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Solid phase micro-extraction in a miniature ion trap mass spectrometer

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Fiber introduction mass spectrometry (FIMS), a variation of solid-phase microextraction (SPME) and membrane introduction mass spectrometry (MIMS), is employed with a miniature mass spectrometer. The inlet system, constructed of commercially available vacuum parts, allows the direct introduction of the SPME needle vacuum chamber into the mass spectrometer. Thermal desorption of the analyte from the poly(dimethylsiloxane) (PDMS) coated fiber was achieved with a built in nichrome heater, followed by electron ionization of the analytes internal to the cylindrical ion trap (CIT). The system has been tested with several volatile organic compounds (VOC) in air and to analyze the headspace over aqueous solutions, with limits of detection in the low ppb range. The signal rise (10–90%) and fall (90–10%) times for the system ranged from 0.1 to 1 s (rise) and 1.2 to 6 s (fall) using heated desorption. In addition, this method has been applied to quantitation of toluene in benzene, toluene, xylene (BTX) mixtures in water and gasoline. This simple and rapid analysis method, coupled to a portable mass spectrometer, has been shown to provide a robust, simple, rapid, reproducible, accurate and sensitive (low ppb range) fieldable approach to the effective *in situ* analysis of VOC in various matrices.

Introduction

There is current emphasis in analytical instrumentation on the miniaturization of lab scale instruments and the construction of fieldable systems.[1,2] Such systems are highly desirable for *in situ* analysis of trace level constituents in air or water.[3,4] Because the compounds of interest often occur at low levels in complex mixtures, their detection can represent a great challenge and require a highly selective and sensitive analytical method. Methods that are both rapid and also provide some degree of preconcentration are highly desirable. The success of membrane introduction mass spectrometry (MIMS) when employing a miniature mass spectrometer and used for air analysis, illustrates this point.[5,6] Membrane introduction (inlet) mass spectrometry (MIMS),[7] uses semi-permeable, hydrophobic membranes (often poly(dimethylsiloxane), PDMS) which selectively concentrate analyte from the matrix (often aqueous solutions, but also air samples) by hydrophobic interactions at the surface, followed by selective diffusion, and evaporation of the analyte from the membrane surface directly into the high-vacuum of a mass spectrometer.

Solid-phase microextraction (SPME), an attractive alternative to most of the conventional sampling techniques, has gained widespread acceptance and is advantageously used in many analytical procedures.[8–12] SPME has become particularly popular as a sampling method prior to GC and GC-MS analyses since it integrates sampling, extraction, concentration, and sample introduction procedures into an easy, rapid, sensitive, and single solvent-free step. SPME uses a small piece of fused-silica fiber coated with a stationary liquid phase to absorb or adsorb the analytes and to concentrate them on the fiber. Fibers with a variety of sorbents are available, and poly-(dimethylsiloxane) (PDMS) is a major SPME coating material for volatile organic chemical (VOC) and many semi-volatile organic chemical (SVOC) analyses. SPME is normally coupled with GC-MS, but a simpler coupling of SPME to MS *via* a short GC transfer line has been described to achieve higher sample throughput and to characterize complex mixtures.[13]

Similarly to SPME, MIMS also integrates easy, rapid, solvent-free, and sensitive VOC and SVOC sampling, extraction, concentration, and introduction all into a single step and has also been applied extensively in many analytical procedures.[14–18] Note that MIMS is not usually employed with chromatography (although exceptions occur[19,20]). In spite of this there is a close relationship between MIMS and SPME, especially when the recently introduced single-sided MIMS (SS-MIMS),[21] is compared with the SPME variant termed fiber introduction mass spectrometry (FIMS) introduced by Meurer *et al.*[13] Although SS-MIMS offers the lowest limits of detection of these methods (sub-ppb range) with short sampling times (1–10 s), and a large dynamic range (4 orders of magnitude), due to the large surface area of the PDMS used, it suffers from the need for helium sweep gas and has a relatively complicated design that requires non-commercially available parts. The FIMS method overcomes some of these limitations and gives low detection limits, low ppb range for 5 min sampling, rapid responses (30 s of single ion monitoring signal), and is suited to direct coupling to a small mass spectrometer. Commercially available SPME fibers, fused-silica coated with poly(dimethylsiloxane) (PDMS), can be used. The PDMS coated SPME fiber was found to efficiently preconcentrate analytes (VOC and SVOC) and allowed simple introduction and thermal desorption directly into the ionization region. Quantitation of volatile (VOC) and semivolatile (SVOC) organic chemicals (carbon tetrachloride, benzene, toluene, xylenes, γ-terpinene, diisoamyl ether, chlorobenzene, polyaromatic hydrocarbons and herbicides) have been quantitated using FIMS from aqueous solutions at low-ppb to ppt levels using either SPME headspace or solution extraction.

The purpose of this study was to combine and characterize the performance of the FIMS preconcentration method when used with a recently developed miniature cylindrical ion trap

(CIT) mass spectrometer capable of field analysis. The analytical performance of the inlet system was evaluated in terms of (1) the rise and fall times (10–90%) of the analytes, (2) limit of detection (LOD), (3) linear dynamic range, and (4) precision and accuracy.

Experimental

Mass spectrometer

These experiments were performed on a second generation miniature mass spectrometer (version 7.0) based on a miniature cylindrical ion trap mass analyzer (r_o = 2.5 mm) and a membrane introduction system. This instrument (136 W, 28 × 70 × 18 cm, 17 kg, including battery pack), which will be fully described in a forthcoming article, is much smaller than the previous generation prototype miniature mass spectrometer (version 5.0, 200–300 W, 40 × 60 × 50cm, 55 kg, including battery pack), fully described elsewhere,[6,22] although it retains all of the features of the previous instrument. The instrument, as used for these experiments, is fitted with an electron ionization source, has an upper mass/charge limit of ~ 260 Th (Thomson = Dalton charge^{-1}), and uses a resonant ejection at q_z = 0.808, β_z = 0.7, f_{eject} = 700 kHz, with detection by an off-axis external channeltron electron multiplier. For single-stage MS experiments, the scan function employed had five periods: a 5 ms delay period, 50 ms ionization time (electrons allowed into trap to ionize neutral vapors), 20 ms ion cooling period, 15 ms analysis time, and a 15 ms delay period, for a total scan time of 105 ms.

Sample preconcentration and introduction system

A custom interface, Fig. 1, was constructed for use as the sampling system. The SPME fiber (24 gauge), coated with 100 μm nonbonded polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA) was held in a commercially available manual SPME Fiber Holder (Supelco, Bellefonte, PA). The vacuum interface for the sampling system was constructed from a 25 mm Quick Flange (QF25) blank stub (MDC Vacuum Products, Hayward, CA) with a 1/16 inch od stainless steel tube fitted through 1/8 inch Swagelok fittings (Swagelok Corporation, Solon, OH) held in place by 1/8 to 1/16 inch polytetrafluoroethylene (PTFE) reducing ferrules (Alltech, Deerfield, IL). At the high-pressure end of the swagelok fittings a GC septum (Thermogreen LB-2 3/8 inch diameter, Supelco, Bellefonte, PA) allowed introduction of the needle and fiber assembly to the vacuum system. This arrangement isolated the stainless steel tuning allowing a current (500 mA) to be passed through a nichrome wire (30 gauge, type A, 2.4 Ω, Kanthal Corporation, Stamford, CT) coiled around the fiber, in order to rapidly heat the membrane material and thus desorb accumulated analyte. This heater is continually on; therefore upon insertion into the vacuum system the fiber is heated immediately.

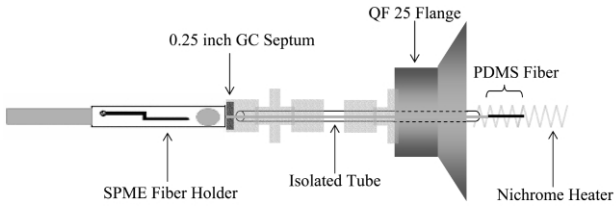

Fig. 1 Schematic of sample preconcentration and inlet system. The SPME fiber is introduced through a GC septum into the vacuum system *via* a series of swagelok connectors coupled to a QF25 vacuum flange. An isolated 1/16 inch od stainless steel tube was held at an elevated potential to allow resistive heating of a nichrome wire to heat the PDMS and desorb accumulated analyte.

Sample preparation

For air samples, a 1 mL sample of the analyte of interest was placed into a 1 L sealed container containing ambient air and liquid–vapor equilibrium was allowed to be reached. The analyte concentration in the gaseous headspace solution was calculated based on the known vapor pressure of the analyte.[23] An aliquot of this gas mixture was sampled with a gas-tight syringe fitted with a shutoff valve (Hamilton, Reno, NV). The sample was injected at a controlled flow rate (0.1 to 5.0 mL min^{-1}) using a syringe pump (Model 22, Harvard Apparatus, Holliston, MA) into the flowing stream (100 to 450 mL min^{-1}) of Grade D OSHA breathable air (BOC Gases, Murray Hill, NJ).

Aqueous solutions were prepared using double-deionized water by serial dilution of 1 mg mL^{-1} methanol solutions. The analyte solutions (10 mL) were placed into 20 mL headspace vials (Supelco, Bellefonte, PA), which were sealed with septum caps, and SPME extraction was performed at room temperature (23 °C) with constant stirring at 1200 rpm for static headspace extraction.

Chemicals

All compounds were obtained from Sigma-Aldrich Corporation (Milwaukee, WI) and were used without purification. A gasoline sample (Amoco unleaded, regular grade) was purchased from a local gas station and analyzed within 4 h.

Results and discussion

The performance of the system was established with air and aqueous headspace samples. For air analysis, the system was optimized with methyl salicylate and the analytical performance was established for this compound, as well as others. The limit of detection (S/N = 3 in the full scan mass spectrum) was determined for methyl salicylate and naphthalene in air. Both compounds were shown to have an LOD of 25 ppb using a 3 min sampling time and sample flow rate of 200 mL min^{-1}. The system response to methyl salicylate in air, shown in Fig. 2, was found to be linear (y = 0.0039x + 0.0669) from 50 ppb to 800 ppb, with an R^2 value of 0.9954. A mass spectrum of 50 ppb methyl salicylate in air is shown in the inset of Fig. 2. The plot is linear to the high end of the tested range, which was limited

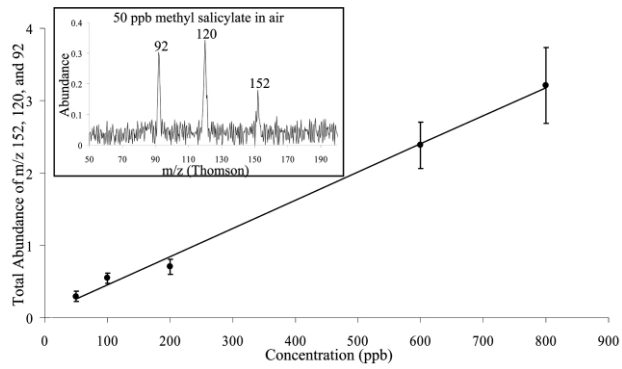

Fig. 2 Total abundances of characteristic ions of methyl salicylate (*m/z* 152, 120, and 92) as a function of methyl salicylate in air concentration. Note the linear response (y = 0.0039x + 0.0669, R^2 = 0.9954) which is maintained from the limit of detection, 25 ppb, up to 800 ppb. A mass spectrum of 50 ppb methyl salicylate in air is shown in the inset.

by the sample preparation technique, although linearity is expected to be lost at high concentration with longer exposure time. The relative standard deviation of the technique is less than 10%, which is typical for SPME.[24]

The conditions used in the above experiments for extraction from air samples were previously optimized with methyl salicylate. In these optimization studies the parameters studied were extraction time, analyte flow rate, and desorption temperature. Data in Fig. 3A (using 400 ppb methyl salicylate in air with a flow rate of 200 mL min^{-1}) indicate that the optimum extraction time is 3 min, during which time it is assumed that the equilibrium concentration of the sample between PDMS and air is achieved. After this period of time, the signal decreases slightly, due to air stripping the methyl salicylate out of the PDMS. The extraction efficiency of the technique is dependent on the sample flow rate. Too fast a flow rate does not allow the sample to mix completely while too slow a rate results in the fiber having contact with less sample over a given extraction time. As shown in Fig. 3B, optimum extraction for the sample of 400 ppb methyl salicylate in air, using a 3 min extraction, occurs at a flow rate of 190 mL min^{-1}. The effect of temperature of the PDMS during desportion was also studied. As expected, elevated desorption temperatures gave larger signals with faster rise and fall times as established using 3,4-dichlorotoluene. At elevated temperatures the 10–90% rise time was 1 s and the 90–10% fall time was 6 s, while at room temperature the 10–90% rise time was 2 s and the 90–10% fall time was 13 s. It was found that there is no detectable analyte carry over between runs that use an elevated temperature. Based on these results all quantitative data with air samples were acquired with a flow rate of 200 mL min^{-1} and a 3 min exposure time under elevated temperature desorption. These optimized conditions are expected to be concentration and compound dependent; therefore conditions must be optimized for each sample if it is necessary to achieve highest performance.

The system was tested further with a variety of saturated solutions of volatile and semivolatile organic compounds in air. Very strong signal was observed after a 5 s exposure time to acetophenone (522 ppm), toluene (37 ppth), methyl salicylate (45 ppm), α-terpinene (unknown concentration since vapor pressure is not known), 3,4-dichlorotoluene (414 ppm), dimethyl methylphosphonate (1266 ppm), *p*-nitrotoluene (216 ppm), naphthalene (111 ppm), and nitrobenzene (322 ppm). This indicates the flexibility of the PDMS to extract a variety of organic compounds.

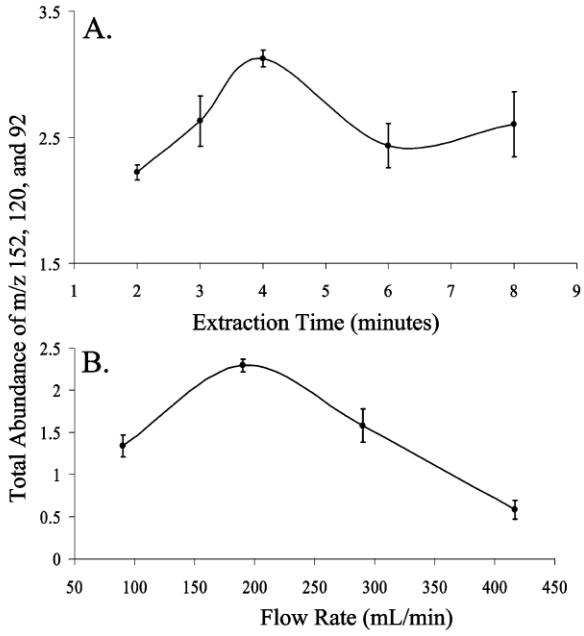

Fig. 3 Optimization of performance of the inlet system. A. Extraction time *versus* total abundances of characteristic ions of methyl salicylate (*m*/*z* 152, 120, and 92), indicating that 3 min is optimum for 400 ppb methyl salicylate in air at a 200 mL min^{-1} flow rate. (B.) Sample flow rate *versus* total abundances of characteristic ions of methyl salicylate (*m*/*z* 152, 120, and 92), showing that 190 mL min^{-1} yields best results for 400 ppb methyl salicylate in air and a 3 min extraction time.

The system performance in sampling the headspace over aqueous samples was explored with toluene as analyte. With an exposure time of 5 min, the limit of detection (S/N = 3; full mass spectrum not single ion monitoring) was found to be 1 ppb in water. As shown in Fig. 4, the system response was linear ($y = 0.005x + 0.5672$) from the limit of detection, 1 ppb to 200 ppb, with an R^2 value of 0.9996. After this point linearity was lost, due to saturation of the membrane. A mass spectrum taken after a 5 min sampling period of the headspace over 5 ppb toluene is shown in the inset of Fig. 4.

The system was tested further using α-terpinene in water. The multiple ion monitoring trace of characteristic ions, Fig. 5, shows a 10–90% rise time of 0.1 s and 90–10% fall time is 1.2 s for 1 ppm α-terpinene. The inset in Fig. 5 is the full mass spectrum of 1 ppm. The limit of detection for this compound is 100 ppb from the full mass spectrum. Detection limits for single or multiple ion monitoring were not rigorously established but are estimated to be 10 times lower.

The limits of detection for toluene and methyl salicylate can be compared with those from other MIMS experiments, both conventional and trap and release MIMS,[25,26] performed using the same miniature mass spectrometer, fitted with a PDMS membrane system described elsewhere.[5] Using this higher

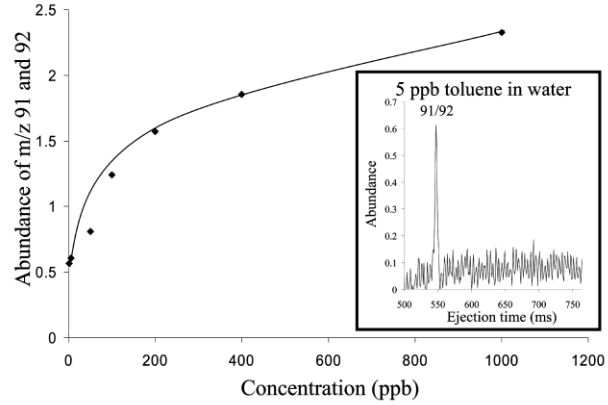

Fig. 4 Analytical performance when sampling headspace over aqueous toluene solutions. Limit of detection is 1 ppb with 5 min exposure. Linearity of response ($y = 0.005x + 0.5672$, R^2 value of 0.9996) occurs from concentrations corresponding to the limit of detection up to 200 ppb. A mass spectrum of 5 ppb toluene sample is shown in the inset.

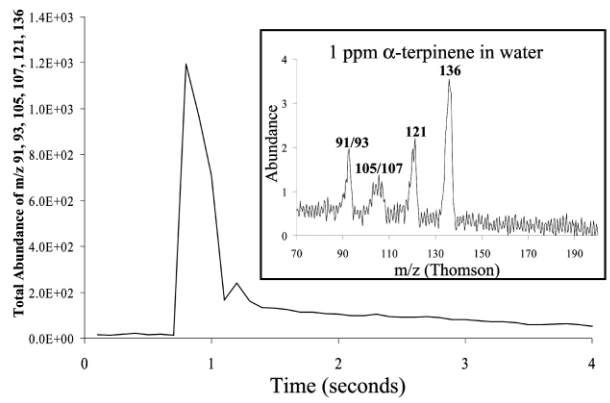

Fig. 5 Multiple ion monitoring trace of headspace sampling (5 min) of 1 ppm α-terpinene. The system has a 10–90% rise time of 0.1 s and 90–10% fall time is 1.2 s. A full mass spectrum of 1 ppm α-terpinene is shown in the inset.

surface area PDMS, the limits of detection for methyl salicylate were determined to be 30 ppb for a 10 s trapping time and 24 pptr for the extreme case of a 20 min trapping period. Assuming there is a linear correlation between time of trapping and limit of detection, it is estimated that the LOD for a 3 min preconcentration time using the trap and release MIMS method would be 26 ppb for methyl salicylate in air. This is very similar to the current results which show a limit of detection of 25 ppb using the FIMS technique. Using this same membrane system, 23 ppb toluene in air was detected on-line, using standard MIMS techniques. This is only an order of magnitude poorer that the current method's LOD for toluene, which requires a 5 min preconcentration time.

Mixture analysis capabilities of the system were investigated using benzene, toluene, xylene (BTX) mixtures. The importance of BTX analysis is highlighted in the fact that although gasoline contains a mixture of approximately 280 different hydrocarbons in the range of C-4 to C-12, its ecotoxicology is usually determined by quantitation of these relatively water-soluble mono-aromatic components, as mandated[27]in 2002 by the United States Environmental Protection Agency (US-EPA) standard test methods (D5769–98).[28]

A series of standards of benzene, toluene, and *p*-xylene in water in a 2:1:2 ratio was prepared in the 500 to 4000 ppb range. A calibration curve for toluene in the BTX matrix was constructed; it gave $y = 0.86914x + 1.109$, with an R^2 value of 0.999. Using this calibration curve, an "unknown" BTX mixture was analyzed for toluene content. The abundance of the *m*/*z* 91 ion was 1.549 V, which after application to the calibration curve yields an *x*-value of 0.51 ppm, a concentration of 510 ppb. The actual concentration of the toluene in this solution was 500 ppb, giving an accuracy of 2% for this single measurement. As observed with other trap-and-release MIMS experiments,[5,29,30] temporal separation occurs as seen by the fact benzene desorbs from the PDMS before toluene or *p*-xylene.

The standard addition method was used to analyze the toluene content in a gasoline sample. The gasoline was diluted to 10 ppm gasoline in water. Addition of toluene at the 500, 1000, and 2000 ppb concentration levels was used to construct a calibration curve. Each point was performed in triplicate and showed RSD of less than 10%. The regression line, $y = 0.3491x + 0.5642$, $R^2 = 0.9557$, allowed calculation of the *x*-intercept = −1.616. Therefore, the concentration of toluene in the diluted solution was 1.6 ppm. This corresponds to 16 ± 2% in original gasoline.

Conclusions

This study has shown that a SPME fiber can be directly coupled to a miniature mass spectrometer, as a simple and relatively fast preconcentration step for aqueous and air samples, with promising implications for field analysis. Trace level detection of a variety of volatile organic compounds has been shown in air and water matrices. Trace level detection in the low parts-per-billion range has been demonstrated using relatively rapid preconcentration times of 3–5 min, for compounds of interest such as toluene and methyl salicylate. Linearity of response, reproducibity, and accuracy were investigated. The system was also applied to a determination of unknown levels of toluene in a benzene, toluene, xylene aqueous mixture. In addition, this technique was used to quantitate the levels of toluene in a gasoline sample, using the standard additions method. Future work will include use of other SPME coatings, actual field analysis, and optimization of the system performance by implementation of direct desorption of the analyte into the ionization region of the mass spectrometer, a step expected to significantly improve the sensitivity of the technique.

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