International Journal of Mass Spectrometry 353 (2013) 26–35

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Characterization of a membrane inlet interfaced with a compact chemical ionization FT-ICR for real-time and quantitative VOC analysis in water

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ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form 1 July 2013
Accepted 1 July 2013
Available online 12 July 2013

Keywords:
MIMS
CI-MIMS
Compact FT-ICR/MS
Water analysis
PDMS properties
Photodegradation

ABSTRACT

A Chemical Ionization Membrane Introduction Mass Spectrometer (CI-MIMS) was evaluated, for use in the analysis of volatile organic compounds (VOCs) in aqueous solutions. The mass spectrometer was a compact high resolution FT-ICR/MS (Fourier Transform Ion Cyclotron Resonance, Mass Spectrometer) using Chemical Ionization by proton transfer from H_3O^+. The membrane inlet setup was based on a flat sheet PDMS membrane. Five VOCs (toluene, benzene, p-xylene, methanol and, phenol) were studied for their enrichment, response time, temperature dependence and pressure, dependence. The permeate concentrations were proportional to the feed concentrations. The enrichment factors varied from 7.7 (methanol) to 6000–9000 (xylene). The best enrichments were observed for the most hydrophobic compounds as was expected based on their octanol–water, partition coefficients. The response times were less than 1 min with the exception of phenol, which exhibited a response time of 5 min, due to its larger size and higher polarity compared with the other compounds.

The individual membrane permeabilities of water and the analytes increased with temperature. This temperature dependence enabled the determination of the activation energies of permeation. The methanol diffusion coefficient exhibited unique temperature dependence behavior, suggesting the existence of a transition temperature in the silicone membrane for methanol. Increasing the feed, pressure from 1 to 20 bar resulted in a linear increase in the enrichment factor of methanol, while the permeate pressure remained constant. Over 20 bar, the permeate pressure collapsed due to membrane, compression, and the enrichment factor leveled off.

A photodegradation experiment was successfully performed, and the CI-MIMS system was demonstrated to enable quantitative analysis in real-time.

1. Introduction

Volatile organic compounds (VOCs) dissolved in trace amounts in natural or treated water present a growing environmental concern. Benzene and its methyl or ethyl derivatives (BTEX), phenol derivatives and halogen compounds, such as trihalomethanes (THM), are among the most significant environmental pollutants. The ability to analyze multiple compounds in extremely dilute aqueous solutions is necessary to determine the composition of environmental samples. Novel in situ and real-time analyses are being used in field studies to evaluate the occurrence of highly toxic compounds or to rapidly identify target analytes in such applications as exhaust fumes analysis [1,2], polymer analysis [3] or electrochemical processes [4]. Nonetheless, the real-time analysis of complex mixtures remains a challenge in analytical chemistry.

The most common methods used for VOC analysis are based on gas chromatography (GC), which is often coupled with mass spectrometry [5]. Sampling and sample preparation may involve the direct injection of aqueous solutions, liquid–liquid extraction, headspace analysis using preconcentration by either cryogenic trapping or by solid-phase microextraction (SPME) followed by desorption, or dynamic headspace analysis using purge-and-trap systems [6–9]. These techniques are remarkably efficient and sensitive but require in-lab sample collection and do not allow on-site and continuous real-time measurements.

The direct and quantitative in-time analysis of trace VOCs in air can be performed efficiently in compact mass spectrometers using controlled chemical ionization (CI), which is a soft and selective

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http://dx.doi.org/10.1016/j.ijms.2013.07.001

ionization technique [10]. The most widely used CI reaction is the proton transfer reaction (PTR) [11]. PTR is very efficient for the analysis of a large variety of VOCs, such as oxygenated compounds, aromatics and nitrogenous compounds. Some molecules may induce fragmentation, such as in the dehydration of alcohols with three or more carbons [12] or long-chain aldehydes [13], the C—C bond cleavage of long-chain alkenes [14] or terpenes [15], alkene loss from protonated esters [16] and the formation of NH_4^+ from branched primary amines [17].

Chemical Ionization mass spectrometry (CIMS), and in particular PTR-MS, was first developed using drift tubes with quadrupole mass spectrometers [18] and has now been extended to various other instruments, such as Time-Of-Flight mass spectrometers [19] or Fourier Transform Ion Cyclotron Resonance mass spectrometers (FT-ICR/MS) [20]. FT-ICR/MS is characterized by its remarkable mass resolution [21]. Our group, which is associated with a university spin-off company (AlyXan), recently designed and built a compact FT-ICR/MS [20] suited for chemical ionization mass spectrometry and analytical applications. These instruments performed direct, real-time, quantitative analysis of VOC mixtures in air in the ppm range [3,22].

The present study aims to extend the method developed for air samples to similar direct analyses of trace VOCs in aqueous solutions.

The introduction of the sample was achieved using a membrane inlet (MI). The membrane is typically composed of PDMS, a hydrophobic polymer [23]. To extend the capacity of the MIMS technology to various solvents, and in particular to semivolatile solvents, various materials were proposed for use in the membrane inlet, including Nafion [24], allyl alcohol [25], Teflon and polyurethane [26]. The membrane serves two functions: (i) it acts as a physical barrier between the aqueous sample to be introduced in the mass spectrometer and the low-pressure gas phase, and (ii) it leads to the preferential pervaporation of VOCs over water and can also produce analyte preconcentration.

Membrane pervaporation techniques have been used for numerous applications in chemical analysis [30] and in water cleanup, such as VOC removal from industrial wastewaters [27–29]. For analytical applications, the membrane inlet has been coupled to several types of instruments, including gas chromatographs [31,32] and mass spectrometers. A number of reviews present the evolution of the MIMS technique for various applications, from BTX analysis to the analysis of low-concentration polar compounds such as drug residues [23,33,34]. Membrane Inlet Mass Spectrometry (MIMS) allows the direct mass spectrometric detection of VOCs in aqueous solutions [33,35–37] as well as in other environmental matrices, such as air or soil [34,35], and is commonly used with electron ionization (EI). However, EI produces highly fragmented molecules, complicating the identification of compounds in the highly complex mixtures that are commonly found in natural environments. In contrast, chemical ionization (CI) offers the advantages of soft and selective sample ionization and improved sensitivity. The first precursor ions to be used in CI were O_2^+ [38] and NO^+ [39], and, more recently, MI-PTR-MS (membrane inlet-proton transfer reaction mass spectrometry) has been performed using the soft and general precursor H_3O^+ [40]. MI-PTRMS has also been shown to allow the direct analysis of dilute aqueous solutions [41]. FT-ICR mass spectrometry provides the advantage of allowing low pressure introduction of the gaseous sample into the ICR cell, employing pressures of less than 10^{-5} mbar, which are easily achievable in the permeate under appropriate membrane conditions. Thus, dilution with a carrier gas is unnecessary, in contrast to PTR-MS instruments. Effective preconcentration by the membrane is expected and should lead to an improvement in sensitivity compared with gaseous samples.

Toward this goal, we built a membrane inlet for direct solution sampling, coupled it to a compact FT-ICR mass spectrometer and tested the sampling apparatus using solutions of known concentration. In this report, we describe this new analytical device and report its analytical performance. We studied the dependence of enrichment on the experimental conditions and present a photodegradation experiment conducted using CI-MIMS as an example of the real-time application of our system.

2. Experimental methods

2.1. Experimental setup

The flat sheet membrane was secured between 2 stainless steel (SS) rectangular plates (cf. Fig. 1). Each stainless steel plate contained a linear channel 4 cm long, 1.5 mm wide and 1.5 mm deep. The flat sheet membrane was used to cover the channels over a large area to prevent leaks. The total exchange area was 60 mm^2. The membrane was composed of a silicone elastomer (Goodfellow Cambridge Ltd., Huntingdon, UK, MQ/VNQ/PMQ/PVMQ film SI301025) equivalent to the Silastic® elastomer typically employed for MIMS. Film thicknesses of 50 μm and 125 μm were tested. Aqueous samples were flowed over the membrane using a peristaltic pump (Masterflex® Numeric L/S1.6–100 rpm) at a constant flow rate of 100 mL/min. The water supply system was closed to allow recirculation of the samples. A 1/4″ PFA tubing (0.047 in. ID) was used for the sample feed tube, except in the peristaltic pump, where Viton® FDA tubing (tubing 17, Masterflex®) was used. The permeate was pumped continuously by a 70 L/s turbomolecular pump to the mass spectrometer (Balzers Pfeiffer®, TMU065) through a 1/4″ SS tube inserted in the center of the channel on the vacuum side. The permeate pressure was measured in the ICR cell vacuum chamber. Under typical conditions, the permeate pressure was approximately 10^{-5} mbar.

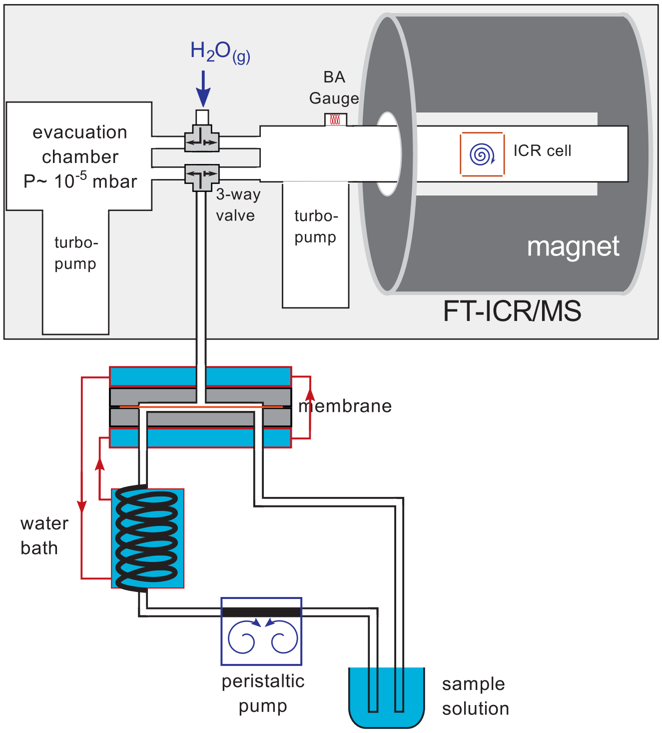

Fig. 1. Scheme of the experimental apparatus, comprising water circulation, a membrane assembly and an FT-ICR mass spectrometer. The ICR vacuum chamber is displayed on the right, and the evacuation line is displayed on the left.