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Technical Notes

Reversed-Phase Membrane Inlet Mass Spectrometry Applied to the Real-Time Monitoring of Low Molecular Weight Alcohols in Chloroform

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Reversed-phase membrane inlet mass spectrometry incorporating a hollow-fiber Nafion membrane has been evaluated for the determination of low molecular weight alcohols in chloroform. The hydrophilic Nafion membrane preferentially transports methanol and ethanol, allowing percentage concentrations of the alcohols to be determined in a chloroform matrix. A linear response was observed for ethanol over the working range 0.5−2.5%, with a limit of detection of 0.1%. The application of reversed-phase membrane inlet mass spectrometry using a Nafion membrane to the monitoring of a chloroform recovery process has been investigated using a residual gas analyzer. Evolving methanol and ethanol concentrations were determined in real time and compared favorably with off-line determinations by gas chromatography.

Membrane inlet mass spectrometry (MIMS) is an interfacing technique based on the selective transport of analytes across a membrane that has a low permeability for the sample matrix.[1−4] The use of nonpolar membranes in hollow-fiber or sheet form to exclude polar solvents and allow the pervaporation of organic analytes is termed normal-phase MIMS. For example, previous work has employed polydimethylsilicone membranes to extract volatile organic compounds (VOCs) from aqueous systems.[5−8] Conversely, the use of a membrane introduction technique that allows the passage of more polar materials, termed reversed-phase MIMS (RP-MIMS), has been less well-studied.[9−12]

Microporous polypropylene[9] has been used by Lauritsen et al. for the RP-MIMS analysis of organic compounds, such as methanol, ethanol, dimethyl sulfoxide, and benzene in hexane. Similarly, Kasthurikrishnan et al.[10] used zeolite-filled poly(dimethylsiloxane) microporous membranes for the analysis of benzene, carbon tetrachloride, chlorobenzene, toluene, and *trans*-1,2-dichloroethane in methanol and hexane. However, microporous membranes lack the selectivity of semipermeable membranes, because transport is determined by laminar flow through the pores rather than diffusion across the membrane. The high sample flow through microporous membranes also usually requires that analyses are carried out using solvent chemical ionization mass spectrometry (CI-MS).

A poly(ethylene terephthalate) membrane was used by Bohatka et al.[11] to determine selectively traces of water in butanol, hexanol, and octanol, and Bauer et al.[12] employed a poly(vinyl alcohol) (PVA) membrane in the RP-MIMS analysis of VOCs, including acetone, methyl ethyl ketone, methanol, and tetrahydrofuran, in hexane. Although the PVA membrane discriminated against the solvent, hexane was used as the reagent gas for CI analysis. Maden et al.[13] investigated the use of a polyimide membrane for the RP-MIMS analysis of water, ethanol, chloroform, acetone, acetic acid, and ethyl acetate in hexane. The polyimide was permeable to polar compounds, including water or ethanol, but showed limited discrimination against the permeation of nonpolar compounds, such as chloroform and ethyl acetate. The flux of hexane permeating the membrane was sufficiently high that EI spectra were observed to have CI characteristics.

Nafion is an ionic polymer with a tetrafluoroethylene backbone and perfluorinated ether side chains terminating in sulfonic acid

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sites.[14] The hydrophilic character of the sulfonic acid groups gives a very high affinity for water and other polar compounds, such as alcohols,[15−17] which can absorb into a Nafion membrane, but nonpolar compounds have a much lower affinity. Once absorbed into the wall of the Nafion membrane, polar analytes diffuse across the membrane via association with neighboring sulfonic acid groups. Nafion has been widely used for drying vapor streams as a consequence of this hydrophilicity.[18−21]

In this paper, we report the use of a RP-MIMS configuration incorporating a semipermeable Nafion membrane for the selective permeation of the low molecular weight alcohols methanol and ethanol in a chloroform matrix. We believe that the experiments reported here describe the first use of Nafion as a RP-MIMS membrane for low molecular weight polar analytes in an organic solvent. Membrane performance was characterized with respect to response time and the selectivity of the membrane. This RP-MIMS approach, using a portable residual gas analyzer (RGA), has been evaluated for a process-monitoring application involving distillation of an alcohol/chloroform mixture and has been referenced against GC-based quantification. We investigated this particular solvent system because of an interest in evaluating an on-line analytical system capable of real-time determination of alcohols in chloroform.

EXPERIMENTAL SECTION

All chemicals were obtained from Aldrich (Gillingham, Dorset, U. K., and Milwaukee, WI) and used without further purification.

(a) Characterization of Nafion Membrane Performance for RP-MIMS. The RP-MIMS interface used for the characterization of the Nafion membrane (Figure 1a) was based on the design of a normal-phase MIMS configuration previously reported.[5] The interface was mounted inside the oven of a Hewlett-Packard HP 5890 GC, which was coupled to a HP 5970 quadrupole analyzer. The interface consisted of a Nafion membrane (0.014-in. i.d., Omnifit Ltd, U.K.) located inside a short section (50 mm) of 1/8-in. stainless steel tubing. The ends of the Nafion membrane were fitted tightly onto two lengths of 0.25-mm-i.d. fused-silica tubing, one of which was connected to the GC injector, and the other, to the mass spectrometer ion source. The whole assembly was made vacuum- and water-tight using stainless steel compression fittings (1/16 × 1/16 × 1/8 in.). The sample was introduced into the interface using a peristaltic pump such that it flowed over the outer surface of the Nafion membrane. Pervaporating analytes were transferred to the mass spectrometer in a stream of helium and analyzed using full scan mode in the mass range m/z 10−120 at a scan rate of 2.4 scans/s. A standard solution containing ethanol (1% v/v) and methanol (5% v/v) was prepared in chloroform [Caution: suspected cancer agent, danger of serious damage to health by prolonged exposure through inhilation and if swallowed]. An aliquot (50 μL) of the standard solution was introduced into the interface using a syringe with the membrane maintained at a temperature in the range 40−100 °C.

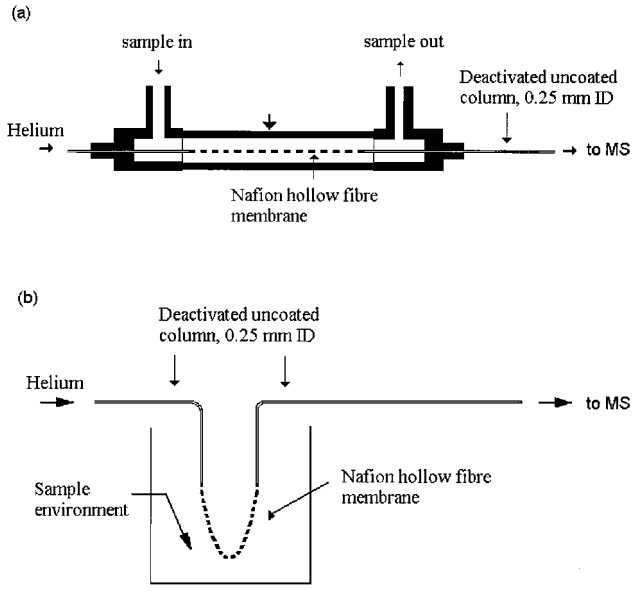

Figure 1. Schematic diagram of the RP-MIMS interfaces incorporating a Nafion hollow-fiber membrane employed for (a) system characterization and (b) real-time process monitoring.

A simplified membrane interface was used for on-line applications. (Figure 1b). This interface consisted of the same Nafion membrane (0.014-in. i.d.) fitted tightly onto two lengths of 0.25-mm-i.d. fused-silica tubing, using wire to secure the membrane to the tubing, which were connected to the GC injector and mass spectrometer ion source. The membrane was immersed in the sample for analysis. Mass spectra were recorded in full scan mode over the mass range m/z 10−120 at a scan rate of 2.4 scans/s. Response time and linearity were investigated via a standard additions approach as follows: The membrane was introduced into 100 mL of a stirred solution of 4% methanol in chloroform. Every 5 min, 0.5 mL of ethanol was added to the mixture, and the m/z 29 and 45 responses were monitored with time.

(b) Distillation of Chloroform/Alcohol Mixtures. The simplified MIMS interface configuration (Figure 1b) was used for the on-line investigation of chloroform/alcohol mixtures during a distillation process. The QMS 300 quadrupole-based RGA system (Stanford Research Systems (SRS), Stanford, CA) was operated under the following conditions: data were typically acquired in SIM mode using m/z settings appropriate for the analytes of interest (m/z = 45 for ethanol, m/z = 29 for methanol, and m/z = 35 for chloroform). The differentially pumped sampling/transfer line was actively heated to 60−70 °C to ensure no condensation of solvent vapor. Distillations were run on a 0.5-L scale using a LabMax automated lab reactor system (Mettler Toledo Inc., Hightstown, NJ) under typical process conditions. Condensed distillate collected in a receiving flask was monitored in real time by MIMS. Samples for comparative GC analysis were collected from the same flask periodically.

(c) Gas Chromatographic Analysis. Complimentary quantitative data for reference and comparison was obtained via analysis by GC/MS. A Hewlett-Packard HP 5890 GC and HP 5972 quadrupole analyzer were employed. The method used a Restek

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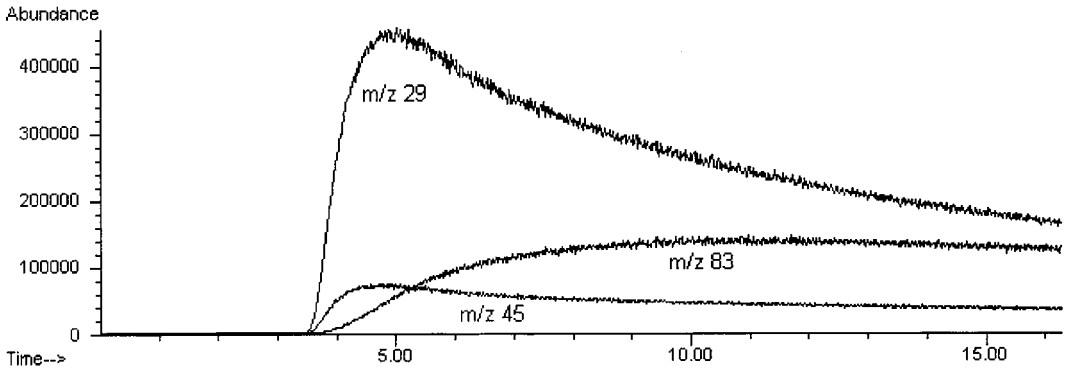

Figure 2. Mass chromatograms for the analysis of 5% v/v methanol and 1% v/v ethanol in chloroform by RP-MIMS using a Nafion membrane.

(Bellefonte, PA) DB Stabilwax column (30 m × 0.25-mm i.d.). The oven temperature was programmed as follows: 40 °C for 5 min, followed by a ramp at 20 °C/min to 200 °C.

RESULTS AND DISCUSSION

The studies described here were pursued with two objectives. The first was to perform a laboratory-based characterization of the behavior of the Nafion membrane for the analysis of mixtures of low molecular weight alcohols in chloroform. The second objective was to design and perform experiments to test the feasibility of a process application of the Nafion membrane in a RP-MIMS application involving a recovery process for chloroform by distillation in which methanol and ethanol concentrations represent important parameters.

(a) Characterization of Nafion Membrane under RP-MIMS Conditions. The performance of the Nafion hollow-fiber membrane for reversed-phase membrane inlet mass spectrometry (RP-MIMS) was investigated initially using the interface configuration shown in Figure 1a. The interface is based on a design previously reported for normal-phase MIMS.[5] The mass chromatogram obtained following exposure of the Nafion membrane to a pulsed sample injection of a mixture of chloroform, methanol (5%), and ethanol (1%) is shown in Figure 2. The responses for methanol and ethanol (m/z 29 and 45) rise rapidly following the introduction of the sample and begin to level off before a significant chloroform response (m/z 83) is detected, reflecting the selective permeation of the polar alcohols through the hydrophilic membrane. The higher diffusion coefficient for methanol leads to a faster initial rate of rise in the response curve.[22,23] The ability of the Nafion membrane to discriminate against the nonpolar chloroform solvent is apparent from the relative intensities of the chloroform and alcohol traces, which allows the membrane to be exposed directly to the mixture without the much higher concentration of the chloroform saturating the mass spectrometer. Ion intensities for m/z 29, 45, and 83 indicate that the Nafion membrane discriminates in favor of methanol and ethanol by factors of 67 and 55, respectively, relative to chloroform, assuming equal analyte responses. This discrimination allowed EI spectra to be recorded, although weak ions corresponding to protonated molecules characteristic of RP-MIMS applications were observed in some cases. The performance of the Nafion membrane was investigated over the temperature range 40−100 °C, and the optimum performance for the membrane was observed at 40 °C. At higher temperatures, the alcohol and chloroform responses were both reduced, and the highest temperature (100 °C) led to membrane failure.

An alternative procedure for the determination of methanol and ethanol in chloroform using normal-phase MIMS was also investigated. This involved extracting the methanol and ethanol into water by liquid−liquid partitioning, followed by partial degasification prior to analysis of the aqueous phase by MIMS using a polydimethylsilicone membrane. This approach allowed methanol and ethanol concentrations to be determined, although the trace levels of chloroform present in the aqueous phase were preferentially transported across the silicone membrane. However, this normal-phase procedure had to be carried out off-line and was, therefore, not readily amenable to on-line real-time process monitoring applications.

The linearity of the response for ethanol using the RP-MIMS method was determined over a working range of concentrations from 0.5 to 2.5% v/v. Figure 3 displays the data obtained during an RP-MIMS analysis in which additions of 0.5 mL of ethanol were made to 100 mL of ethanol-stabilized chloroform (starting concentration of ethanol, 5.7 g/L). The ethanol response (m/z 45, $C_2H_5O^+$) increases with each addition, but the m/z 29 response associated with methanol falls as a result of the dilution of the sample. A good linear response ($r^2 = 0.9959$) was observed for ethanol over the range by normalizing the mass spectrometry response for ethanol to the total ion current and correcting for volume changes.

(b) Real-Time Monitoring of Chloroform/Alcohols Distillation. The application of the RP-MIMS interface has been investigated for the real-time monitoring of methanol and ethanol concentrations in chloroform during a process distillation. This ternary system contains azeotropes that hamper the recovery of the halogenated solvent. As such, the alcohol concentrations (in particular ethanol) represent a critical quality parameter in this recovery process.[24] The RGA system was chosen for the analysis, because it has realistic process use possibilities.

A distillation of a solution of 4% (v/v) methanol as a cosolvent in chloroform containing 0.75% (v/v) ethanol as a stabilizer was

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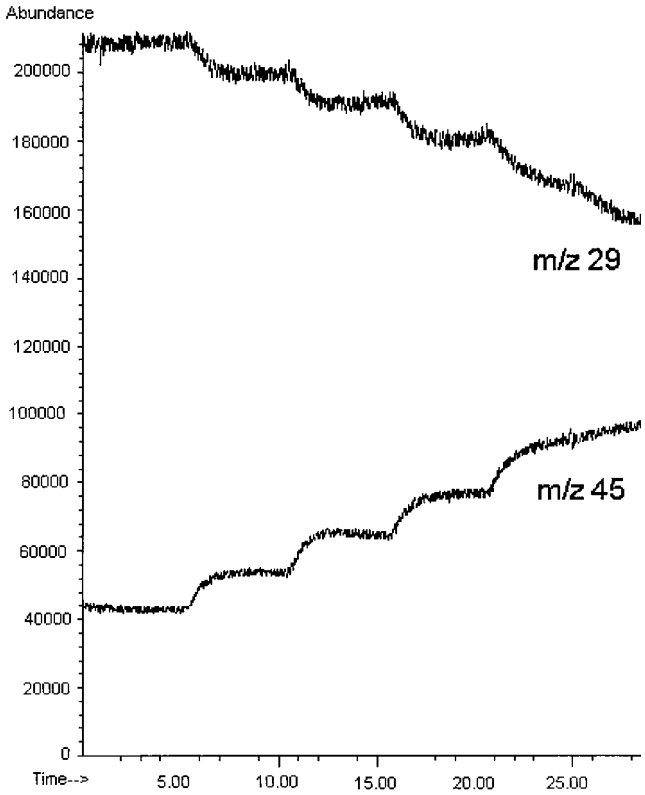

Figure 3. Mass chromatograms for the analysis of 5% v/v methanol in chloroform on addition of 0.5-mL aliquots of ethanol.

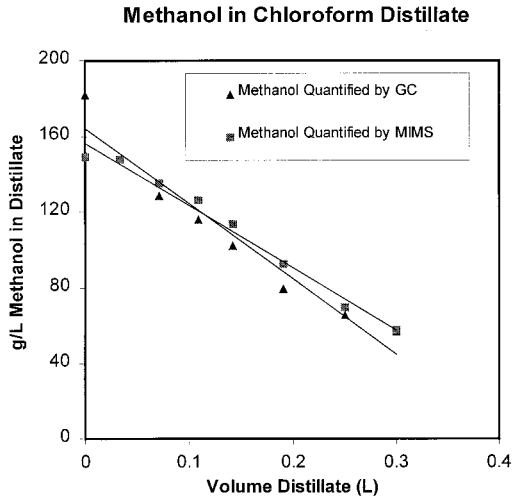

Figure 4. On-line monitoring of methanol in a distillation condensate by RP-MIMS and GC.

carried out, and the condensed distillate was monitored by RP-MIMS using the RGA. Normalized ion ratios 29/35 (COH^+/Cl^+) and 45/35 ($C_2H_5O^+/Cl^+$), relative to chloroform, were monitored for methanol and ethanol, respectively. These experiments were carried out in the laboratory at the 0.5-L scale. Sampling via RP-MIMS was carried out as described above. Data for monitoring the change in methanol and ethanol concentration are summarized in Figures 4 and 5.

The results obtained via mass spectrometry were referenced to data quantified by GC/MS. For referencing purposes, the MIMS results were scaled by a single GC/MS quantification. In the data shown in Figure 4, the reference point for quantification

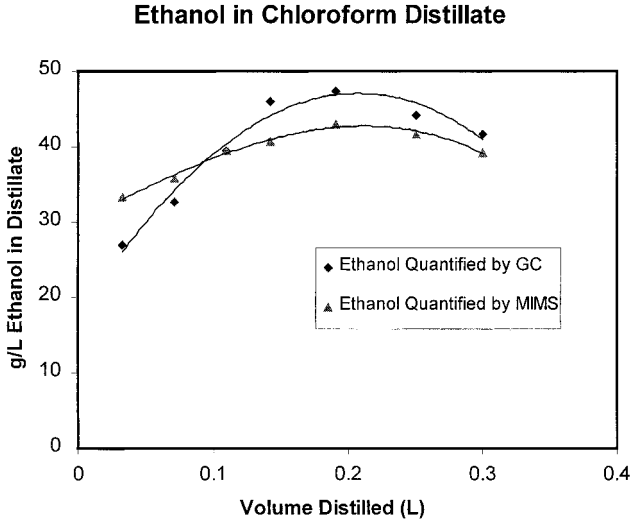

Figure 5. On-line monitoring of ethanol in a distillation condensate by RP-MIMS and GC.

is the point at 0.03 L of distillate where the data points for the two different techniques overlap. The results for the RP-MIMS and GC analysis show that the methanol concentration decreases during the evolution of the distillation process (Figure 4). Early fractions of the distillation are enriched with the more volatile alcohols that subsequently decrease in concentration in the collected distillate as less alcohol-enriched fractions are collected. In practice, this concentration could be monitored to a predetermined point, after which collection for solvent recovery of chloroform would begin. The portion of distillate that was being monitored would be reserved for an alternative recovery treatment being overly enriched in alcohols. The graph shows that the time evolution of the methanol concentration in chloroform distillate data obtained on-line by RP-MIMS using a Nafion membrane compares favorably with GC data for the condensate. The main difference is that the slope of the function obtained by using RP-MIMS is slightly less negative. The source of this difference is not yet clear; however, it may be related to a delay in the transfer of the alcohol across the membrane. The variation in the concentration of ethanol during the distillation, monitored by RP-MIMS and GC, is shown in Figure 5, where the quantitative reference was performed at 0.1 L distillate collected. The data sets for both methods show an initial increase in ethanol concentration, which reaches a maximum when the volume of distillate is ca. 0.2 L, before falling slightly. These results indicate that the RP-MIMS method also has potential for the monitoring of ethanol. The advantages of the MIMS approach, especially in comparison to an optically based method, is that real-time monitoring of methanol and ethanol during the distillation process is possible because of the ability of the mass spectrometer to distinguish between the alcohols.

CONCLUSIONS

The use of a hydrophilic Nafion membrane in the RP-MIMS analysis of mixtures of methanol, ethanol, and chloroform has been demonstrated. The membrane discriminates against the nonpolar chloroform, allowing the alcohols to be determined at concentrations below 0.5% v/v. The direct on-line introduction of sample mixtures into the reversed-phase membrane interface is

a convenient alternative to the lengthy off-line procedure required for normal-phase MIMS. The potential of RP-MIMS with a RGA for process monitoring has been investigated for evolving methanol and ethanol concentrations during a chloroform distillation process. The analyzer has been shown to be able to track vapor-phase compositions in real time, with reasonable accuracy and sensitivity. We have demonstrated a semiquantitative capability with a minimal approach toward calibration. A primary focus for further work will be to determine more precise methods toward calibration. Although these will not be required in all applications, a thorough understanding of this area is important.

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