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Quantitation of trace phenolic compounds in water by trap-and-release membrane introduction mass spectrometry after acetylation

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Trap-and-release membrane introduction mass spectrometry (T&R-MIMS) with a removable direct insertion membrane probe (DIMP) is used to quantitate a variety of trace phenolic compounds in water after acetylation. The procedure is simple, rapid and robust, producing linear and reproducible responses for phenolic compounds with varying polarities. Acetylation minimizes the polarity effects of ring substituents; hence, T&R-MIMS of the acetylated phenols provides lower and more uniform limits of detection (LODs) (2–15 $\mu g\,L^{-1}$) than those obtained by direct T&R-MIMS analysis of the non-derivatized phenols. Copyright © 2008 John Wiley & Sons, Ltd.

Phenols are a common and important class of pollutants.[1] These polar and relatively acidic compounds may occur in domestic and industrial wastewaters, natural waters, and potable water supplies. Chlorination of such waters may also produce odorous and objectionable-tasting chlorophenols. Phenols, chlorophenols and other related compounds are toxic to humans and aquatic organisms and therefore their detection and quantitation at trace levels are important.[2,3] Several analytical techniques are used to identify and to quantitate phenolic compounds in water. Liquid or gas chromatographic methods are employed but their detection limits are often too high.[4] However, the chromatographic performance can be enhanced considerably by derivatization, and acetic anhydride has been used to derivatize phenols directly in water.[5]

Membrane introduction mass spectrometry (MIMS)[6–10] is a well-established technique for the direct analysis of volatile organic compounds (VOCs) in aqueous matrices. The introduction of analyte into the mass spectrometer in MIMS occurs through a polymeric membrane, which is selective for small and less polar organic compounds relative to water. However, for the analysis of polar or even semi-polar organic compounds (SVOCs), conventional MIMS is normally unsatisfactory due to inefficient permeability or selectivity; hence, the detection limits are often too high to be useful.

Ojala *et al*.[11] studied the applicability of MIMS to the analysis of phenolic compounds in water by direct analysis and analysis after acetylation of the phenolic compounds and showed that off-line acetylation of phenols in water enhances conventional MIMS detections limits (30 $\mu g\,L^{-1}$ for phenol, 60 $\mu g\,L^{-1}$ for pentachlorophenol and 1000 $\mu g\,L^{-1}$ for nitrophenol) by nearly 2 orders of magnitude, obtaining limits of detection (LODs) in the range of 0.5 $\mu g\,L^{-1}$ for phenol, 5 $\mu g\,L^{-1}$ for pentachlorophenol and 10 $\mu g\,L^{-1}$ for nitrophenol. Using a conventional MIMS system coupled to flow injection analysis (FIA), that is, a FIA-MIMS system with on-line acetylation, we showed[12] the high sensitivity of this method for the quantification of the phenolic compounds in water, with LODs of the order of 0.5 $\mu g\,L^{-1}$ for phenol and 20 $\mu g\,L^{-1}$ for 2,4,6-trichlorophenol. FIA-MIMS was, however, unable to detect pentachlorophenol in water. The use of MIMS following acetylation to transform phenols into their respective less polar acetyl esters seemed therefore to be a promising approach to the detection of a wider range of phenols in environmental water samples with similar LODs.

Various trapping methods combined with conventional MIMS have also been designed recently to gain more selectivity or to enhance the LODs of compounds which are difficult to measure using conventional MIMS.[13–15] In the trap-and-release (T&R)-MIMS method developed by Leth and Lauritsen,[16] the membrane is kept cold during sample loading by the flow of the solution. During this period, the semi-polar analytes permeate the membrane and are continuously accumulated, owing to their low volatility, on the external surface of the membrane. Then, to release the analytes to the gas phase, the solution flow is replaced by a flow of air by the introduction of an air plug. The flow of air causes rapid heating and desorption of the analytes from the external surface of the membrane to the ion source gas-phase environment of the mass spectrometer, in which the gaseous analytes are then ionized and detected. The filament provides both the heat for desorption and the electron beam for electron ionization (EI) of the gaseous analytes. In general, the obtained LODs for chlorophenols were 10–100 times lower than those obtained by conventional MIMS. Lauritsen and Ketola[17] demonstrated the use of T&R-MIMS for the quantitative determination of SVOCs, such as acetylsalicylic acid, caffeine and 4-phenylphenol, with LODs of 250, 600 and

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2 μg L^{-1}, respectively. For 4-phenylphenol, the LOD was lowered by a factor of 50 compared with those possible with conventional MIMS.

T&R-MIMS has been applied to the analysis of phenols and chlorophenols,[16] and a good detection limit for pentachlorophenol (10 μg L^{-1}) was obtained. The results for more volatile compounds such as phenol (200 μg L^{-1}) and 4-chlorophenol (170 μg L^{-1}) were, however, less satisfactory. T&R-MIMS provides therefore a quite broad range of LODs for phenol analysis in water (10–200 μg L^{-1}). In the present study, we used a T&R-MIMS system based on a removable direct insertion membrane probe (DIMP)[18–20] to quantitate phenolic compounds in water. The use of a removable DIMP and two EI filaments promotes faster and more uniform membrane heating that enhances sensitivity and reduces memory effects. In addition, the use of a simple acetylation procedure before analysis allowed us to reduce the effects of ring substituents on analyte polarity and thus to obtain a more uniform response as a function of precursor phenol polarities, that is, the LODs were in the low ppb range for all phenols tested with a relatively wide range of polarity for the precursor analyte. This procedure allows therefore combined analysis in water of both volatile (such as phenol) and semi-volatile phenols (such as pentachlorophenol) at trace level (ca. 10 μg L^{-1}).

EXPERIMENTAL

All chemicals were of analytical-reagent grade, and Milli-Q water (Millipore, Billerica, MA, USA) was used throughout. Aqueous standard solutions of the phenols were prepared by dilutions of 1000 mg L^{-1} methanol stock solutions. The off-line acetylation of phenols in the aqueous phase was performed as follows: to each 100 mL test solution, 200 μL of acetic anhydride and 1 g of solid potassium carbonate were added, and the reaction mixture was stirred for 3 min, before being ready for analysis. Mass spectrometry was performed using 70 eV electron ionization (EI) and an Extrel (Pittsburg, PA, USA) mass spectrometer fitted with a high transmission quadrupole mass analyzer. The removable direct insertion membrane probe (DIMP) used in this study has been described by us in detail elsewhere.[18–20] The solutions of phenolic compounds at room temperature (23 ± 1°C) were pumped through the system by an eight-roll peristaltic pump at a rate of 2 mL min^{-1}. The capillary membrane (Silastic medical-grade tubing), with a wall thickness of 0.056 cm, i.d. of 0.063 cm, and o.d. of 0.12 cm, was provided by Dow Corning Co. (Midland, MI, USA).

RESULTS AND DISCUSSION

Signal profile

During the operation of the system for phenol analysis in water, initially a pure water stream is continuously pumped through the membrane; then, a 1 min air plug is introduced (simply by removing the pumping tube from the aqueous sample solution) which results in a peak produced by the desorption and ionization of chemical present in the membrane (chemical noise). This procedure is repeated (twice normally) until the chemical noise is properly minimized. The phenolic solution is then pumped through the system, and during trapping, no signal is detected (phenolic compounds permeate the membrane and are accumulated in its external surface but thermal desorption to the gas phase is irrelevant due to low temperature of the membrane and low volatility of the analytes). When the 1 min air plug is introduced, however, the temperature rises rapidly (due to filament heating), and the pre-concentrated phenolic compounds are

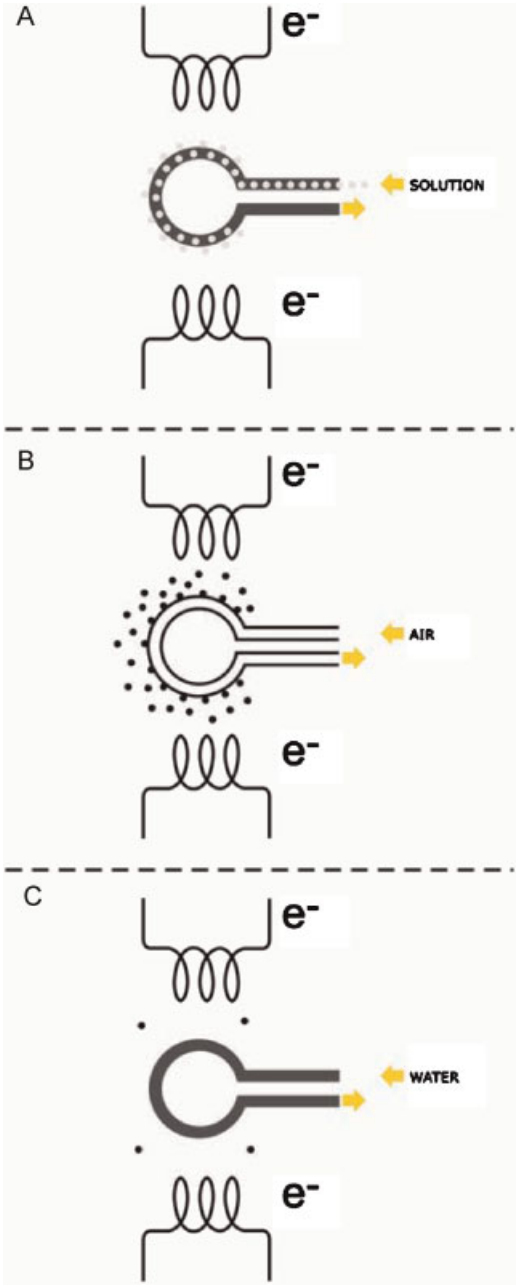

Figure 1. Schematic of the operation of the T&R-MIMS system for the quantitation of acetylated phenolic compounds in water. (A) The analyte solution is pumped through the system, and the analyte (●) accumulates in the external surface of the membrane. The solution cools down the membrane so its temperature remains low. (B) An air plug is pumped through the system. The heat and the electron beam from the filament cause thermal desorption and ionization of the gaseous analyte. (C) Pure water is now pumped through the system for cleaning.

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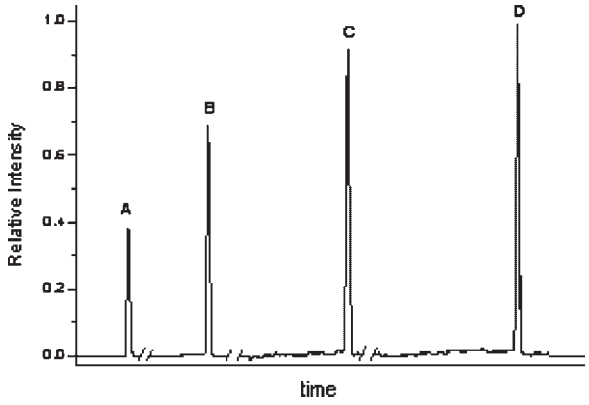

Figure 2. T&R-MIMS responses using SIM (*m/z* 94) for the analysis of a 1000 $\mu g\,L^{-1}$ acetylated phenol aqueous solution as a function of trapping time: (A) 5, (B) 10, (C) 15, and (D) 20 min. For optimum sensitivity and analytical frequency, a trapping time of 15 min (C) was selected. An air plug of 1 min was used, based on previous testing of the system.[18]

thermally and efficiently desorbed (released) to the gas phase. The mass spectrometer response rises and drops sharply now due to ionization and detection of the gaseous analyte, producing a well-defined, narrow, and intense peak (Fig. 1). When the air plug ends, and since room temperature pure water is now flowing through the system, the membrane rapidly cools and the ion signal drops sharply back to the baseline. After sample analysis, cleaning is performed by an additional 1 min air plug. The cleaning peak is much less abundant, and only a single cleaning step is normally required due to the low memory effects of our T&R-MIMS system.[18–20]

Trapping time

Figure 2 shows the T&R-MIMS responses for a 1000 $\mu g\,L^{-1}$ acetylated phenol solution analyzed as a function of trapping time (5, 10, 15 or 20 min). As expected, the sensitivity (maximum peak height) increases (not linearly, however) with trap time and a trap time of 15 min was selected for best sensitivity and analytical frequency.

Analytical performance

Table 1 lists the 70 eV electron ionization (EI) ions used in selected ion monitoring (SIM) to quantitative and to confirm the identity of the seven phenolic compounds tested as their acetates. The $ArOH^+$ most abundant fragment ion was used in SIM for quantitation, and the molecular ion ($ArOAc^{+\bullet}$) was used to confirm the identity of the analytes; hence, to enhance selectivity.

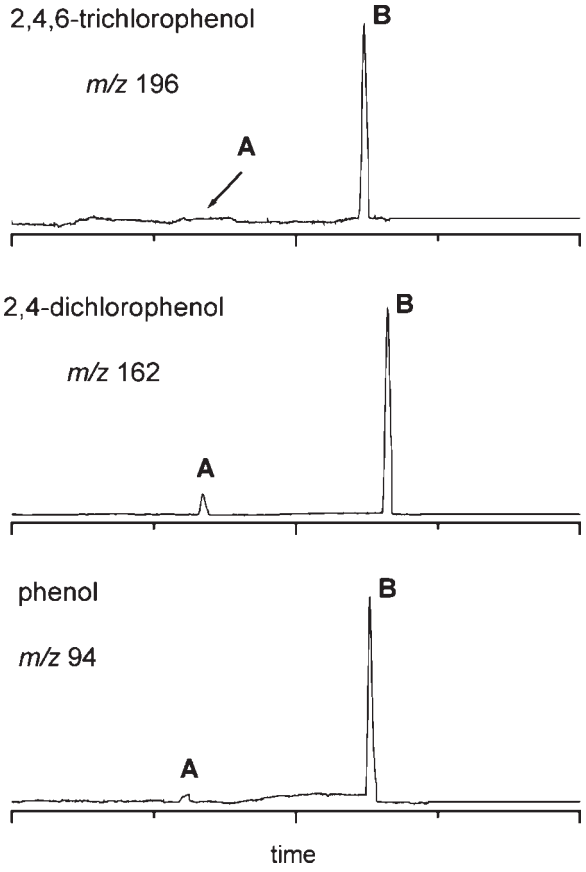

Figure 3. T&R-MIMS responses using SIM for the analysis of a 1000 $\mu g\,L^{-1}$ phenol aqueous solution after 15 min of trapping and 1 min air plug (A) without and (B) with acetylation.

LODs and linearity

Table 1 also lists the LODs and the linear ranges tested for analysis of the acetylated selected phenols by the T&R-MIMS procedure under optimized conditions. Correlation coefficients higher than 0.990 were obtained (6 point and peak height), which demonstrates good linearity and reproducibility. LODs in the narrow 2–15 $\mu g\,L^{-1}$ range were easily attained. A signal-to-noise ratio of 3 was used as a criterion for LOD. It is observed therefore that a simple acetylation procedure before analysis significantly lowers and homogenizes the LOD for phenolic compounds analyzed by T&R-MIMS. For 2,4-6-trichlorophenol, phenol and 2,4-dichlorophenol, for instance (Fig. 3), the LODs in our system were lowered from 1000, 350 and 20 $\mu g\,L^{-1}$ for the unacetylated molecules to 7, 10 and 2 $\mu g\,L^{-1}$ for the

Table 1. Results for the T&R-MIMS quantitation of acetylated phenolic compounds in water

Phenolic compounds	$ArOAc^+$ *m/z*	$ArOH^+$ *m/z*	Linear range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	r
Phenol	136	94	10–1000	10	0.9931
2-methylphenol	150	108	10–1000	6	0.9962
4-chlorophenol	170	128	10–1000	7	0.9901
4-chloro-3-methylphenol	184	142	10–1000	3	0.9943
2,4-dichlorophenol	204	162	10–1000	2	0.9905
2,4,6-trichlorophenol	238	196	10–1000	7	0.9932
pentachlorophenol	308	266	20–1000	15	0.9903

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acetylated phenols, respectively. These enhancements of the LOD are probably the result of the enhanced permeability of the analytes through the methylsilicone membrane and increased desorption efficiency.

Repeatability

The repeatability of the method was tested by comparing the responses for 15 consecutive injections of solutions of the acetylated phenolic compounds at 1000 $\mu g\,L^{-1}$. The relative standard deviations were about 5% in all cases.

CONCLUSIONS

Simple acetylation previous to T&R-MIMS analysis leads to lower and more uniform LODs (2–15 ppb) than with direct T&R-MIMS (ca. 1 ppm) for quantitating phenols in water. The method is simple, rapid, and robust, producing linear and reproducible results. Acetylation minimizes the polarity effects of ring substituents; hence the method is particularly suitable to screen a broad range of trace phenolic contaminants with varying polarities (but similar LOD after acetylation) including complex mixtures in samples of unknown composition.

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