

Trace level analysis of VOCs and semi-VOCs in aqueous solution using a direct insertion membrane probe and trap and release membrane introduction mass spectrometry

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Received 1st November 1999, Accepted 30th November 1999

A new design for a trap and release membrane introduction mass spectrometry (T&R-MIMS) system using a removable direct insertion membrane probe (DIMP) for combined trace level analysis (low or sub ppb range) of volatile (VOC) and semi-volatile organic compounds (SVOCs) is reported. The system differs from the original T&R-MIMS system (M. Leth and F. R. Lauritsen, *Rapid Commun. Mass Spectrom.*, 1995, 9, 591) as it uses a removable DIMP probe to place a capillary membrane loop inside the ion source block exactly between two parallel filaments. The more versatile DIMP-T&R-MIMS system can be operated, during the trapping step of T&R-MIMS analysis, in the standard MIMS mode for VOC detection; during the T&R-MIMS thermal desorption step needed for SVOC analysis, the system permits faster and more uniform heating of the membrane, thus SVOC sensitivity is improved and memory effects are minimized.

Introduction

Membrane introduction mass spectrometry (MIMS)¹ is a recent, fast-growing technique for the analysis of volatile organic compounds (VOCs), especially in aqueous matrixes. From chemical to biochemical and on to physiological monitoring, MIMS has found widespread use; its many advantages include simplicity, speed, high sensitivity, precision, nearly real-time and *in situ* monitoring.¹

MIMS benefits from selective transport of VOCs through a hydrophobic membrane, often of silicone polymer; VOCs are transferred frequently without any extraction or pretreatment from the aqueous matrix directly into a mass spectrometer. The membrane also works as an efficient interface between the matrix and the high vacuum of the mass spectrometer. The VOCs migrate from the aqueous solution to the membrane, concentrate in and diffuse through the membrane, and evaporate from the membrane surface directly into the high vacuum ion source region of a mass spectrometer, in which they are ionized and detected normally at trace levels (low ppbs or less).¹

For the analysis of semi-volatile organic compounds (SVOCs) and polar VOCs in aqueous matrixes, standard MIMS has been, however, unsatisfactory since the detection limits are often too high to be useful. Several approaches have therefore been proposed to improve MIMS detection limits for SVOCs and concurrently to lower the detection limits for VOCs: a typical approach has been to combine MIMS with a pre-concentration (trapping) method, using solid adsorbents,² cryotrapping,³ purging,⁴ headspace trapping,⁵ or analyte ion trapping.⁶ Ultrathin composite membranes (25–0.5 μm)⁷ normally reinforced with a microporous support have also been used to reduce transport time through the membrane. Since the analyte permeability is inversely dependent on membrane thickness, the ultrathin membranes alleviate the effect of low diffusivity or low solubility (or both) of SVOCs in silicone. Chemical derivatization of the SVOCs⁸ or indirect monitoring

of a related VOC analyte can also be useful alternatives for trace SVOC analysis by MIMS; recently, for instance, the selective and sensitive quantitation of cyanogenic glycosides in cassava root extracts was performed *via* hydrolysis and MIMS monitoring of the released ketone.⁹

But so far the most generally applicable approach for trace SVOC analysis by MIMS has been offered by the trap and release MIMS (T&R-MIMS) technique developed by Leth and Lauritsen and co-workers¹⁰ and Matz and Lennemann.¹¹ Poor responses for SVOCs with standard MIMS often result from their inefficient evaporation from the membrane to the gas phase. The original fully-integrated T&R-MIMS system¹⁰ is unique since it uses no external trapping: the SVOCs are preconcentrated inside the membrane itself, before fast thermal desorption¹² promotes efficient transport of the SVOCs into the gas phase. A tubular membrane, mounted between two 1/16 in stainless-steel tubes, passes straight through the ion source, and a long slit parallel to both the membrane and the filament allows heat radiation from the filament to reach the membrane continuously. An aqueous solution of the SVOCs (at near 0 °C or room temperature since the SVOC's solubility in the silicone membrane normally decrease with temperature) is flushed typically for 20 min through the membrane inlet, and during this period the SVOCs dissolve in, diffuse through and concentrate inside the membrane. The cooling fluid is then removed by pumping through the lines a plug of air for typically 50 s;^{10b} when the air plug reaches the membrane, the radiant heat from the filament rapidly heats the membrane to more than 300 °C. As a result, the SVOCs dissolved in the membrane evaporate rapidly, and are efficiently transferred to the gas phase. When compared to standard MIMS, responses are improved, typically 50 or more times higher; hence lower detection limits on the low or sub ppb range are obtained.

We now report on a more versatile and advantageous design for a trap and release MIMS system that uses a removable direct insertion membrane probe (DIMP)¹³ to place a capillary membrane loop inside the ion source block exactly between two parallel filaments. The new, more versatile DIMP-T&R-MIMS system allows combined trace level analysis (low or sub ppb range) of both volatile (VOC) and semi-volatile organic compounds (SVOCs); it promotes, during the thermal desorption step needed for SVOC analysis, uniform and fast membrane heating and efficient ionization. Hence, sensitivity is enhanced and memory effects are reduced.

Experimental

MS detection (scan speed of typically 6 spectra min^{-1}) was performed using 70 eV electron ionization and an Extrel (Pittsburgh, PA) mass spectrometer fitted with a high transmission (3/4 in) quadrupole. The standard ion source was used with just a minor modification: the id of one of the two gas entrance lines was enlarged to 1/2 in (see Fig. 1). The aqueous solutions were prepared in distilled water by serial dilution of 1 mg mL^{-1}

methanol solutions of the analytes. The solutions at room temperature (23 ± 1 °C) were pumped through the system by an eight-roll peristaltic pump at the rate of 2 mL min^{-1} . The capillary membrane was provided by Dow Corning Co. (Silastic Medical-grade tubing) with a wall thickness of 0.022 in, an id of 0.025 in, and an od of 0.047 in. The capillary membrane was expanded by hexane soaking and then fitted to the 1/24 in steel tubes of the DIMP probe; after hexane evaporation, a strong seal was attained.

Results and discussion

The DIMP-T&R-MIMS system

Design. Fig. 1 displays the orthogonal cross-sections of the DIMP-T&R-MIMS system with the DIMP probe (A) with a 1/2 in long capillary membrane loop (B) shown *in situ* in the ion source (D). In the original T&R-MIMS system¹⁰ the membrane and the stainless-steel tubings were mounted and fixed directly in the source. In the DIMP-T&R-MIMS system, however, the capillary membrane (B) is fixed into a removable DIMP probe (A), and a ceramic probe adapter (F) is used to ensure proper sealing. By finely adjusting the position of the DIMP probe, the membrane loop (B) can therefore be placed exactly between the two filaments (C) so as to ensure efficient ionization but particularly faster and more uniform heating. Heating of the whole membrane loop is actually attained by rotating the probe, thus slightly de-aligning the membrane loop so as to allow the upper filament to heat both the external surface of the upper loop face and the internal surface of the bottom loop face, and the bottom filament to heat both the external surface of the bottom loop face and the internal surface of the upper loop face. This uniform heating substantially reduces memory effects, as discussed below. The removable probe is also advantageous in

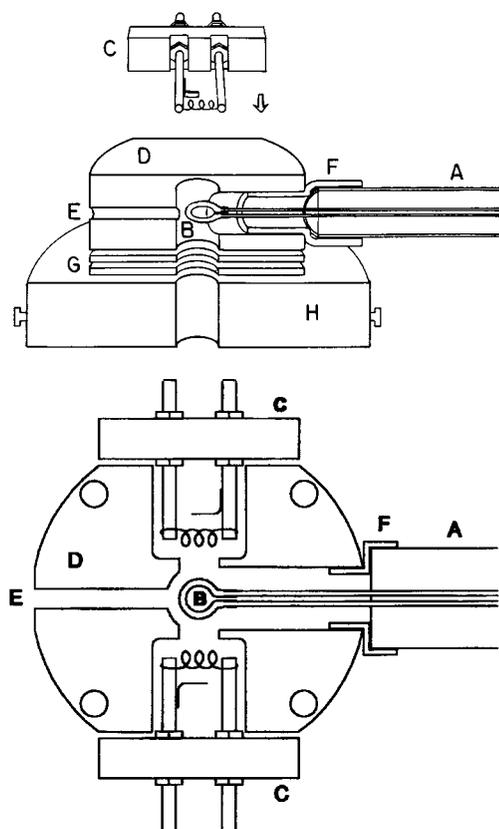


Fig. 1 Orthogonal cross-sections of the DIMP-T&R-MIMS system: the highlighted items are: A, DIMP probe; B, capillary membrane loop; C, filaments; D, ion source block; E, CI gas entrance; F, ceramic probe adapter; G, focusing lenses; and H, ion source holder.

other ways: it allows faster membrane replacement since it eliminates the need for instrument venting; the DIMP probe is only used when needed, and other standard or MIMS probes can be used and introduced *via* the same probe inlet system; the ion source can also be used for standard MS analysis.

Operation. Similarly to the original T&R-MIMS system,¹⁰ the DIMP-T&R-MIMS system can be operated either in the standard MIMS mode (more suitable for VOC detection)^{10b} or in the T&R-MIMS mode. For SVOC or combined VOC and SVOC analysis, a room temperature aqueous solution of the analyte is pumped typically for 10–20 min through the system to preconcentrate the SVOC inside the membrane, which is kept cold by the flowing fluid. During the SVOC preconcentration time, VOC analysis is performed by standard MIMS.¹ Then, an air plug of typically 40 s is introduced (simply by removing the pump tube from the aqueous sample solution) in the liquid flow. To end the air plug, the pump tube is introduced into room temperature distilled water, and water is pumped through the membrane for an additional 40 s. Then, for cleaning, two 40 s air plugs with a 1 min interval are sequentially introduced in the liquid flow.

Signal profile. Fig. 2 shows a typical signal profile for DIMP-T&R-MIMS analysis of a 500 ppb aqueous solution of β -naphthol using selective ion monitoring of the analyte molecular ion of m/z 144. As the solution starts flowing through the system (a), the signal rises and soon levels off at a relative low intensity, corresponding to the response for the system in its standard MIMS mode. During the 10 min of pumping, the SVOC is not efficiently transferred to the gas phase, but it dissolves, permeates and gets concentrated in the membrane. Then, a 40 s air plug is introduced (b); when the plug reaches the membrane (c), the temperature rises rapidly, the preconcentrated SVOCs are thermally and efficiently released to the gas phase, hence the signal rises and then drops sharply producing a well-defined, narrow, and for β -naphthol a nearly 50 times more intense, desorption peak. When the air plug ends (d), and since room temperature water is now flowing through the system, the membrane rapidly cools down and the ion signal drops sharply.

Memory effects. To clean the membrane of residual SVOCs, two additional 40 s air plugs with a 1 min separation are introduced just after sample analysis. The residual SVOCs are removed mostly during the first cleaning air plug (e, Fig. 2) and cleaning is clearly completed after the second air plug since the resulting desorption peak (f) is nearly as abundant as that continuously produced by heating the membrane alone, that is, from the membrane chemical noise.^{10a}

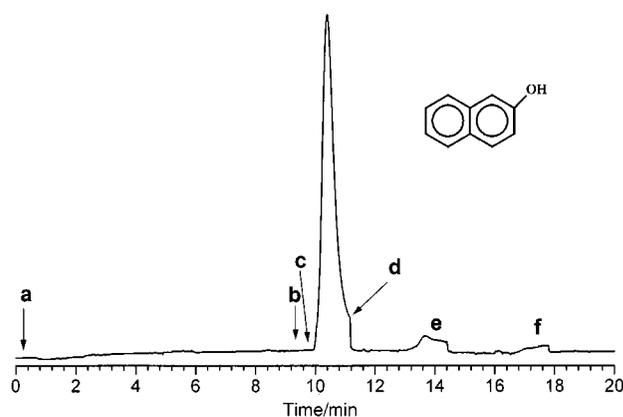


Fig. 2 DIMP-T&R-MIMS signal profile using selective ion monitoring (SIM) for 500 ppb aqueous solution of β -naphthol. a, Pumping starts; b, air plug is introduced in the system; c, air plug reaches the membrane loop; d, air plug ends; e, first cleaning air plug; and f, second cleaning air plug.

In the original T&R-MIMS system,¹⁰ which used a single filament, the 'dark' face of the capillary membrane was not sufficiently heated during the desorption step. Responses were therefore not as high and the system was found to be particularly sensitive to undesirable memory effects.^{10b} The uniform heating of the membrane loop provided by the DIMP-T&R-MIMS design results in uniform thermal desorption thus improving sensitivity while reducing memory effects.

Full mass spectra acquisition. The duration of the DIMP-T&R-MIMS peak is short, but long enough so as to allow the acquisition of many full mass spectra of the SVOCs; this is particularly useful for secure analyte identification and mixture analysis. Fig. 3 shows examples of the full mass spectra obtained for DIMP-T&R-MIMS analysis at the time of maximal desorption for aqueous solutions (500 ppb) of three representative SVOCs: β -naphthol, benzo(a)pyrene, and nicotine. Naturally, however, the more sensitive selective ion monitoring (SIM) scan mode should be applied for trace level analysis.

Other parameters. Relative and substantial gains (no lower than 50) for several SVOCs, broad dynamic range, high linearity and reproducibility, and low detection limits (low to sub ppbs) have been appropriately demonstrated for the original T&R-MIMS system.¹⁰ These parameters will not be discussed in detail here since our preliminary results for the new DIMP-T&R-MIMS system have indicated similar performance. The preliminary results for several SVOCs (β -naphthol, benzo(a)pyrene, nicotine, phenanthrene, salicylic acid, lactic acid, DMSO, and caffeine) as compared to those using a standard MIMS probe¹⁴ and to those reported for the original T&R-MIMS system¹⁰ point, however, to a 5–10-fold improved sensitivity (owing likely to the faster and more uniform

heating), and hence, to even lower detection limits of SVOCs in aqueous solutions when using the new DIMP-T&R-MIMS system.

Conclusion

The use of a removable direct insertion membrane probe (DIMP) in a trap and release membrane introduction mass spectrometry system is shown to be advantageous. The new DIMP-T&R-MIMS system is more versatile; it can work efficiently and sequentially in both the standard MIMS and T&R-MIMS modes for combined VOC and SVOC analysis, and can be used only when needed, thereby allowing replacement with other MIMS or standard probes, and the standard operation of the mass spectrometer. With the DIMP probe, the capillary membrane loop is placed inside the ion source block exactly between two parallel filaments. Fast and uniform heating of the membrane loop during the T&R-MIMS thermal desorption step is therefore accomplished; sensitivity is improved and memory effects are minimized.

Acknowledgements

This work has been supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq).

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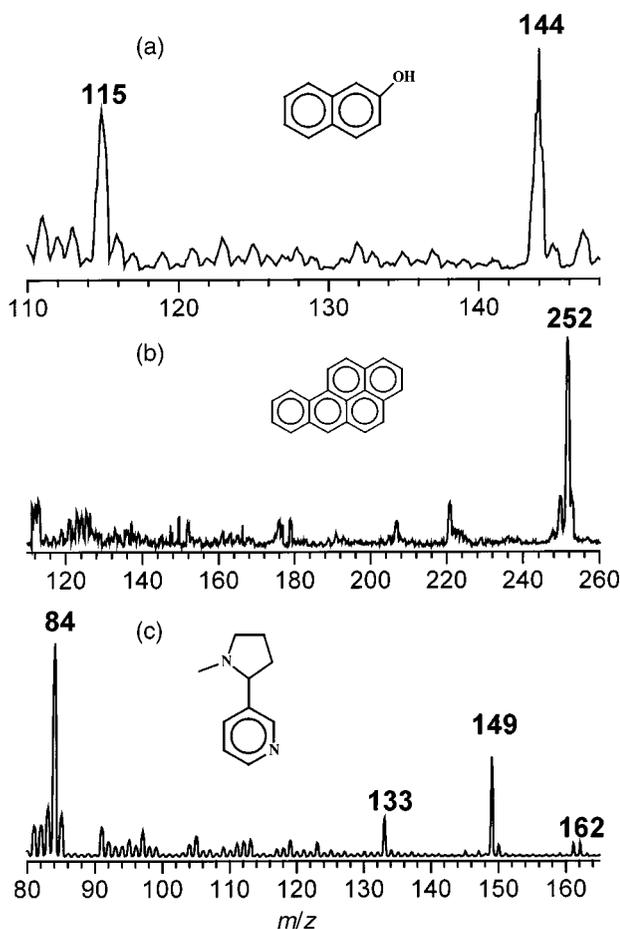


Fig. 3 DIMP-T&R-MIMS 70 eV EI mass spectra for 500 ppb aqueous solutions of (a) β -naphthol; (b) benzo(a)pyrene; and (c) nicotine. Note in (c) the ion of m/z 149 corresponding to plasticizers present in the membrane.

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Paper a908654d