCs. Dynamic headspace methodology, i.e. purge-and-trap (P&T), provides high sensitivity for residual solvents, but more complex instrumentation is required [75, 80, 81]. Furthermore, the adsorbents used in P&T may lead to unreliable quantitative results due to easy breakthrough of highly volatile compounds when Tenax is used as an adsorbent or due to freezing of the cold trap when carbon-based adsorbents are used. Furthermore, significant memory effects may occur with P&T after the analysis of samples containing high concentrations of VOCs. Headspace solid phase microextraction (SPME) has also been applied for residual solvents in pharmaceutical products [82]. The method is relatively simple and provides more than sufficient sensitivity. However, all the methods based on headspace techniques are time-consuming due to long equilibrium times, extraction times and the time needed for GC separation of VOCs [82]. Fast gas chromatography has been used in the analysis of residual solvents [83]. Although the analysis time is short, sample extraction or headspace equilibrium time is still needed before the analysis.

## 1.5 Analysis of aqueous samples

### 1.5.1 Volatile organic compounds in water

As mentioned earlier (Section 1.4.1), volatile organic compounds are widely used in industry and therefore they also occur in nature. Two important groups

of VOCs are volatile organic sulphur compounds (VOSCs) and terpenes. VOSCs are present in industrial wastes, particularly in effluents of the pulp and paper industry. Other natural sources of VOSCs are volcanoes, oceans, soils, vegetation, fossil fuel combustion and solvent releases [84, 85]. Since VOSCs are toxic, corrosive and they have low odour threshold values [86], highly sensitive methods are required for their detection in the environment.

Several different chromatographic methods have been developed for the detection of VOSCs [87–89]. A purge-and-trap gas chromatographic method with flame photometric detection has been shown to give ng/l-level detection limits for VOSCs [90–94]. A Hall electrolytic conductive detector was used in the analysis of volatile sulphides in water after degassing the solution and cryogenically trapping the volatiles [95]. In addition, static headspace gas chromatography with chemiluminescence detection has been used in the analysis of volatile sulphur compounds in brandies [96].

Mono- and sesquiterpenes are common constituents of volatile oils and several woods contain extractable terpenes, and they are found for example in the condensation waters of pulp and paper mills [97, 98]. Monoterpenes exist as hydrocarbons or as oxygenated compounds such as aldehydes, alcohols, ketones, esters or ethers. The solubility of mono- and dicyclic terpene hydrocarbons in water is low (10–30 mg/l). However, monoterpenes containing the hydroxyl group have 10–100 fold solubilities compared to terpene hydrocarbons [99]. Due to their low solubility in water, terpene hydrocarbons have relatively high Henry's law constants [100–101] and therefore they partition predominantly into the atmosphere [102]. For this reason they have been analysed more often in air [103–106] than in water.

Gas chromatography and gas chromatography- mass spectrometry have been used to analyse different terpenes from wood and water samples after extraction [107–112]. Headspace methods have been used in the analysis of terpenes from essential oils, plant products and in aroma constituents [113–115]. Furthermore, headspace methods have been used in quantitation of volatile constituents, for example terpenes in juices [116–118]. However, only one article reporting the measurement of terpenes from water by the static headspace method was found in the literature [119]. The detection limits obtained for terpene hydrocarbons were approximately 5 µg/l.

### 1.5.2 Phenolic compounds in water

Phenol and related compounds are used in large quantities in industry. As a result of emissions, accidents and other releases they also occur in the environment. Phenols are highly toxic and can cause serious taste and odour contamination and therefore their analysis even at low concentrations is very important [120, 121]. However, the analysis of phenolic compounds is difficult due to their high polarity. The separation of phenolic compounds from water by solvent extraction is particularly difficult and the recoveries are not satisfactory.

Direct measurement of phenolic compounds in water using high performance liquid chromatography (HPLC) is possible, but the detection limits are rather high, about 100 µg/l [122, 123]. Several concentration methods may be used to obtain better overall detection limits [124–130]. Solid-phase microextraction [131–132] has also been applied to the analysis of phenolic compounds. Low detection limits with good precision were obtained, but the absorption time of one sample, about 40–50 minutes, limited the usefulness of the method for on-line applications. Various derivatives [133] have also been used but acetylation of phenols after solvent extraction is one of the most frequently used derivatisation techniques. It is also possible to carry out acetylation in aqueous solution [134–136]. This derivatisation method, followed by solvent extraction and gas chromatographic analysis, has produced much better results than the reversed order method, in which the phenols are first extracted and then derivatised, due to better recovery of the phenols. With the direct acetylation in water, recoveries of about 100% could be obtained [134]. A modified MIMS-method, trap-MIMS has been used for the analysis of chlorophenols from water samples [45]. Recent developments in the analysis of phenolic compounds in water samples are focused on solid phase extraction of phenols [137], or aim to develop new sorbents and to test and compare them both in off- [138] and on-line methods [139]. On-line liquid-solid extraction using LiChrolut EN sorbent followed by liquid chromatography with coulimetric detection generated parts per trillion levels detection limits [140]. Alberici et al. [141] has presented an application for phenol analysis from water, namely flow injection coupled with MIMS with on-line derivatisation.

## 1.6 Aims of this work

The aims of this work were:

- to develop purge-and-membrane inlet mass spectrometry

- to develop the device and methods for VOC-analysis in aqueous and solid samples and to evaluate the method against the traditional methods, mainly static headspace and purge-and-trap gas chromatography-mass spectrometry

- to develop simple and rapid membrane inlet mass spectrometric methods for analysis of volatile organic compounds, especially of terpenes and sulphur compounds in water samples

- to develop a membrane inlet mass spectrometric method for phenolic compounds in water

# 2. Experimental

## 2.1 Membrane inlet mass spectrometry and purge-and-membrane mass spectrometry instrumentation

### 2.1.1 Membrane inlet mass spectrometry

The mass spectrometers used were a Balzers QMG 421C quadrupole mass spectrometer (mass range 1 to 500 amu) equipped with an open cross-beam electron impact (70 eV) ion source and a Balzers Omnistar quadrupole mass spectrometer (mass range 1 to 300 amu) equipped with a closed electron impact ion source (used only in Appendix II to measure linearity and detection limits). Custom-made membrane inlets utilising a sheet membrane, built at VTT Chemical Technology [3], were used in both mass instruments. The temperature of the membrane inlet in both mass spectrometers was typically 70°C. The material of the sheet membrane was polydimethylsiloxane with dimensions: contact area 28 $mm^2$ for QMG 421C and 10 $mm^2$ for Omnistar and thickness 25 μm and 100 μm for PAM and MIMS, respectively. Most of the testing was performed using the selected ion-monitoring mode (SIM). In the analysis of the authentic soil samples the scanning mode was also used, the mass range measured being 46 to 200 amu. During operation of the system a water stream was continuously supplied to the membrane inlet via a peristaltic pump, typically at a flow rate of 10 ml/min and aliquots of sample solution (20–50 ml) were injected into this stream. The water stream was heated to 70°C before the membrane inlet using a heat exchanger, which itself was heated to 70°C with a circulating water bath.

### 2.1.2 Purge-and-membrane (PAM) devices

The preliminary PAM-devices for water and soil samples were simple and they are presented in details in Appendix I. The vial used for the water samples was modified from the commercially available 20 -ml purge vial. A water sample (5 ml) was purged at room temperature with nitrogen at 60 ml $min^{-1}$. The nitrogen stream containing the purged analytes was directed through a sheet membrane inlet. The purge vessel used for soil samples was a standard 20 -ml headspace vial. Glass beads with diameter of 4 mm were added to the bottom of the vial.

Soil sample (5 g) was weighed onto the top of the bead layer and the vial was sealed with a septum. The vial was heated to 80°C in a water bath. The soil sample was purged with nitrogen at 100 ml $min^{-1}$. The nitrogen flow was directed to the bottom of the vial with a stainless steel needle, and the purged analytes were directed through the membrane module.

The first PAM-device (PAM-1) is introduced in detail in Appendix II in both standby and sampling modes of operation. A schematic diagram of PAM-1 is presented in Figure 2.1. The main parts of the device are a membrane inlet mass spectrometer, a convection oven with adjustable temperature up to 300°C, a six-port valve and a custom-made gas flow control unit for purge gas. The gas flow control unit was built using standard Swagelok® parts, a mechanical HP gas chromatograph flow controller, S-series standard needle valves, a Bürkert 127 3-way on/off valve and 1/8" (3.18 mm) or 1/16" (1.59 mm) copper or nickel tubing. All gas lines in contact with the gas stream containing VOCs were 1/16" (1.59 mm) nickel tubing and they were heated to 150°C in order to minimise contamination. The sample vessels were made by cutting off the bottoms of two commercial 10 -ml headspace vials and connecting the truncated vials together at the cut ends. A glass sinter for supporting the sample was mounted on the bottom of the vessel during the manufacturing process.

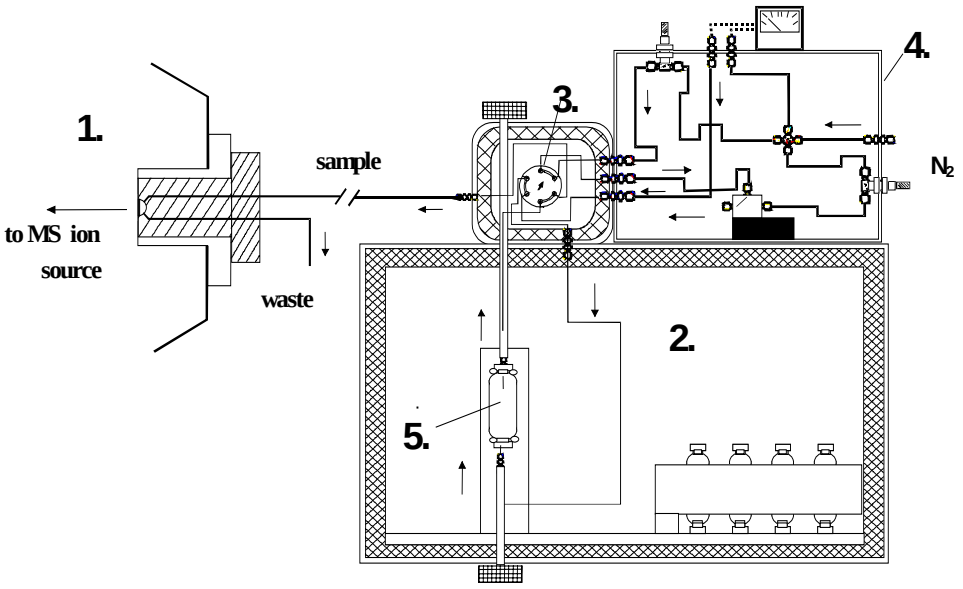



*Figure 2.1. A schematic picture of the PAM-1 showing the sampling mode of operation.*

*Arrows indicate the direction of gas flow.*

*1. Membrane inlet mass spectrometer*

*2. Convection oven*

*3. Six-port valve*

*4. Gas flow control unit for purge gas*

*5. Sample vessel*

A schematic diagram of the second semi-automatic purge-and-membrane mass spectrometric apparatus (PAM-2) [IV] is presented in Figure 2.2 in both standby and sampling modes of operation. The main parts of the device are a membrane inlet mass spectrometer, an oven with adjustable temperature up to 200°C, a four-port valve and a mass flow controller. All gas lines in contact with the gas stream containing VOCs were 1/16" (1.59 mm O.D.) EFNi tubing and they were heated to 150°C in order to minimise contamination. A glass sinter for supporting the sample was mounted on the bottom of the vessel during the manufacturing process. The sample was purged with synthetic air at 100 ml $min^{-1}$. The airflow was directed to the bottom of the vial through the septum with a stainless steel needle and the purged analytes were passed over the custom-built membrane inlet to the ion source of a mass spectrometer.

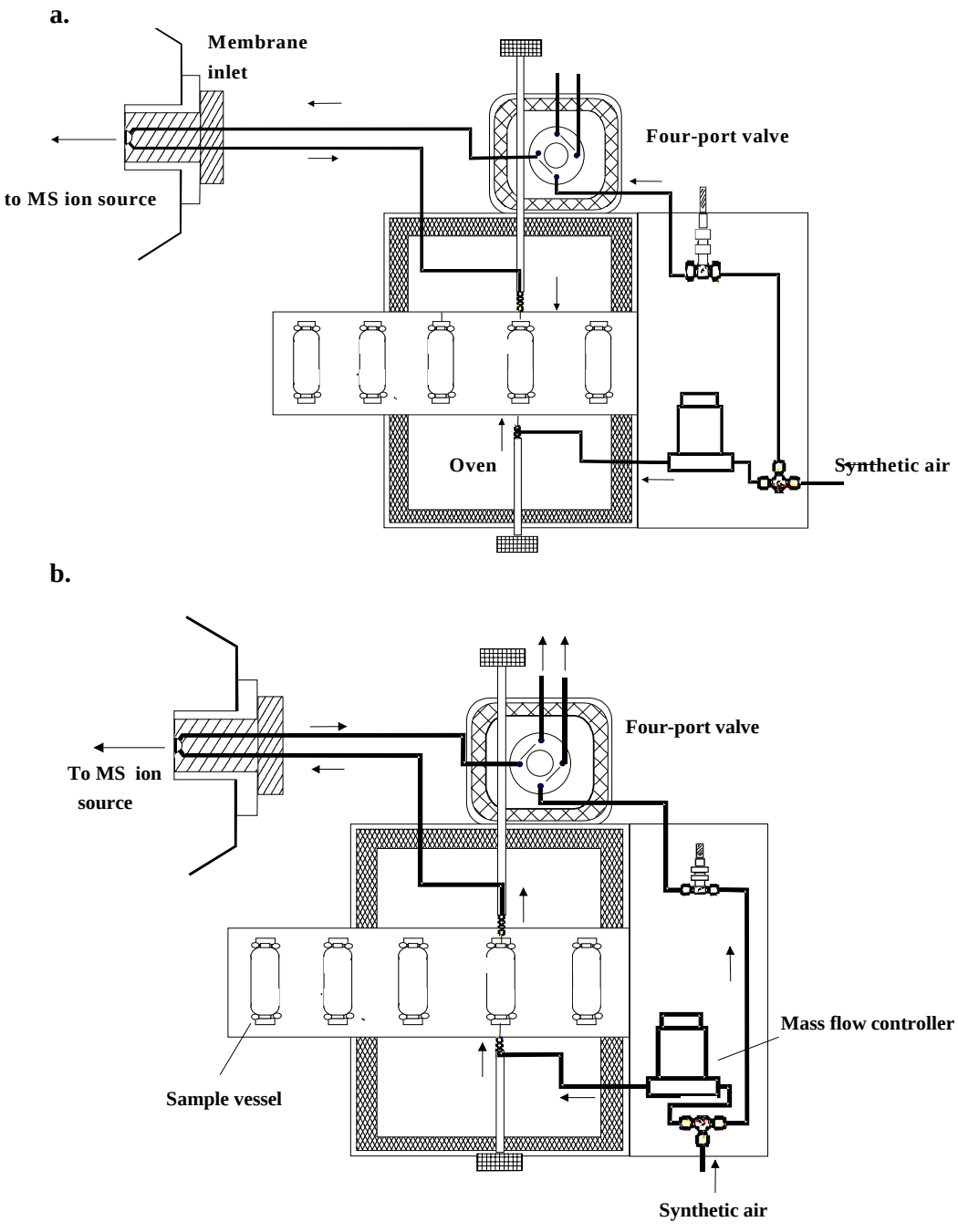



*Figure 2.2. A schematic pictures of the PAM-sampler (PAM-2) showing (a) the stand-by mode of operation and (b) the sampling mode of operation. Arrows indicate the direction of gas flow.*

Identification and quantitation of different compounds in water samples were performed using a calculation program (Solver) designed at VTT Chemical Technology [49]. This calculation program uses a modified algorithm of the general deconvolution method, which assumes that the intensity of any mass-to-charge ratio (m/z) is a linear function of the concentration of the chemical compounds which contribute to that particular m/z.

## 2.2 Chromatography

### 2.2.1 Static headspace gas chromatography

The static headspace system used in this experiment was a gas chromatograph equipped with two FIDs and a headspace sampler. Two columns were used, an SPB-1 (30m x 0.32mm x 1.0 µm) and a DB-1701 (30m x 0.32mm x 1.0 µm). The temperature program used was optimised for the separation of terpenes and it was 45°C, 5 min $\xrightarrow{10°C/\text{min}}$ 210°C, 10 min. The temperatures of the injector and detectors were 220°C and 250°C, respectively. In addition, the temperatures of sample vials and of the transferline between the headspace autosampler and the GC were 80°C and 120°C, respectively.

### 2.2.2 Purge-and-trap gas chromatography-mass spectrometry

The purge-and-trap gas chromatograph-mass spectrometer consisted of an LSC 3000 purge-and-trap sampler, an HP 5890 Series II gas chromatograph equipped with a DB-1 capillary column, 30 m x 0.32 mm id, film thickness 1.0 µm and a JMS-AX505WA mass spectrometer with electron impact ionisation at 70 eV. The conditions of the purge-and-trap sampler were: sample temperature 200°C, purge time 6 min, dry purge time 2 min, desorption temperature 225°C (trapping temperature 25°C), desorption time 4 minutes and cold trap temperature -120°C. Helium was used as a purge gas with a flow rate of 40 ml $min^{-1}$. The GC temperature program was: 30°C (5 min) to 110°C (20°C $min^{-1}$) and then to 300°C (10°C $min^{-1}$), held for 5 min. The carrier gas was helium. The scan range m/z was 29–400 (1.5 sec/scan).

### 2.2.3 Gas chromatograph with electrolytic conductivity detector

A gas chromatograph (HP 5890 Series II) equipped with ELCD (ELCD 4420), and a DB-624 column (30m x 0.53mm x 3.0 μm) was used. The temperature program used was: 40°C, 3 min, $\xrightarrow{10°C/min}$ 210°C. The temperatures of the injector and of the detector were 250°C and 930°C, respectively.

### 2.2.4 Portable gas chromatograph

The portable gas chromatograph used in the field tests was an HNU 311 GC equipped with a PID (10.2 eV source). Manual injection of headspace air was used, and the temperature of the injector and detector was 100°C. Isothermal analysis was used, with an oven temperature of 70°C. The column used was a Wcot Ultimetal CP sil 5 CB steel column with dimensions: 25 m, 0.53 mm ID and with a stationary phase thickness of 5.0 μm.

### 2.2.5 High performance liquid chromatography

Liquid chromatographic experiments were carried out using a high performance liquid chromatograph (HP 1090) in combination with an autoinjector, an autosampler and a diode array detector. A reversed phase analytical column (Hypersil 100 mm x 2.1 mm i.d., 5μm) with a linear gradient elution (10% methanol/acidic water $\xrightarrow{10\,min}$ 100% methanol, flowrate 0.4 ml/min) was used to separate compounds and a diode array detector (wavelength 225 nm) was used for detection.

## 2.3 Chemicals, samples and sample pretreatment

All chemicals used in this work were the purest available and were obtained from well known deliverers. Volatile organic compounds [I–IV], volatile organic sulphur compounds [V], terpenes [VI] and phenolic compounds [VII] are presented in detail in connection with each application. All calibration standards were made in methanol and diluted with deionised water or methanol. The soils used in testing were sand, commercial garden soil and peat. The water and organic content of the soils were determined by drying samples at 102°C and

thereafter burning off the organic compounds at 550°C. The authentic water and soil samples used in testing were obtained from customers of VTT Chemical Technology. The moisture contents of the soil samples were not measured. The acetylation of phenolic compounds before the MIMS-analysis is presented in Appendix VII. The preparation of vapour fortification standards and ageing of soil samples are described in connection with the second PAM-sampler [IV]. The pharmaceutical products used in testing [III] were commercially available drugs and the preparation of standards are described in detail in Appendix III.

# 3. Results and discussion

## 3.1 Development of purge-and-membrane mass spectrometry for the analysis of volatile organic compounds in solid samples

### 3.1.1 Development of purge-and-membrane samplers

The preliminary tests were carried using the experimental set-up presented in Appendix I. The purge vessel used for soil samples was a disposable 20 -ml headspace vial, which can also be used for sampling. Glass beads were put on the bottom of the vial and soil sample (5g) was weighed on top of the beads. The flow of nitrogen was directed from the bottom of the vial through the beads in order to disperse the flow through the whole sample. Heating of the soil was used to induce the desorption of VOCs from soil samples. As an example Figure 3.1 shows the analysis of VOCs in an authentic soil sample [I]. The peak shapes of toluene and xylenes differ from that of fluorotoluene, because they had been adsorbed more tightly in soil than fluorotoluene, which was added to the samples just before the analysis.

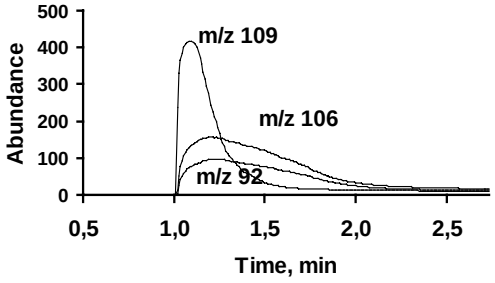



*Figure 3.1. Analysis of toluene (m/z 92) and xylenes (m/z 106) in a soil sample by PAM-MS with fluorotoluene (m/z 109) as internal standard.*

The first PAM-MS instrument (PAM-1) is presented in detail in Appendix II and a schematic picture is presented in Figure 2.1 in the sampling mode. The advanced second semi-automatic PAM-MS-instrument (PAM-2) is presented in Figure 2.2 both in the sampling and stand-by mode [IV]. This PAM-2-instrument was developed on the basis of the PAM-1-device, oven size was optimised and all the lines were made as short as possible. In the PAM-1-version the

sampling occurred through a six-port valve. In order to minimise contamination in the new instrument the six-port valve was replaced with a four-port valve and sampling did not occur through the valve as in the first version. All the lines of the PAM-2-device were made of electro-formed nickel (EFNi) tubing, also to minimise possible memory effects. The sample holder has places for five samples in order to allow pre-heating of the following samples during analysis of the previous one. As can be seen from Figures 2.1 and 2.2 the PAM-2-device is simpler to build and use than the PAM-1-device. In addition, it is smaller and easily portable.

The measurement procedure with the PAM-device starts by pre-heating the sample in the oven in the sample holder. After a selected pre-heating time, the four-port valve is switched to the sampling position and finally the sampling lines with needles are manually punctured through the sample vessel septa. This last step directs the flow of purge gas through the sample, desorption of VOCs occurs and ion chromatograms or mass spectra for VOCs can be measured with the mass spectrometer. In the stand-by mode a backflush of purge gas flows through all the gas lines in contact with VOCs and the membrane inlet in order to prevent contamination and to provide a constant background for the mass spectrometer.

### 3.1.2 Effects of purge-and-membrane parameters

#### 3.1.2.1 Effects of pre-heating temperature and time [II]

The effects of the pre-heating temperature and pre-heating time on desorption times and desorption peak areas were studied with the PAM-1-device using a selected set of compounds and garden soil as a matrix. The effects of the pre-heating temperature on the desorption times of the selected compounds are presented in Table 3.1 and as an example the effect of pre-heating temperature on the recovery curve of toluene measured from garden soil at various pre-heating temperatures is presented in Figure 3.2. The yield curves of toluene provide a clear visual demonstration of the effects of increasing pre-heating temperature on desorption times, i.e. desorption times decreased considerably when the pre-heating temperature was increased.

*Table 3.1. Effects of pre-heating temperatures on desorption times of a selected set of compounds (pre-heating time 20 min).*

| | Temperature, °C / Desorption time, s | | | |
|---|---|---|---|---|
| Compound | 50 | 65 | 80 | 95 |
| Benzene | 34 | 22 | 16 | 11 |
| Toluene | 51 | 33 | 22 | 12 |
| 1,2,4,5-Tetramethylbenzene | nm | 227 | 175 | 154 |
| 1,2-Dichloroethene | 34 | 22 | 13 | 7 |
| Trichloroethene | 41 | 26 | 14 | 8 |

nm not measured

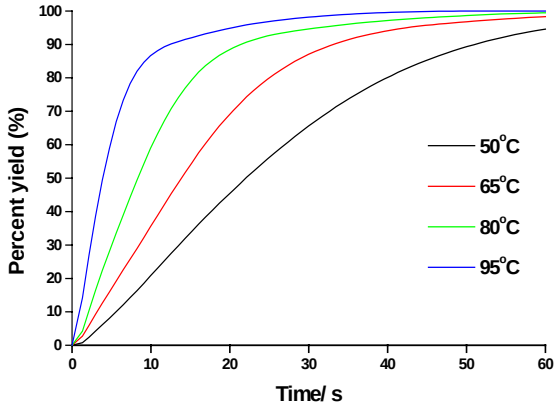



*Figure 3.2. The effect of pre-heating temperature on desorption time of toluene from the garden soil.*

It was observed that desorption peak areas decreased as the pre-heating temperature increased, and the peak height of the desorption peaks increased slightly as the pre-heating temperature increased. Higher desorption peaks are observed at higher pre-heating temperature, because the amount of VOCs in the headspace of the sample vessels increases as a function of temperature due to the increased vapour pressures. However, the desorption peak areas decrease because at higher pre-heating temperatures a smaller portion of VOCs is sampled due to rapid desorption times and due to the fact that only a small part of the VOCs in the purge gas stream is sampled via the membrane inlet. On the basis of the results presented a pre-heating temperature of 80 °C was selected for use in further studies of soil samples [II].

The effect of pre-heating temperature (30–70ºC) on desorption efficiency was also studied for VOC-analysis in spiked prepurged pharmaceutical material containing ibuprofen. The spectra recorded at higher temperatures than 50°C showed ions of ibuprofen due to its vaporisation, which caused a strong background and led to decreased selectivity in the analysis of VOCs. Therefore, the maximum temperature of the sample must always be below that which produces appreciable vapour pressure of the drug substance or excipients in a medical product or other solid samples. For this reason a pre-heating temperature of 40°C was used for pharmaceuticals in all further experiments [III].

Different pre-heating times, 0, 5, 10, 15, 20, 30 and 40 minutes were also tested, but no significant differences in desorption times or desorption peak areas were observed after five minutes preheating time, a result which is in good agreement with our earlier static headspace gas chromatographic results [142]. A pre-heating time of at least 10 minutes was used in subsequent studies. For pharmaceuticals a pre-heating time of 20 minutes was observed to decrease slightly the purge times needed for complete purging of VOCs from the samples.

#### 3.1.2.2 Effects of purge gas [II]

The effects of purge gas on the desorption peak areas and on the desorption times were studied using helium, carbon dioxide, nitrogen or synthetic air as purge gas. Garden soil was used in these experiments and selected compounds were spiked to a concentration of about 2 mg/kg two days before analysis. The effects of various purge gases on the desorption peak areas are presented in Table 3.2. It can be seen that the differences in the desorption peak areas between the various purge gases are not very great for any of the compounds used in testing. From Table 3.2 it can be also observed that the relative standard deviations in the desorption peak area determinations are generally of the same order of magnitude for all the purge gases. In addition, it was observed that the desorption times were the same for all the purge gases. On the basis of these results nitrogen and synthetic air were selected as purge gases for further studies. The low price of these gases also influenced this selection, and purified air is relatively easy to make using mobile air purifiers, a fact which is important when a purge gas is selected for on-site applications of the PAM-MS method.

*Table 3.2. Effect of purge gas on peak areas (four or five replicate measurements) of a selected set of compounds. Garden soil was used in testing.*

| Gas | Compound/ Peak area | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | MTBE | | 1,1,1-Trichloroethane | | o-Xylene | | Tetrachloroethene | |
| | Mean | RSD % | Mean | RSD % | Mean | RSD % | Mean | RSD % |
| Synthetic air | 4500 | 4.6 | 3900 | 4.1 | 31000 | 3.1 | 10000 | 1.9 |
| Helium | 6200 | 9.4 | 3700 | 9.3 | 40000 | 2.2 | 13000 | 5.6 |
| Carbon dioxide | 4200 | 9.4 | 3400 | 12.3 | 34000 | 3.6 | 12000 | 5.6 |
| Nitrogen | 5900 | 3.1 | 3900 | 2.5 | 38000 | 2.5 | 13000 | 4.2 |

RSD Relative standard deviations

### 3.1.3 Effects of soil conditions

#### 3.1.3.1 Effects of methanol concentration of the samples [II]

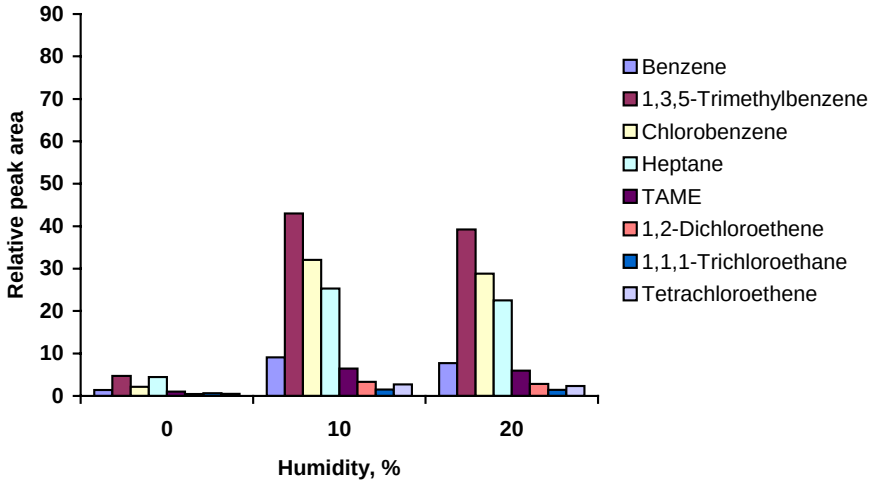
The effects of methanol concentration on desorption peak areas were studied because the standard mixtures for spiking and calibration were made in methanol. This was done by spiking garden soil samples (5 g) with selected VOCs (MTBE, 1,1,1-trichloroethane, o-xylene, tetrachloroethene and m-fluorotoluene, each at a concentration of 0.2 mg/kg) and changing the amount of methanol in the samples. The desorption peak areas of all the analytes decreased considerably as the methanol content increased from 20 µl to either 110 or 210 µl, the decrease being typically at least 50%. The reason could be that the solubility of the analysed compounds in methanol is good and therefore the desorption from methanol is more difficult than from soil. In order to minimise the effect of methanol its amount in further analyses was reduced to 5 or 10 µl/sample. Water or water/methanol is often added to solid samples in the analysis of VOCs by the headspace method in order to simplify preparation of a standard sample; the preparation of headspace standard samples in water is easier than in solid material [74, 79]. However, in our experiments addition of water or water/methanol to the pharmaceutical product resulted in strong foaming due to increased surface tension of the liquid caused by the excipients in the pharmaceutical material. Despite addition of antifoaming agent to the sample, it was necessary to decrease the purge flow rate (from 100 to 40 ml $min^{-1}$), which led to significantly increased analysis times. It was found that the analysis of residual solvents directly from dry solid material is faster and easier than after

addition of water or water/methanol to the sample. Furthermore, the mass spectra of the samples including methanol/water showed significantly increased background due to saturation of the ion source with methanol. In order to avoid the increased background in mass spectra the amount of organic solvent in the sample should not exceed 10 µl.

#### 3.1.3.2 Effects of soil type and moisture content of the sample on sorption

Some preliminary tests were carried out using the first PAM-device (PAM-1) [II] but the second device (PAM-2) was used for the thorough tests [IV]. The effects of soil type and moisture on desorption peak areas of selected compounds and on their desorption times were studied using garden soil, sand and a mixture of sand and garden soil (50/50 w-%). Three replicates of each analysis were made. The moisture contents of samples were 0, 10 and 20%. A selected set of test compounds was used, e.g. benzene, toluene, o-xylene, 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, chlorobenzene, 1,2-dichloro-ethene, trichloroethene, 1,1,1-trichloroethane, tetrachloroethene, heptane, MTBE and TAME. These compounds represent typical contaminants in polluted soil samples. Figure 3.3 shows the desorption peak areas from two different soil types at three different moisture contents.

a.




b.

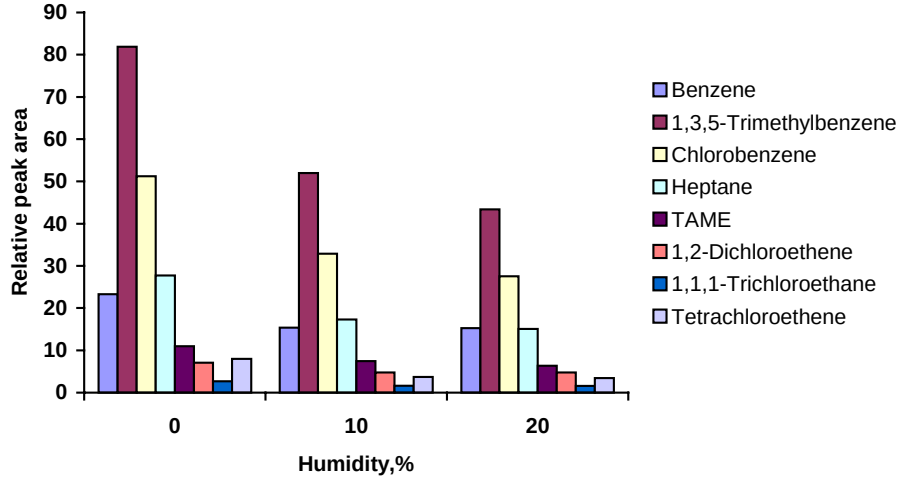



*Figure 3.3. The effect of moisture on peak areas for commercial garden soil (3.3.a) and sand (3.3.b).*

The highest peak areas were obtained from dry sand, especially for trimethyl-, tetramethyl- and chlorobenzenes (Fig. 3.3.b). In the case of garden soil samples the highest peaks were obtained from the sample with 10% moisture. For both soil types only minor differences in desorption peak areas were observed between 10 and 20% moisture. The greatest difference in peak areas was between dry sand and dry garden soil. When analysing typical authentic samples the results of the PAM method can be considered to be independent of soil type for practical purposes, because the authentic samples are never dry. The average moisture content of authentic soil samples (54 samples sent to VTT Chemical Technology for different analysis) was 20%, with variation from 54% to 4%, and more than 80% of samples had a moisture content higher than 10%. Furthermore if authentic samples are dry (moisture less than 5%), it can be assumed that most of the VOCs have evaporated with water.

*Table 3.3. The desorption times, defined as the time between 0 and 90% of the desorption curve, of selected compounds from different soil types and moisture levels. The errors in the desorption times are estimated to be ±15%.*

| | | Soil type/Desorption time, s | | |
|---|---|---|---|---|
| Compound | Moisture, % | Sand | Sand/Garden soil (1:1) | Garden soil |
| Benzene | 0 | 20 | 36 | 43 |
| | 10 | 17 | 24 | 27 |
| | 20 | 19 | 25 | 26 |
| o-Xylene | 0 | 23 | 70 | 84 |
| | 10 | 22 | 57 | 77 |
| | 20 | 19 | 68 | 67 |
| 1,3,5-Trimethylbenzene | 0 | 21 | 83 | 98 |
| | 10 | 20 | 68 | 93 |
| | 20 | 18 | 70 | 83 |
| Tetrachloroethene | 0 | 22 | 44 | 59 |
| | 10 | 21 | 39 | 49 |
| | 20 | 17 | 34 | 44 |
| MTBE | 0 | 24 | 42 | 44 |
| | 10 | 25 | 26 | 27 |
| | 20 | 27 | 24 | 23 |

As an example of the effect of moisture on the desorption times, typical results are presented in Table 3.3. The moisture content of a sample had no significant effect on the desorption times in sand samples, but in the case of garden soil the longest desorption times were recorded from dry samples. Desorption times of 1,2,4,5-tetramethylbenzene and trichloroethene from dry garden soil were so long that they could not be measured. A general trend was that desorption times increased when the garden soil content, i.e. the content of organic matter in the sample increased. In addition, desorption times normally decreased when the water content of the sample increased. Desorption times of benzene, o-xylene and MTBE for sand/garden soil mixtures and garden soil at 20% moisture content were the same. The reason for the difference between our earlier results [II, III] and the results presented here [IV] are not clearly understood, but the difference might be due to the different spiking procedure. In the earlier study the volume of the spiking methanol solution was 100 µl, instead of the 10 µl volume used in this study.

In conclusion, both soil type and moisture content have an effect on peak areas. Highest peak areas were obtained from dry sand and lowest areas from dry garden soil. In addition, moisture content had an inversely proportional effect on the desorption times in the case of garden soil. An increasing amount of garden soil in the sample lengthened desorption times in most cases with the sole exception of MTBE.

#### 3.1.3.3 Linearity, repeatability and detection limits

The detection limits obtained in the preliminary tests varied from 1–20 µg/kg, indicating the high sensitivity of the method. Relative standard deviations were calculated using six replicates and they were lower than 14% with internal standard and varied from 19–58% without the internal standard. The linearity of the method was tested using seven different concentrations between 0.1 and 100 mg/kg. Linearity was good, correlation coefficients being higher than 0.997 [I].

Detection limits for soil samples obtained with the first PAM-device (PAM-1) were of the same order of magnitude as in the preliminary measurements, linear dynamic ranges for selected compounds were wide, from 100 µg/kg to at least 1g/kg, and the repeatability was good (RSD varied from 2–12%) [II]. The detection limits, dynamic ranges and repeatability were also tested with pharma-

ceuticals. Detection limits varied from 0.05 mg/kg for benzene to 0.1 mg/kg for e.g. toluene and chloroform. Dynamic ranges were 0.3–300 mg/kg for all the measured compounds and relative standard deviations were less than 18% [III].

The linearity of the second PAM-device (PAM-2) was tested using eleven compounds listed in Table 3.4. Six concentrations of the compounds (0.5–50 mg/kg) in methanol were spiked to natural sand samples (moisture 17%) and analysed after two days of storing. Good linearity was obtained, with correlation coefficients varying from 0.990 for 1,2,4,5-tetramethylbenzene to 1.000 for 1,3,5-trimethylbenzene [IV]. Detection limits (S/N=3) were measured for the same compounds (1–200 µg/kg) from three different matrices, namely dry and wet Fluka sand (moisture 17%) and wet garden soil (moisture 17%). From Table 3.4 it can clearly be seen that larger amounts of moisture and organic matter in the samples increased the detection limits, possibly due to the higher capacity of soil to bind analyte when the organic matter or water content in samples increased. Measured detection limits were of the same order of magnitude as those obtained in the preliminary tests and with the first PAM-device.

*Table 3.4. The detection limits (S/N=3) of selected compounds measured from dry sand, moistened sand (moisture content 17%) and moistened commercial garden soil (moisture content 17%). Detection limits were measured using the SIM-technique and estimated using the desorption peak heights.*

| Compound | Ion m/z | Soil type/ Detection limit, µg/kg | | |
|---|---|---|---|---|
| | | Dry sand | Moist. sand | Moist. garden soil |
| Benzene | 78 | 5 | 10 | 15 |
| Toluene | 92 | 5 | 10 | 30 |
| o-Xylene | 106 | 5 | 8 | 50 |
| 1,3,5-Trimethylbenzene | 105 | 2 | 4 | 40 |
| 1,2,4,5-Tetramethylbenzene | 119 | 2 | 4 | 40 |
| 1,2-Dichloroethene | 61 | 10 | 50 | 50 |
| Trichloroethene | 97 | 20 | 70 | 70 |
| 1,1,1-Trichloroethane | 130 | 50 | 100 | 150 |
| Tetrachloroethene | 166 | 10 | 40 | 80 |
| MTBE | 73 | 50 | 100 | 100 |
| TAME | 73 | 40 | 80 | 90 |

Repeatability of the PAM-method was tested using (PAM-2) and spiked garden soil samples. Four compounds, namely MTBE, 1,1,1-trichloroethane, o-xylene and tetrachloroethene were used in spiking. Ten replicates were measured and the relative standard deviation varied from 4.2% for o-xylene to 7.7% for 1,1,1-trichloroethane. The relative standard deviations calculated using *m*-fluorotoluene as an internal standard varied from 2.5% for tetrachloroethene to 3.4% for 1,1,1-trichloroethane. According to these results the repeatability of the PAM-2-method is very good. These results, like those obtained with the PAM-1-equipment, are better than those obtained with the preliminary PAM-method. This is due to the fact that the constructed PAM-apparatus makes working simpler and more reliable [IV]. The better PAM-sampling device gave better repeatability but it had no significant effect on detection limits and linearity.

#### 3.1.3.4 Ageing the soil samples

In order to define the effect of ageing on the desorption of the compounds from different soils, spiked samples were stored for different times before analysis. Another aim of this study was to define the length of time for which the soil samples can be stored before analysis. Two types of samples namely dry Fluka sand and moistened garden soil (moisture 17%), were used in these experiments. The same compounds as in the linearity tests (Table 3.4) were used in spiking. The storage times before analysis were one day, two weeks, and one, two, four and six months. Both peak areas and the desorption times for six samples of each storing time were measured. *m*-Fluorotoluene was used as an internal standard, added prior to analysis. For the data treatment the analyte peak areas/internal standard peak area of the samples stored for one day were given a value of unity and all the other desorption peak areas were normalised relative to these values. Figure 3.4 summarises the results, showing the mean of the normalised peak area value of each of the compounds and the corresponding mean standard deviation values.

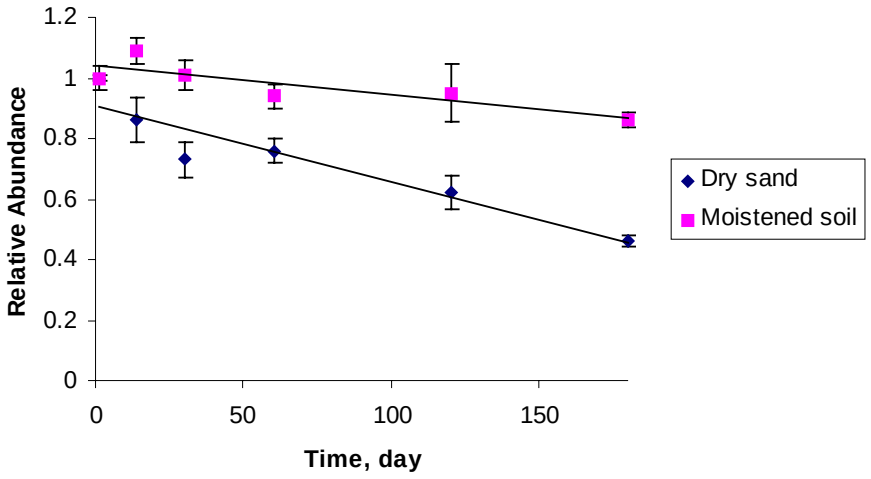



*Figure 3.4. The effect of ageing on peak area using the dry sand and moistened garden soil. The averages and standard deviations of all compounds are presented.*

The storage time of up to two weeks had no significant effect on peak areas in garden soil, but in the case of dry sand the peak areas decreased by 14% on average (Figure 3.4). In the case of garden soil only a rather small decrease of peak areas was observed over six months of storage (on average 14%), but in sand samples the final area was on average only 46% of the original. Especially for tri- and tetrachloroethene the decrease was significant, since the desorption peak areas decreased from 1 to 0.07 and 0.17, respectively. According to our studies, storage had no effect on the desorption times in sand samples but in garden soil samples after six months of storage the desorption times for substituted benzenes were about twice as long as in the beginning. The results obtained show that soil samples can be stored in closed bottles for two weeks before analysis without very significant loss of even the most volatile compounds. The difference in results between soil type may originate from either soil type or moisture. The garden soil contains more organic matter and therefore it can possibly adsorb more volatile components. On the other hand it has been reported that it can be difficult to desorb volatile compounds from dry soil samples [61]. According to the results of Kolb et al. [61] the time of adsorption has an effect on the recovery of desorption; the recovery of trichloroethene after three hours of adsorption was 91%, whereas after two days of adsorption the recovery was only 27%.

### 3.1.4 Comparison of PAM method with traditional analytical methods

#### 3.1.4.1 Analysis of VOCs using vapour fortification soil standards

The preparation of homogenous and reliable soil standards for VOC-analysis is very difficult because of the high volatility of the compounds to be analysed. Therefore the vapour fortification method was used to make identical standard soils for comparison of different analytical methods [143]. The preparation of vapour fortification standards is not trouble-free. Hewitt [143] used tetraglyme to dilute standard compounds to the desired concentration before making soil standards. We noticed in some cases that empty glass vials also adsorbed almost the same amount as the soil samples. Instead of tetraglyme we used methanol as a diluting agent and in this case practically no adsorption on empty vials was observed. Two examples of the results of these tests are presented in Table 3.5. One sample was contaminated with a mixture of compounds presented in Table 3.5 and the other was contaminated with petrol. The PAM-MS analysis was performed using selective ion monitoring (SIM) technique. The results are means of five replicate samples, and two HSGC (Lab1) analyses were performed from each bottle. The samples analysed by Lab 2 with the HSGC and portable HSGC were taken from the same bottles. All the GC results agreed well with each other but the PAM -results were about 3- or 4-fold for the first sample. It has also been noticed earlier [69, 143] that differences of this magnitude in the analysis of soil samples may occur when samples are analysed using different techniques. However, the analytical results of PAM-MS and HSGC of soil samples contaminated with petrol by vapour fortification methods agree well with each other. It is worthy of note that TAME and MTBE have very similar mass spectra, and therefore cannot be analysed separately with PAM-MS. The result for xylenes also includes all xylene isomers and ethylbenzene, and the results for tri- and tetramethylbenzene are the sums of all isomers in the PAM-MS analysis. For HSGC-analysis only single isomers of tri- and tetramethylbenzenes were chosen, namely 1,2,4-trimethylbenzene and 1,2,3,5-tetramethylbenzene.

*Table 3.5. The results of soil samples prepared by the vapour fortification method.*

| Compound | PAM-MS | | HSGC Lab 1 | | Portable HSGC | | HSGC Lab 2 | |
|---|---|---|---|---|---|---|---|---|
| | Content mg/kg | RSD (%) | Content mg/kg | RSD (%) | Content mg/kg | RSD (%) | Content mg/kg | RSD (%) |
| Benzene | 44 | 12 | 16 | 12 | 15 | 12 | 15 | 16 |
| Toluene | 47 | 10 | 29 | 9 | 36 | 8 | 29 | 13 |
| MTBE | 63 | 12 | 17 | 12 | 15 | 10 | 15 | 13 |
| Heptane | 42 | 16 | 12 | 9 | nm | nm | nm | nm |
| Trichloroethene | 45 | 12 | 25 | 9 | nm | nm | nm | nm |
| 1,2,3,5-Tetramethylbenzene | 103 | 9 | 45 | 9 | nm | nm | nm | nm |
| TVOC[a] | 343 | 8 | 144[b] | 9 | 137[c] | 8 | nm | nm |
| Petrol contaminated soil sample | | | | | | | | |
| Benzene | 23 | 4 | 19 | 14 | nm | nm | nm | nm |
| Toluene | 150 | 5 | 174 | 12 | nm | nm | nm | nm |
| Xylenes | 180[d] | 9 | 177 | 12 | nm | nm | nm | nm |
| Ethylbenzene | [d] | | 40 | 12 | nm | nm | nm | nm |
| Tetramethylbenzene | 2.7 | 22 | 4.2[e] | 6 | nm | nm | nm | nm |
| Trimethylbenzene | 128 | 2 | 49[f] | 9 | nm | nm | nm | nm |
| Aliphates | 102 | 6 | nm | nm | nm | nm | nm | nm |
| MTBE | 225[g] | 6 | 119 | 16 | nm | nm | nm | nm |
| TAME | [g] | | 39 | 14 | nm | nm | nm | nm |
| TVOC[a] | 812 | 5 | 1032[b] | 13 | nm | nm | nm | nm |

[a]TVOC (total volatile organic compounds) is the sum of identified compounds and unknown compounds. The amount of unknown compounds was estimated using toluene (Lab 1) or xylene (Lab 2). In PAM-MS TVOC is the sum of analysed compounds. TVOC of the petrol contaminated soil sample calculated equally from the results of HSGC Lab 1 is 622 mg/kg.

[b] Estimated with toluene

[c] Estimated with xylene

[d]The sum of xylenes and ethylbenzene. [e]Only 1,2,3,5-tetramethylbenzene. [f]Only 1,2,4-trimethylbenzene. [g]The sum of MTBE and TAME.

nm not measured

### 3.1.4.2 Analysis of authentic samples

Three authentic soil samples were analysed with the first PAM-MS device combined with the Solver calculation program [49], PAM-MS method with selected ion monitoring (SIM) and a headspace gas chromatographic (HSGC) method (Table 3.6). Samples 1 and 2 were clay and sample 3 was moist sand.

The results obtained with the three different methods were in relatively good agreement. The amount of toluene could not be determined reliably with the SIM method due to large amounts of xylenes and ethylbenzene, which have spectral overlap with toluene. Note also that the mass spectra of MTBE and TAME (*tert*-amyl methyl ether) are so similar that neither Solver nor SIM can quantitate them separately, but their total amount was in good agreement with the amount obtained with the HSGC method [II].

*Table 3.6. Quantitative results of some authentic soil samples.*

| | | Analysis method /content, mg/kg | | |
|---|---|---|---|---|
| Sample | Compound | Solver | SIM | HSGC |
| 1 | Toluene | 1.8 | nm | 2.8 |
| | Xylenes[1] | 19 | 17 | 10 |
| | MTBE | 43[2] | 31[2] | 31 |
| | TAME | [2] | [2] | <1 |
| 2 | Toluene | 1.0 | nm | 3.1 |
| | Xylenes[1] | 7.3 | 9.6 | 2.6 |
| | MTBE | 18[2] | 21[2] | 17 |
| 3 | Toluene | 1.3 | nm | 2.4 |
| | Xylenes[1] | 8.9 | 7.5 | 10 |

[1] Results are sums of xylenes and ethylbenzene

[2] Results are sums of MTBE and TAME

Some authentic pharmaceutical samples were analysed using the PAM-1-equipment [III]. Figure 3.5 shows the mass spectra measured by PAM-MS for two different pharmaceutical products containing ibuprofen from two different manufacturers. Since the membrane does not provide any separation, the mass spectra are mixtures of several VOCs. The spectra measured are different, indicating different manufacturing processes of the products. Without identifying individual VOCs in the sample, the shape of the spectrum can be used for the control or identification of the manufacturing process. The results show that PAM-MS/Solver can identify the main VOCs, but that P&T-GC/MS [III] better identifies VOCs with low concentrations (below 0.5 mg/kg).

The PAM-MS method combined with the Solver software was compared with a P&T-GC/MS method in identification of VOCs from two different pharmaceutical products. The following compounds could be identified using both methods: benzene, toluene, 2-pentene, chloroform and methylpentane. Concentrations of these compounds, determined with both methods, varied in the range of 0.1–0.7 mg/kg. In addition to the major compounds some other VOCs, such as cyclohexane, were identified by the P&T-GC/MS [III].

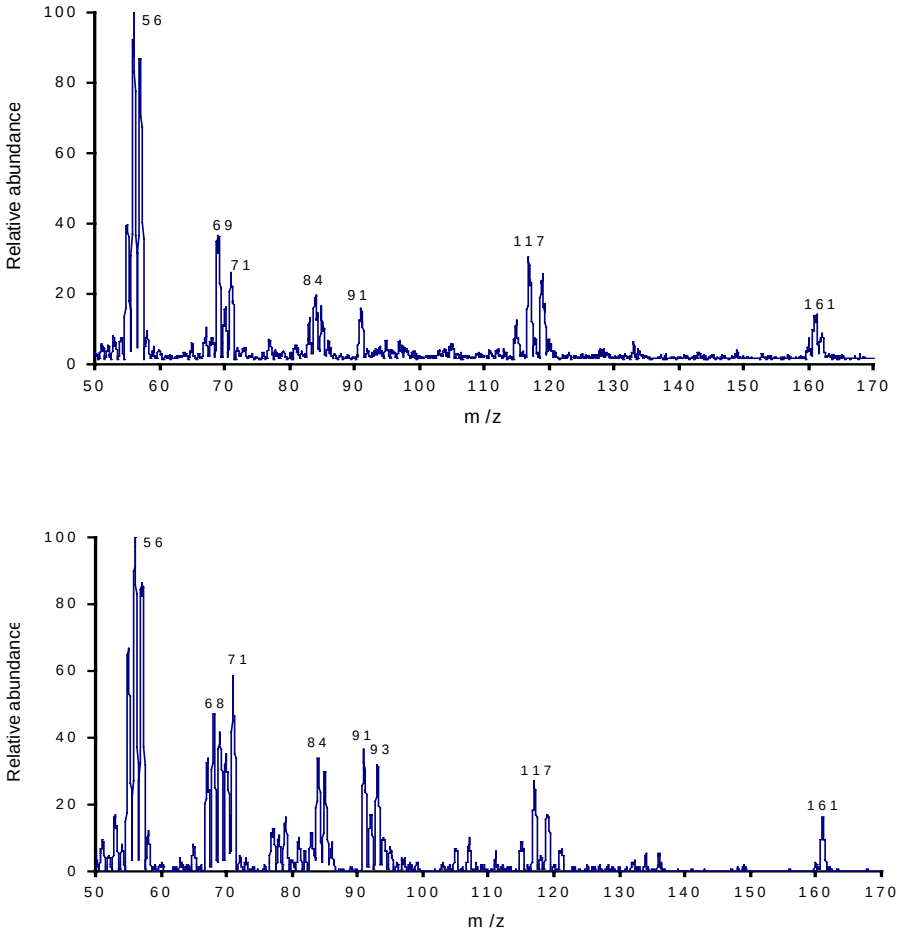
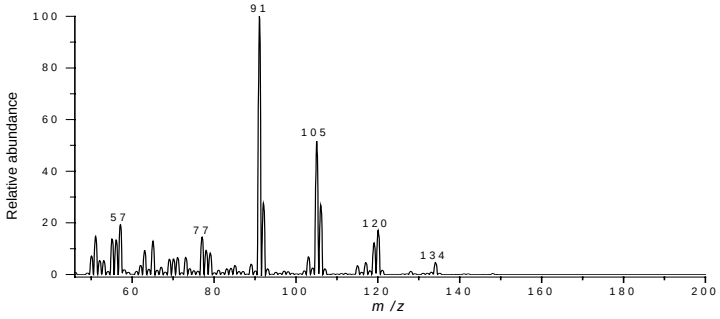


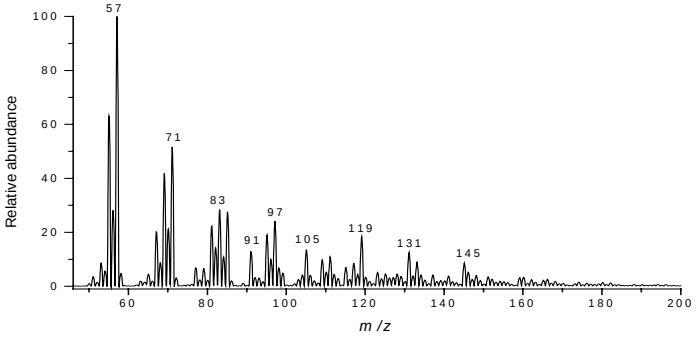

*Figure 3.5. Mass spectra of two different pharmaceutical products containing ibuprofen.*

Numerous authentic and spiked soil samples were also analysed with different techniques, namely the PAM-2-device with selected ion monitoring (SIM) and two headspace gas chromatographic (HSGC) methods [IV]. The samples analysed were typically contaminated by petrol or diesel oil. As an example the mass spectra of a soil sample spiked with petrol (3.6 a), a soil sample spiked with diesel fuel (3.6 b) and an authentic soil sample (3.6 c) are presented in Figure 3.6. It can be observed that the authentic sample is probably contaminated with both petrol and diesel fuel, because the characteristic ions m/z 91, 105 and 120 of the aromatics in petrol and the typical ions m/z 57, 71 and 83 of diesel components are present. Figure 3.6 demonstrates that the mass spectra of unknown samples can be used to aid identification of the source of contamination.

a)




b)




c)

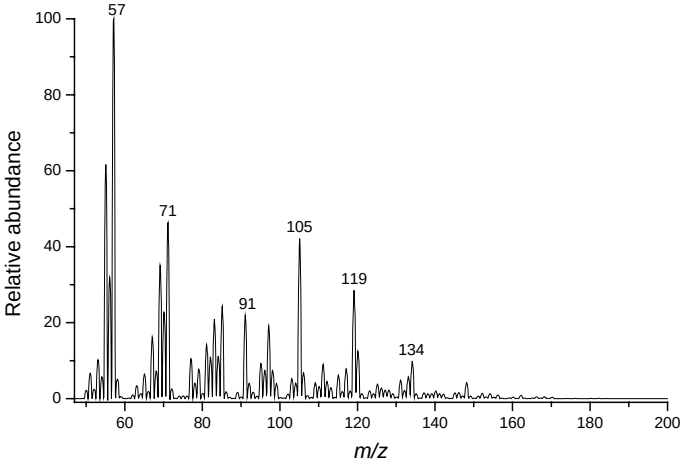



*Figure 3.6. A mass spectrum of (a) a petrol-spiked soil sample, (b) a diesel fuel-spiked soil sample, and (c) an authentic soil sample contaminated with both petrol and diesel fuel.*

As an example, quantitation results of two authentic soil samples are presented in Table 3.7. The results obtained with the three different methods are in relatively good agreement.

*Table 3.7. The analytical results of two authentic soil samples measured by PAM-MS and HSGC.*

| Compound | Sample/Content, mg/kg | | | | | |
|---|---|---|---|---|---|---|
| | Sample 1 | | | Sample 2 | | |
| | PAM-MS | HSGC Lab 1 | Portable HSGC | PAM-MS | HSGC Lab 1 | Portable HSGC |
| Benzene | 6.3 | 5.0 | 17 | nd | 0.1 | 1.0 |
| Toluene | 140 | 110 | > 140 | 6.8 | 7.0 | 19 |
| Xylenes | 680[a] | 610 | > 350 | 23[a] | 43 | 70 |
| Ethylbenzene | [a] | 130 | 110 | [a] | 5.8 | 16 |
| Tetramethylbenzene | 100 | 27[b] | nm | 9.2 | 6.1[b] | nm |
| Trimethylbenzene | 1000 | 280[c] | nm | 52 | 33[c] | nm |
| Aliphates | 400 | nm | nm | 26 | nm | nm |
| MTBE | 18 | 32 | 37 | nd | nd | nm |
| TVOC[f] | 2400 | 2900[d] | > 490[e] | 120 | 240[d] | 300[e] |

[a] The sum of xylenes and ethylbenzene. [b] Only 1,2,3,5-tetramethyl-benzene. [c] Only 1,2,4-trimethylbenzene.

[d] estimated with toluene. [e] Estimated with xylene.

[f] TVOC (total volatile organic compounds) is the sum of identified compounds and unknown compounds in the HSGC-analysis and the sum of identified compounds in the PAM-analysis. The amount of unknown compounds was estimated using toluene (Lab 1) or xylene (Lab 2).

nd= not detected

nm=not measured

As a summary of the vapour fortification samples (79) and authentic samples (35) analysed, Figure 3.7 shows the correlation between the results obtained with the PAM-MS method and the HSGC method of Lab 1 in logaritmic scale. The compounds analysed are mainly those presented in Table 3.5. The slope of the line is 0.900 and the coefficient of regression (r) is 0.848. In addition, Students t-test was used to compare the results obtained with PAM-MS and the HSGC methods. The t-value obtained from samples was lower than theoretical value (0.718 and 2.00, respectively, 2-sided test), which indicates that the results of the two methods have no significant differences at the 5% confidence level. The correlation between the results of two methods at lower concentration level (less

than 60 mg/kg) is not as good as at higher concentration level (Appendix IV, Figure 5), but the results are on the same order of magnitude. Some of the results are close to the detection limits of the HSGC- method, which cause inaccuracy to the results. The uncertainty of the measurement at low concetrations level is typically at least 50%. The evaporation of VOCs during the sample pretreatment in the HSGC-method has more effect on the results at low concentrations level. An additional reason for the deviation between the HSGC and the PAM-MS results may be the small amount (5 g) of sample used, because authentic soil samples are not necessarily very homogenous, and due to the volatile compounds to be analysed they cannot be homogenised very well.

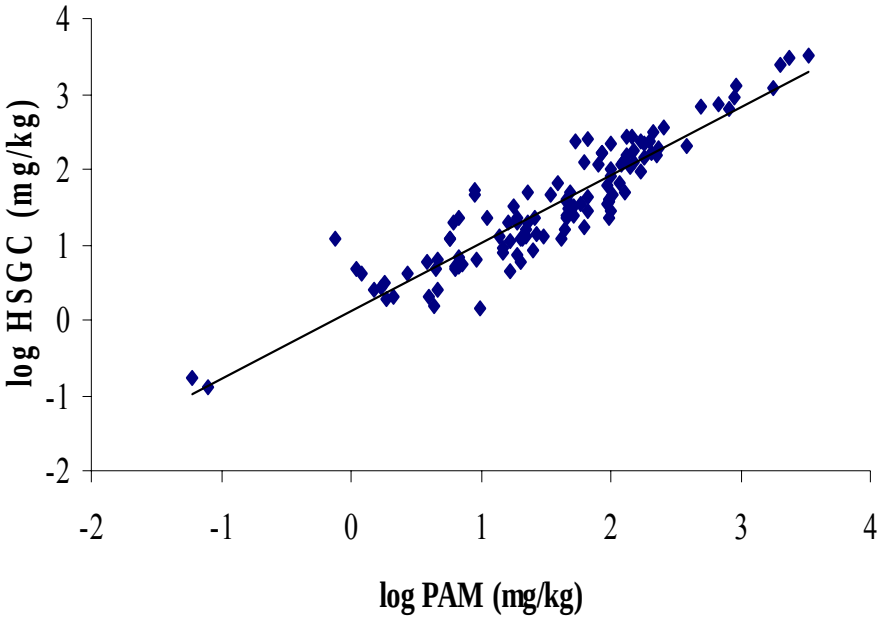



*Figure 3.7. The correlation of the results obtained by HSGC and PAM-MS. Both vapour fortification and authentic samples are included.*

## 3.2 Analysis of organic compounds in aqueous samples

### 3.2.1 Analysis of volatile organic compounds

The analysis of volatile organic compounds such as aromatic and chlorinated hydrocarbons and different solvents from water samples was the first experiment of our studies with MIMS [31, 43, 142]. The analyses of different sulphur compounds and terpenes were the next applications [V, VI]. The first measurements were carried out using hollow fibre membrane inlet, but the ease of use and lower detection limits obtained with the sheet membrane made this alternative preferable. The capillary membrane has also been used in gas chromatography-mass spectrometry [31]. The capillary inlet was installed in the column oven at the site of the capillary column and the carrier gas was used to purge volatiles from water. Volatile organic compounds in water samples were analysed mainly with MIMS-techniques but some tests were performed using the preliminary PAM- device (see Chapter 2.1.2). Different well known analytical methods have been used to confirm the results obtained with MIMS. The detection limits and linear dynamic ranges of different techniques are presented in Tables 3.8 and 3.9.

*Table 3.8. Detection limits and linear dynamic ranges of selected VOCs measured by different techniques.*

| Compound | MIMS/SIM | | P&T | | HSGC/FID | |
|---|---|---|---|---|---|---|
| | Detection limit, µg/l | LDR µg/l | Detection limit, µg/l | LDR µg/l | Detection limit, µg/l | LRD µg/l |
| Benzene | 0.1 | 0.1–1000 | 0.2 | 0.2–20 | 4 | 4–100000 |
| Toluene | 0.1 | 0.3–1000 | 0.2 | 0.2–15 | 3 | 3–380000 |
| Xylenes | 0.1 | 0.1–5000 | 0.2 | 0.2–15 | 4 | 4–100000 |
| Trichloroethene | 0.1 | 0.1–1000 | 0.2 | 0.2–20 | 8 | 8–100000 |
| 1,1,1-Trichloroethane | 0.6 | 0.6–5000 | 0.2 | 0.2–15 | 30 | 30–100000 |
| Trichloroethene | 0.1 | 0.1–1000 | 0.2 | 0.2–20 | 8 | 8–100000 |
| Carbon tetrachloride | 0.5 | 0.5–5000 | 0.2 | 0.2–20 | 40 | 40–100000 |
| | MIMS/SIM | | HSGC/ELCD | | HSGC/FID | |
| Ethanethiol | 0.1 | 0.1–1000 | 5 | 5–500 | 10 | 10–100000 |
| Dimethyl sulphide | 0.5 | 0.5–5000 | 5 | 5–500 | 10 | 10–100000 |
| Carbon disulphide | 0.1 | 0.1–1000 | 1 | 1–100 | nd | |
| Ethylmethyl sulphide | 0.5 | 0.5–5000 | 5 | 5–500 | 10 | 10–100000 |
| Thiophene | 0.5 | 0.5–5000 | 10 | 10–1000 | 10 | 10–100000 |
| Dimethyl disulphide | 0.5 | 0.5–5000 | 5 | 5–500 | 20 | 20–100000 |
| | MIMS/SIM | | - | | HSGC/FID | |
| α-Pinene | 0.2 | 0.2–300 | - | - | 2 | 2–300 |
| Camphene | 0.5 | nm | - | - | 2 | 2–300 |
| β-Pinene | 0.2 | nm | - | - | 3 | nm |
| Myrcene | 0.2 | 0.2–300 | - | - | 2 | 2–300 |
| Δ-3-carene | 0.5 | nm | - | - | 2 | nm |
| α-Terpinene | 0.5 | 0.5–300 | - | - | 2 | 2–300 |
| Limonene | 0.5 | 0.5–300 | - | - | 2 | 2–300 |
| Linalool | 0.5 | nm | - | - | 30 | nm |
| Geraniol | 2 | 2–300 | - | - | 100 | nm |
| Longifolene | 2 | 2–300 | - | - | 5 | 5–300 |
| Cedrene | 0.5 | nm | - | - | 5 | 5–300 |

nm=not measured, nd= not detected, SIM= selected ion monitoring, FID=flame ionisation detector, ELCD=electrolytic conductivity detector, - = terpenes have only been analysed with two analytical methods.

The detection limits of MIMS are well comparable with those obtained with the other methods. The linear dynamic ranges of compounds measured by the MIMS method are three or four orders of magnitude. Due to the limited capacities of the adsorbent and cryofocusing traps, the linear dynamic ranges for

P&T-GC/MS are much narrower, likewise the linear dynamic ranges obtained with HSGC/ ELCD were about two orders of magnitude. The widest linear dynamic ranges are obtained with HSGC/FID up to six orders of magnitude. The only exception is terpene compounds, the poor solubility of which in water prevented the measurement of high concentrations.

*Table 3.9. The detection limits for selected compounds in water obtained with PAM-technique [I].*

| Compound | Detection limit, µg/l |
|---|---|
| Toluene | 0.1 |
| o-Xylene | 0.2 |
| 1,4-Dichlorobenzene | 2 |
| Dichloromethane | 0.3 |
| Trichloroethene | 0.3 |
| MTBE | 10 |
| Di-isopropyl ether | 40 |
| Ethyl acetate | 60 |
| Butyl acetate | 4 |
| Phenol | 700 |
| Ethanol | 1000 |

The detection limits obtained with MIMS and PAM (preliminary tests) are in the same order of magnitude in the case of aromatic and chlorinated hydrocarbons. The detection limit for MTBE is also similar to that measured with MIMS (3 µg/l) [142]. However, the detection limit for phenol obtained with PAM is 100–1000 fold higher compared to that obtained with MIMS (Table 3.12).

The accuracy of the MIMS method for VOCs was tested earlier with samples spiked with aromatic and chlorinated hydrocarbons and by analysing authentic water samples by different analytical methods, namely HSGC and P&T-GC/MS. Mean standard deviations were 13%, 6% and 16% for MIMS, HSGC and P&T-GC/MS, respectively [43].

In order to confirm the accuracy, water samples were spiked with two different concentrations of sulphur compounds and analysed with MIMS/SIM, MIMS combined with the Solver program and HSGC combined with either FID or ELCD. In the Solver calculation, the concentrations were calculated using the

mass spectrum of a known sample mixture as calibration standard. MIMS without Solver allowed reliable quantitation only for compounds without overlapping peaks, for example m/z 84 (thiophene) and m/z 94 (dimethyl disulphide). However, ethanethiol and dimethyl sulphide cannot be quantified by MIMS/SIM, because all their major peaks are at the same m/z value. However, with the Solver program, reliable quantitation was possible. Ethylmethyl sulphide was also difficult to analyse in spiked mixtures using the MIMS/SIM because its base peak (m/z 61) overlaps with minor peaks from ethanethiol, dimethyl sulphide and dimethyl disulphide. This also explains the high relative difference values in the case of MIMS/SIM method (see Table 3.10). The results obtained for these two samples with each of the methods are in very good agreement, except that carbon disulphide could not be detected with FID. Both gas chromatographic methods gave good results above the 10 µg/l level. The sensitivity of FID was not sufficient for reliable quantitation below 10 µg/l. At the lower (µg/l) level MIMS/Solver was the only method which gave good results for all the compounds analysed.

*Table 3.10 The results of spiked samples analysed by MIMS/Solver, MIMS/SIM, GC-FID and GC-ELCD.*

| Compound | Spiked µg/l | MIMS/ Solver µg/l | MIMS/ SIM µg/l | Ion, monitored m/z | GC-FID µg/l | GC-ELCD µg/l |
|---|---|---|---|---|---|---|
| Ethanethiol | 115 | 108 | 227 [a)] | 62 | 99.5 | 101 |
| Dimethyl sulphide | 134 | 103 | [a)] | | 133 | 118 |
| Carbon disulphide | 202 | 207 | 156 | 76 | nd | 232 |
| Ethylmethyl sulphide | 10.6 | 19.4 | 42.1 | 61 | 12.8 | 16.6 |
| Thiophene | 23.4 | 28 | 30.4 | 84 | 26.7 | 30.2 |
| Dimethyl disulphide | 53.1 | 55.8 | 59.5 | 94 | 50.1 | 47.7 |
| Ethanethiol | 11.5 | 8.91 | 19.7 [a)] | 62 | 6.7 | 7.4 |
| Dimethyl sulphide | 13.4 | 9.13 | [a)] | | 15.7 | 9.7 |
| Carbon disulphide | 20.2 | 17.3 | 15.1 | 76 | nd | 17.2 |
| Ethylmethyl sulphide | 1.06 | 0.90 | 3.52 | 61 | 8.5 | nd |
| Thiophene | 2.34 | 1.36 | 2.14 | 84 | 5.3 | nd |
| Dimethyl disulphide | 5.31 | 4.16 | 4.66 | 94 | nd | 3.8 |

[a)] Result is the sum of ethanethiol and dimethyl sulphide
nd=not detected
SIM selected ion monitoring
Solver is a calculation program for the analysis of multicomponent mass spectra.

As an example of high sensitivity of MIMS, a mass spectrum of $CS_2$ measured at a concentration level of 1µg/l is presented in Figure 3.8. The sensitivity was sufficient to detect the characteristic isotope peaks of molecular ion for sulphur compounds M and (M+2), for $CS_2$ at m/z 76 and m/z 78.

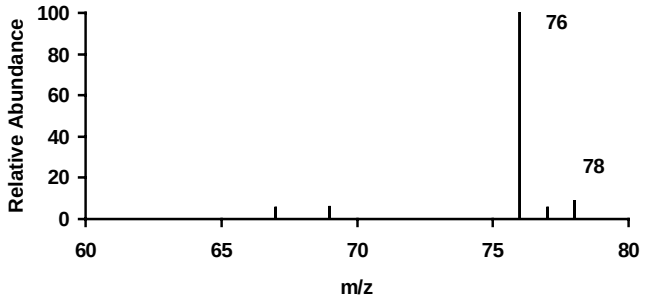



*Figure 3.8. A mass spectrum of $CS_2$ (1 µg/l).*

The results of authentic water samples analysed for terpenes by using the HSGC and MIMS methods are presented in Table 3.11.

*Table 3.11. Terpene concentrations of authentic water samples measured by MIMS/Solver and static headspace gas chromatography [VI].*

| Sample | Monoterpenes, µg/l | | Sesquiterpenes, µg/l | | Total, µg/l | |
|---|---|---|---|---|---|---|
| | HSGC | MIMS | HSGC | MIMS | HSGC | MIMS |
| 1 | 48 | 160 | 100 | 69 | 150 | 230 |
| 2 | 32 | 98 | 72 | 62 | 100 | 160 |
| 3 | 61 | 110 | 110 | 70 | 170 | 180 |
| 4 | 36 | 74 | 67 | 49 | 100 | 120 |
| 5 | 530 | 410 | 370 | 370 | 900 | 780 |
| 6 | 1500 | 1500 | 580 | 650 | 2100 | 2100 |
| 7 | 730 | 440 | 260 | 320 | 1000 | 760 |
| 8 | 1900 | 1800 | 540 | 750 | 2400 | 2600 |
| 9 | 860 | 610 | 330 | 450 | 1200 | 1100 |
| 10 | 23000 | 37000 | 3700 | 5700 | 27000 | 42000 |

Due to the extreme similarity of the mass spectra of monoterpenes the individual compounds cannot be separated on the basis of the measured MIMS mass spectrum. This is also true for sesquiterpenes. Quantitation by both methods was performed using an external standard method. The total amounts of mono- and sesquiterpenes obtained with both methods were of the same order. The main reason for the differences between the results obtained by the different analysis methods was probably the high concentration of terpenes in the samples, which caused some unhomogeneity and the need to dilute samples before the analysis. Furthermore, some non-terpenic compounds could have been included in the HSGC quantitation because their identifications were not possible using GC-FID.

### 3.2.2 Analysis of phenolic compounds

Phenolic compounds were analysed directly and after acetylation from water using membrane inlet mass spectrometry (VII). Electron ionization mass spectra of the standard compounds were measured by MIMS before and after acetylation. Even at this stage it was observed that the acetylated compounds could be measured at lower levels, since solutions of similar concentrations produced mass spectra with much better signal to noise ratios for the acetylated phenols than for the underivatised compounds. All the measured EI mass spectra agreed very well with the EI mass spectra published in reference mass spectral libraries [144].

The detection limits (Table 3.12) and the linear dynamic ranges for underivatised and acetylated phenols were measured using the selected ion monitoring (SIM) method. From Table 3.12 it can be seen that acetylation significantly lowered the detection limits, especially in the case of 4-nitrophenol. The detection limit of 4-nitrophenol was lowered from 1000 µg/l to 10 µg/l. This effect is probably due mainly to two factors. Probably the most important of these is the change in the solubility of analytes in the silicone membrane. The more polar underivatised phenols do not dissolve as well in the relatively non-polar membrane material as do the less polar acetylated phenols (i.e. the partition coefficient of acetylated compounds into the silicone is higher than that of underivatised phenols). Another effect is that the phenols with $pK_a$ values below 5.5 (e.g. pentachlorophenol, pKa 4.74 [131]) cannot be analysed very well

directly from water samples at the used pH values of the samples because they are in ionic form and ions do not dissolve in the silicone membrane.

*Table 3.12. Detection limits and linear dynamic ranges of some phenolic compounds measured by MIMS with and without acetylation. [VII].*

| Compound | Detection limit µg/l | Linear dynamic range µg/l | Detection limit after acetylation µg/l | Linear dynamic range µg/l |
|---|---|---|---|---|
| Phenol | 30 | 30–1000 | 0.5 | 0.5–300 |
| 3-Methylphenol | 20 | 20–1000 | 1 | 1–300 |
| 4-Chloro-3-methylphenol | 10 | 10–1000 | 1 | 1–300 |
| 2,5-Dichlorophenol | 5 | 5–1000 | 1 | 1–300 |
| 2,4,6-Trichlorophenol | 5 | 5–1000 | 1 | 1–300 |
| 2,3,4,6-Tetrachloropenol | 10 | nm | 2 | 2–1000 |
| Pentachlorophenol | 60 | nm | 5 | 5–2500 |
| 4-Nitrophenol | 1000 | nm | 10 | 10–10000 |

nm not measured

Membrane inlet mass spectrometry was also tested in the analysis of complex phenol mixtures in which the concentration of each analyte was about 1 mg/l. For all the analytes characteristic ions can be seen, i.e. the molecular ion and the ion formed by the loss of neutral ketene from the molecular ion (Figure 3.9)[VII].

Some surface water samples taken from an area contaminated with phenolic resins were also analysed using both the acetylation method and the direct HPLC method presented in the experimental section. The phenolic content of most of the samples was below the detection limits of both methods. Only in one sample were measureable amounts of phenolic compounds observed. The concentrations of these compounds were determined by an external standard quantitation method using the closest concentration of standard solution as calibrant. The concentrations of phenol and methylphenol calculated on the basis of these standards were 34 mg/l and 26 mg/l, respectively. With the HPLC method only phenol could be identified reliably, due to the high background eluting simultaneously with the methylphenols. The concentration of phenol obtained by the HPLC method was 36 mg/l, which agrees very well with the MIMS determination.

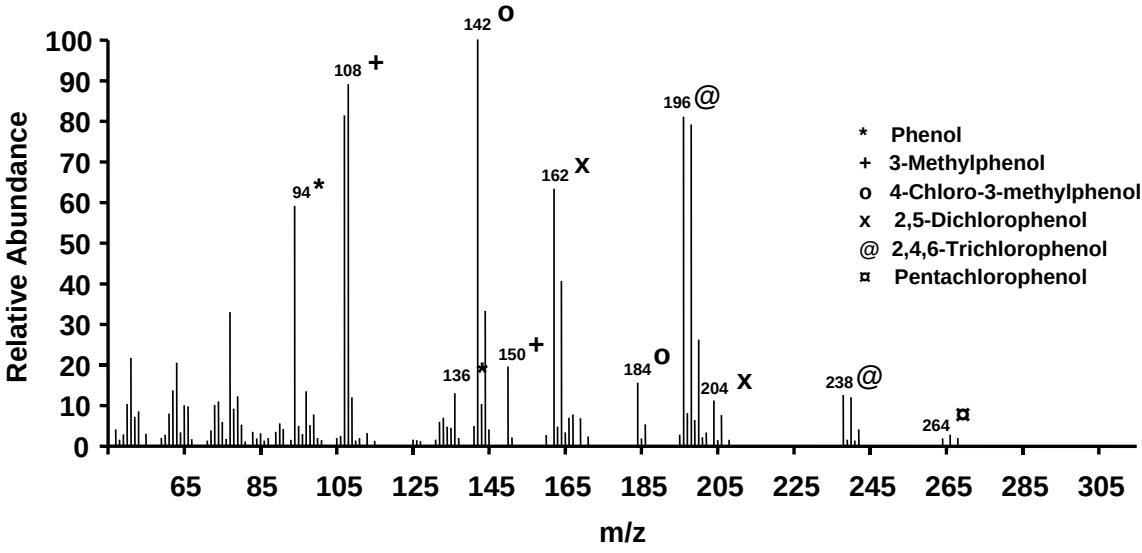



*Figure 3.9. Mass spectrum of a solution containing phenol, 3-methylphenol, 4-chloro-3-methylphenol, 2,5-dichlorophenol, 2,4,6-trichlorophenol and penta-chlorophenol. The characteristic ions of each compound are indicated.*

# 4. Conclusions and future perspectives

The main aim of this work was to develop a purge-and-membrane device for analysis of volatile organic compounds from soil samples. Two PAM-devices were developed and tested in detail in this study. The size of the equipment was diminished significantly (from 49 cm x 45 cm x 63 cm to 35 cm x 20 cm x 48 cm) and therefore the PAM-2-device is easily portable. Portable mass spectrometers are already available and smaller equipments are developed. The evaluation of the analysis method with conventional methods was also an important part of this work. Both vapour fortification samples (79) and authentic samples (35) were used in comparison. The correlation between the results obtained with the PAM-MS method and the HSGC method was good. The slope of the line was 0.900 and the coefficient of regression (r) was 0.848. In addition, Students t-test indicated that the results obtained with the two methods hade no significant differences at the 5% confidence level. The detection limits obtained with the PAM-method were at least as low as with the conventional methods and linear dynamic ranges were wider than with P&T-GC/MS. In the case of pharmaceuticals the results showed that PAM-MS/Solver can identify the main VOCs, but that P&T-GC/MS better identified the VOCs with low concentration (below 0.5 mg/kg). The results also demonstrated that the new PAM-MS method is very promising for the determination of volatile organic compounds in solid samples such as soils, pharmaceuticals and building materials. Other advantages of the method are short analysis times, the non-requirement for chemical pretreatment of samples, and for environmental and health risk reasons the fact that solvents are not used.

Preliminary tests were carried out with the use of PAM-MS for analysis of VOCs from water. The obtained detection limits were of the same order of magnitude as those obtained with the MIMS method for aromatic and chlorinated hydrocarbons. In the case of polar compounds the detection limits were even two or three orders of magnitude higher than with the MIMS method. The suitability of the MIMS method for water analysis resulted in a delay in the further development of the PAM-method for water analysis. For the analysis of VOCs, especially in on-line applications, the PAM-method should be preferred against the MIMS-method because of lower background caused by dirty sample matrix.

The effect of soil composition and humidity on desorption should be tested more thoroughly than it was possible in this work. In order to establish the contamination of soil it would be necessary to know as much as possible about the behaviour of different compounds and matrices in different conditions. Furthermore, the ageing test should be carried out in more detail than hitherto. The results would then be more precise, with only one variable changing at a time. The results of the ageing tests can possibly be utilised in the estimation of the length of time since contamination. The PAM-device needs further development towards full automation.

The MIMS-method was developed for the analysis of sulphur compounds, terpenes and phenolic compounds in water. Sulphur compounds and terpenes were also analysed using different chromatographic methods. The same conclusions as with the PAM-method are valid with MIMS methods. Detection limits, linear dynamic ranges and repeatability are comparable to those obtained with the conventional methods. The HSGC/FID method had the widest linear dynamic ranges and the P&T the narrowest. In the case of terpenes their low solubility in water limited the linear dynamic ranges. It is worthy of notice that MIMS-Solver was the only reliable method (of four) to measure low concentrations of sulphur compounds. The MIMS-method combined with the Solver program made possible to calculate the amounts of monoterpenes and sesquiterpenes in water samples. Phenolic compounds were analysed both directly from water and after acetylation in the aqueous phase. Acetylation of phenolic compounds decreased the detection limits from fivefold (di- and trichlorophenols) to 100-fold (4-nitrophenol).

The greatest disadvantage of both PAM- and MIMS-methods is that there is no separation of compounds before analysis. The use of MS-MS-techniques, alternative ionisation techniques such as chemical ionisation, proton transfer reaction and charge exchange or of effective calculation programs can circumvent this shortcoming. The temperature-programmed desorption MIMS method currently under development may be one answer to this problem. A new version of the Solver program will shortly be released and it may allow more accurate quantitation without separation of compounds.

In conclusion, the PAM-method is well suitable for the analysis of volatile organic compounds in solid samples, the results are accurate and repeatable and

the detection limits are sufficient low. The MIMS-method was tested thoroughly for water analysis and good results were also obtained for semivolatile compounds. Both methods are suitable for on-line and on-site analysis.

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Author(s)
Ojala, Marja

Title

# Novel membrane inlet mass spectrometric methods for analysis of organic compounds in aqueous and solid samples

Abstract

Different volatile organic compounds (VOCs) are widely used in industry and due to accidents and fuel emissions the compounds can be discharged into the environment, causing contamination of soil and groundwater. Because of their toxicity the analysis of VOCs is very important. The traditional analytical methods for VOCs, such as static and dynamic headspace gas chromatography-mass spectrometry, are time consuming and difficult to apply in on-line analysis or even on-site analysis. For this reason, a purge-and-membrane mass spectrometric (PAM) method was developed for analysis of VOCs in solid samples. Two versions of PAM-devices are introduced in this study. The characteristics of the method, such as linear dynamic ranges (at least five orders of magnitude), detection limits and repeatability, are presented. The detection limits varied between 5 and 150 µg/kg depending on compounds and soil type, and the repeatability was good when an internal standard was used (RSD < 14%). The effects of soil parameters such as humidity and the content of organics on desorption were studied. Both soil type and moisture content had an effect on peak areas. In addition, moisture content had an inversely proportional effect on desorption times in the case of garden soil. Furthermore, the effects of PAM-parameters such as the preheating time and temperature are presented in detail. Even a preheating time of only ten minutes was suitable for analysis. The use of different purge gases was studied. In addition, an application of the analysis of VOCs in pharmaceuticals is presented. Some preliminary tests for water analysis with PAM were carried out. The results obtained with the PAM-method for soil samples were compared with those of static headspace gas chromatography. Both spiked and authentic soil samples were used in analysis and two different laboratories took part in the testing. The agreement between testing methods and laboratories was good. The results show that the new PAM-MS method is very promising for the determination of volatile organic compounds in solid samples. Other advantages of the method are short analysis times (only a few minutes per sample), the non-requirement for pretreatment of samples, and for environmental and health risk reasons the fact that solvents are not used.

A membrane inlet mass spectrometry (MIMS) method was developed for testing volatile organic sulphur compounds, terpenes and phenolic compounds in water samples. Different conventional chromatographic methods were used to compare results. Detection limits obtained were at the low ppb level. Analysis times are short, only a few minutes, and no pretreatment of the samples is needed. Phenolic compounds were analysed both directly from water and after acetylation in aqueous phase. The detection limits obtained after acetylation increased from 5-fold for di- and trichlorophenols to 100 fold for 4-nitrophenol. The MIMS-method combined with the Solver program made it possible to calculate the amounts of monoterpenes and sesquiterpenes in water samples. It is worthy of notice that MIMS-Solver was the only reliable method (of four) to measure low concentrations of sulphur compounds in water samples.

Keywords

volatile organic compounds, membrane inlet mass spectrometry, determination, soil analysis, aqueous systems, pharmaceuticals, chromatography, samples, pretreatment, phenols

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