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Internally heated membrane interfaced to a gas chromatography flame ionization detector

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ABSTRACT

Volatile Organic Compounds (VOCs) mixtures in aqueous solutions have been investigated using a simple and efficient all-in-one on-line sampling, isolation, enrichment and pre-concentration internally heated membrane connected to a gas chromatography flame ionization detector (GC-FID). In our previous study with the internally heated membrane, no GC column was used in the instrument. In this new study, we introduce a GC column in the instrument design and this makes it possible for mixtures to be investigated. This new experimental design enabled high resolution separation of analyte mixtures capable of being adsorbed, diffused, and desorbed from the device for detection with an FID. With the new design we present data from investigation of competitive adsorption effects on the membrane. The data showed that analyte adsorption and diffusion onto the membrane can be affected when mixtures of analytes are introduced. The application of multiple linear regressions approach to the data enabled us to correct for the problem of competitive adsorption. Analyte adsorption and diffusion was affected by the diffusion coefficients of the analytes; the higher the diffusion coefficient the better the extraction from the membrane. Increasing the sampling time from 1 to 4 min increases the response by 77%. The sampling time responses were linear up to 4 min sampling time. Above 4 min sampling time, the data deviate from linearity. The effect of adding salt to standards has no effect on analyte absorption onto the membrane. The detection limits for key VOCs studied with an internal standard calibration ranged from 0.2 to 194 ng cm^{-3}.

1. Introduction

The development and validation of sample introduction techniques in analytical instruments for the analysis of volatile organic compounds (VOCs) is important for the surveillance of environmental and clinical samples. In recent time, most sample introduction techniques used with analytical instruments have used direct injection [1], solid phase microextraction (SPME) [2–5], headspace analysis [6–8], purge and trap [9], pyrolysis [10], solid phase aroma concentrate extraction (SPACE) [11], electrospray ionization [12–14], exponential dilution [15–17], and recently stir bar sorptive extraction (SBSE) [18] to name a few. All of these techniques with the exception of headspace analysis and purge and trap require an extra sample preparation step before any sample analysis can be initiated. More specifically, headspace analysis has disadvantages in that the blocking syringe injection poses a major problem. Cleaning blocked syringes, in addition, to keeping the syringe warm at all times for each injection can be time consuming, delaying the rate at which data is generated. Purge and trap analysis also requires a lot of time in preparing the sample and making sure a gas tight system is created before analytes can be successfully adsorbed onto the adsorbent bed. SPME and SBSE are simple solvent-less techniques that can allow extraction and concentration in a single step [3,18]. However, it should be noted that analysis time is also extended for these two sample introduction techniques. There is clearly a need for the development of sample introduction techniques that require no sample preparation before analyses of VOCs in environmental and clinical samples.

Membrane sample introduction (or inlets) was combined with mass spectrometry and first reported by Hoch and Kok back in 1963 [19] during their study of the kinetics of photosynthesis gases. The same sample introduction technique combined with a gas chromatography mass spectrometry (GC/MS) was demonstrated in 1969 [20]. In recent years advances in membrane inlets owed its current development to the exploitation of modern interfacing with MS, GC and GC/MS. Applications developed include environmental analysis [21,22], on-line process control [23,24], flavors and fragrances, pharmaceutical quality control and chemical and biological reaction monitoring [25,26].

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In membrane inlets, VOCs are transported in a matrix of interest to the desired instrument and can be divided into three steps:

I Selective adsorption of analyte at the membrane surface. This adsorption is controlled by hydrophobic/hydrophilic interactions between the sample and the membrane material.
II Permeation through the membrane, controlled by diffusion of the analyte across a concentration gradient, normally the rate-determining step of the transport process.
III Desorption into the analytical system for detection, which is dependent on the volatility of the analyte.

Several investigations have utilized a variety of membranes [27,28]. However, silicone membranes are most commonly used as it has been noted they perform a genuine extraction of desired analytes from the rest of the sample in real time. The high selectivity of silicone membranes allowed VOCs to be determined in the presence of other components in a complex air or water matrix.

In membrane inlet research, two areas have been the subject of interest: enhancing the sensitivity and selectivity of the technique and extending the range from low molecular weight (high volatility compounds) to polar and less volatile analytes [29]. Most designs employed have been classified into one of three configurations, (a) inlets where the membrane is located at the end of an evacuated transfer line and inserted directly into the sample, [30,31] (b) purge-flow inlets, in which analytes diffusing through the membrane are transported to the ion source in a flow of inert gas, usually helium, [21,32] and (c) the direct insertion interface, where the membrane is placed at the end of a probe which is then inserted into a mass spectrometry vacuum system so that analytes diffusing through the membrane are evaporated directly into the ion source region [33,34]. Some of these designs have made use of an external heater during the release step which tremendously enhanced the range of semi-VOCs to be detected with high sensitivity [21,35–37].

This investigation presents the alternative approach. Our design allowed membranes to be thermally desorbed internally using a temperature program cycle to facilitate the release step and generate low-resolution separations, but improved sensitivity and selectivity of key VOCs and semi-VOCs. The membrane was designed with the capability to change its properties in order to suit its environmental performance. The design also allowed tuning of operational parameters to enhance its performance. This novel sample introduction device enabled the membrane to be heated to whatever temperature fit the operating range of the membrane material. This feature could allow a wide range of compounds to be studied. The detailed drawing of the device, complete description of how the heaters operate, and the theory behind the approach together with the initial investigations establishing effect of temperature programming and concentration for single analytes in the absence of a GC column was described previously [38,39].

This report presents studies on mixtures when the silicone membrane inlet was interfaced through a capillary GC column. Our research investigates competitive adsorption effects on the membrane, sampling time, addition of salt on standards, and the effect of introducing an internal standard. We also perform calibration studies with the internally heated membrane sample introduction unit using a gas chromatography separation stage. The construction of the internally heated membrane GC-FID unit may well be an effective sample introduction interface for conventional analysis in that liquid samples can be analyzed quickly in a short period of time without any sample preparation. We have noted that this approach may well be a better alternative when compared to techniques like headspace or purge and trap specifically for the analysis of VOCs in surface waters, wastewaters, soils, and even clinical samples.

2. Experimental section

2.1. Instrumentation

The fundamental components of the instrument consisted of an internally heated membrane, a CP 9001 gas chromatography (Chrompack UK Ltd., Millharbour, UK) fitted with a flame ionization detector. The sampling unit was constructed from a poly(dimethylsilicone) elastomeric capillary membrane [10 cm long, 1.5 mm O.D., and 0.5 mm I.D.], (Goodfellow Ltd., Cambridge, UK). Separate stainless steel Valco tube connectors (1 cm long, 2 mm O.D., 0.53 mm I.D.) were pushed through both ends of the elastomeric membrane. Because the membrane has elastic properties, this insertion created a gas tight seal. The seal was constantly inspected for leaks. The internal heater was a 125 μm stainless steel wire threaded through the membrane and arranged in a zigzag manner such that it makes electrical contact with the stainless steel tubes. The final arrangement was fitted into a threaded screw PTFE cap (designed by the workshop at the University of Manchester) to fit a 25 mL glass vial (Chromacol Ltd., Herts, UK). The entire vial configuration was held in place by a stainless steel mounting block fitted on top of the GC. The stainless steel Valco tubes on both ends of the membrane were interfaced to a 1/16″ Swagelok straight union. One end of this union was interfaced with the carrier gas, and the other end interfaced to a 75 cm long stainless steel deactivated alumina clad capillary column (0.53 mm I.D.) transfer line. This line was sent through the injector of the GC and interfaced with another 1/16″ Swagelok straight union to the column.

The GC oven was fitted with a DB-5 column, 30 m long×0.25 mm I.D., and a stationary phase thickness of 1 μm (QMX equivalent of DB-5 to J & W, QMX Laboratories Ltd., UK). The outlet of the column was connected to the flame ionization detector of the CP 9001 gas chromatography. Fig. 1 is a summary schematic representation of the experimental arrangement. Oxygen free nitrogen gas was purified by passing it through molecular sieves adsorbent traps. The flow of carrier gas was controlled by needle valves and further by the 2-stage pressure controller of the GC, and monitored with a calibrated digital flow meter.

To operate the internal heater on the membrane, a power transistor controlled from a PCI-6024E data acquisition card (National Instrument) running a LabView code programmed specifically for the

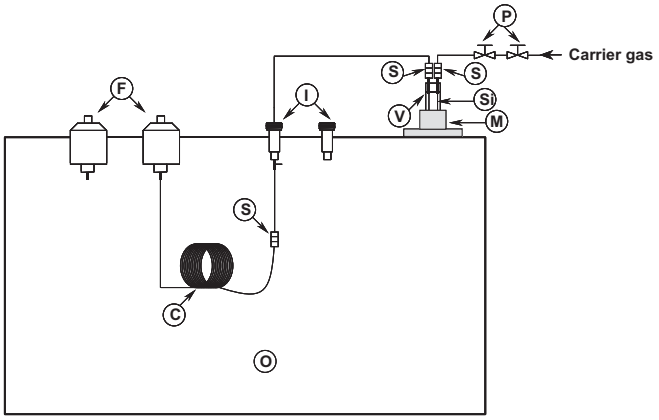

Fig. 1. A schematic diagram of the experimental arrangement used for GC-FID tests. The silicone membrane fitted on a 25 ml vial was mounted on a stainless steel block fitted on top of the CP 9001 gas chromatography. Temperature programming the membrane was achieved by allowing the threaded wire fitted inside the membrane to make electrical contact with the stainless steel tube on both sides of the membrane. The transfer line to the column was always kept hot by the combination of injector and oven temperatures. *S*=1/16″ stainless steel straight unions, *P*=pressure regulators, *V*=25 mL vial, *M*=stainless steel mounting block, Si=poly(dimethylsilicone) membrane, *O*=GC oven, *C*=capillary column, *I*=GC injector, and *F*=FID.