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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

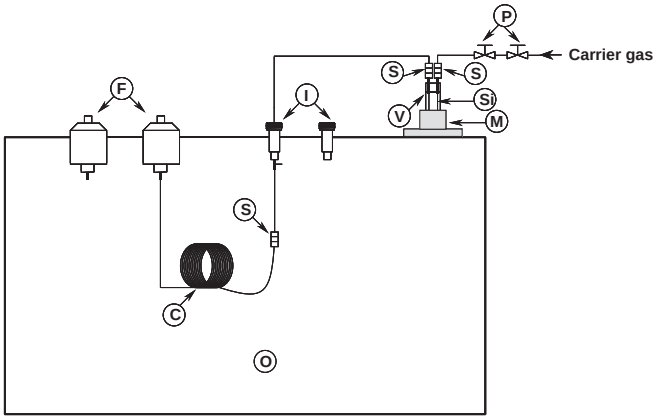

Fig. 1. A schematic diagram of the experimental arrangement used for GC-FID tests. The silicone membrane fitted on a 25 ml vial was mounted on a stainless steel block fitted on top of the CP 9001 gas chromatography. Temperature programming the membrane was achieved by allowing the threaded wire fitted 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.

task was used to control the current in the heating element and hence its temperature. The design of the sampler enabled a range of heating profiles to be used for the internal heater. The different heating profiles will be described later. The external temperature was monitored by mounting a thermocouple outside of the membrane near the carrier gas inlet. The thermocouple responses and FID signals were also captured with the PCI-6024E data acquisition card. Modeling was used previously to describe the theoretical background behind our design. The operation of the internal heater inside the membrane has also been described [38,39]. In this new configuration, the updated operating parameters have been summarized in Table 1.

2.2. Reagents and standards

All vials and separating funnels used in the analysis were washed overnight in Decon (Fisher Scientific, Leicestershire, UK). This was followed by rinsing several times with distilled water (distilled and deionized to 18 MΩ) and then left to bake out overnight in an oven at 200 °C. Aqueous standards were used in this investigation and the following features of the analytes used were taken into account: volatility, low solubility, stability at low concentrations, and risk of contamination between runs. All standards were prepared immediately before use, headspace volumes were minimized and vials sealed at all times to minimize issues of volatility. For low volatility analytes, standards were prepared by placing 24.9 cm^3 of distilled water into a separating funnel. This was followed by adding 0.1 mL aliquot of the analyte to the funnel. The two layers were gently swirled and allowed to equilibrate at room temperature. Saturation was assumed after repeated swirling and allowing the funnel to stand for up to four hours. The saturated solution was decanted from the bottom of the separating funnel into a vial and concentration of the stock solution was calculated from the solubility value of the analyte. Lower concentrations of analytes were prepared by serial dilution using a precision pipette and 18 MΩ distilled water. Precautions were taken to ensure that small droplets of the immiscible analytes did not elute into the vials during the separation process. This could have resulted in pure analytes touching the membrane introducing errors in the data.

Water soluble standards were prepared directly in vials and the solution retained for serial dilution. Contamination checks were addressed by taking blank runs between experiments. It should be noted that several VOC's were investigated in these studies. The VOC's studied were volatiles and semi-volatiles and these were VOCs and semi-VOCs commonly encountered in contaminated water samples. The device was capable of analyzing both VOCs and semi-VOCs, which demonstrates the device versatility.

3. Experimental procedure

3.1. Experiment ♯1: adsorption studies

Two analytes, o-xylene and 2-chlorophenol were chosen to investigate the effect of competitive adsorption on the membrane. These two analytes have different solubility in water and are also common water contaminants. Five concentrations for each analyte (o-xylene: 0.9, 4.4, 9, 18, and 27 μg cm^{-3}; 2-chlorophenol: 5.5, 18, 182, 274, and 456 ng cm^{-3}) were chosen and each varied against the other using a central composite design. The fact that the concentration of o-xylene chosen for this study were a 1000 fold greater than those of 2-chlorophenol was an indication of 2-chlorophenol having a higher diffusion coefficient than o-xylene. In the central composite design, concentrations were varied against each other giving a total of 25 experiments. To generate the data, three replicates were taken for each sample. This gave us a total of 75 experiments. The experimental order was selected based on a random number selection and the experiments carried out over a three-day period. The instrument settings defined in Table 1 was used for these sets of experiments.

3.2. Experiment ♯2: sampling time and addition of salt to standards

Pentanol and propylbenzene were chosen for these studies. Five sampling times from 1 to 5 min were chosen for this investigation. To ensure that concentrations chosen for these studies were within the linear dynamic range for each analyte, a calibration was conducted with the 1 and 5 min sampling time for pentanol and propylbenzene. Based on the data from the calibrations studies, two concentrations for pentanol (64 and 128 ng cm^{-3}) and propylbenzene (1.02 and 2.03 μg cm^{-3}) were chosen for each analyte. Further experiments were conducted on the chosen concentrations from

Table 1
Experimental and instrumental conditions.

Parameter	Setting
Column stationary phase	5% Phenyl and 95% Methyl
Carrier gas flow rate	5 cm^3 min^{-1}
Carrier gas identity	Nitrogen
Membrane identity	Poly(dimethylsilicone) elastomer tube
Membrane length	10 cm
Membrane outer ϕ	1.5 mm
Membrane wall thickness	0.5 mm
Membrane inner ϕ	0.5 mm
Stainless steel wire diameter	125 μm
Desorption temperature	130–150 °C
V_{in} at power supply	12.5 V
V_{in} at interface	12.29–12.47 V
Potentiometer range	0.8 Ω–4.98 KΩ
V_{out} to heater	4.83–5.5 V
Current driving heater	1650–1750 mA
Column head pressure	300 Kpa
Air pressure	150 Kpa
Hydrogen pressure	100 kpa
Injector	SMTD + Splitless + 280 °C
Detector temperature	280 °C
GC program	Start temperature, 50 °C; initial time, 0 min; ramp rate 25 °C/min; final temperature, 250 °C; final time, 0 min.

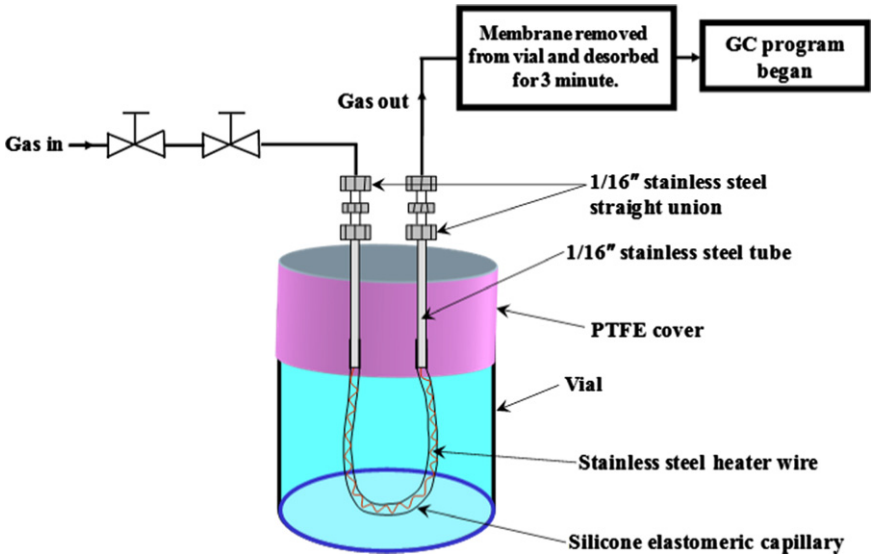

Fig. 2. A schematic diagram showing an expanded view of the internally heated membrane and process illustration of getting sample into the GC system.

1 to 5 min to demonstrate the device sampling time capability. The table below illustrates how the design for this part of the study was conducted.

Pentanol/ppb	Propylbenzene/ppm	
	X_{1i}	Y_{1i}
X_{1j}	1	3
Y_{1j}	2	4

where X_{1i} and Y_{1i}=1.02 and 2.03 μg cm^{-3}, respectively and X_{1j} and Y_{1j}=64 and 128 ng cm^{-3}, respectively.

In the table above, 1 represent a mixed analyte concentration of X_{1i} versus X_{1j} where X_{1i}=1.02 μg cm^{-3} and X_{1j}=64 ng cm^{-3} etc. The experiments for the different sampling time experiments were randomized. The randomization leads us to choose the order to run the experiments. The order that was determined and used to collect the data was 4, 3, 5, 2 and 1 min sampling times. More randomizations were conducted to determine the experimental order for the mixed analyte concentrations.

Salts were added to standards to determine whether this would lead to more analyte uptake on the membrane. The experiment was conducted to compare studies done with solid phase microextraction (SPME). SPME has been determined to increase analyte uptake on a fiber when salts are added to standards [3]. To investigate what effect addition of salt will have on the membrane, a 0.02 g cm^{-3} NaCl solution was used to prepare standards of pentanol. This standard was used to conduct a calibration study at 1 and 5 min sampling time. Three replicates were obtained for each sample. The instrument settings defined in Table 1 were also used for these sets of experiments.

3.3. Experiment ♯3: internal standard calibration with mixtures

Internal standard calibrations were carried out for a range of compounds in mixtures. The mixtures were chosen to reflect different functional group chemistries including-alcohols, aromatics and phenols. The internal standard used for the study of alcohols was octanol whereas that used for the study of aromatics was o-xylene. These two internal standards have similar physico-chemical behavior to our target analytes and are also easily found in future real samples. The concentration range studied for each analyte was randomized for each functional group and three replicates taken for each sample. Table 1 summarized the instrumental settings used for this study.

3.4. Internal heating control on membrane

A LabView code was written for this study to control both the heating and cooling process inside the membrane in addition to collecting the FID responses. This code was installed on a personal computer and the computer linked to the membrane and GC via an interface board. The output bit for temperature program control on the membrane was set between 0–255 bits with delays of 0.025 s. There were three modes of control for the membrane; fully desorbed, ramping, and clear. The fully desorbed mode enabled the membrane to be heated rapidly to the highest temperature possible. The ramping mode enabled temperature programming to be performed on the membrane. All our studies in this investigation used the ramping mode. The clear mode enabled the membrane to return to room temperature conditions, such that any fully desorbed or ramping program is cleared off the membrane. The experimental program was adjusted to fit with the sampling times. For e.g., for a 1 min sample time, the membrane was sampled for 1 min and, desorbed for 3 min before the GC program began. For a 2 min sampling time, the membrane was sampled for 2 min and, desorbed for 3 min before the GC program began. A similar experimental program was followed for the 3, 4, and 5 min sampling times. Fig. 2 is a schematic illustrating how the sample was transferred to the GC instrument.

In this study, the output bit for temperature programming was set to 5 steps s^{-1} and was ramped to 240 steps, with a delay of 0.025 s. The voltage output to the heater was between 4.83 and 5.5 V, thus the ramp rate using this time delay ranged between 4.03 and 4.58 V s^{-1} on the poly(dimethylsilicone) membrane. Voltages between these ranges corresponding to temperatures between 130–150 °C were used on the membrane to thermally release permeated analytes almost at once to the column head. This was followed by separation of analytes with the GC oven temperature program on the GC column. All separated analytes were then detected with an FID.

4. Result and discussion

4.1. Adsorption studies

The design of the membrane unit allowed a wire to be threaded through the central channel of the membrane, see Fig. 2 for details. The inner channel was also designed to incorporate a flow of inert carrier gas, flowing continuously over the wire. When the membrane was placed in contact with a sample matrix, volatile analyte was adsorbed onto the membrane surface and rapidly diffused into the central channel of the membrane. Movement of the analyte within the membrane's channel, and hence the effectiveness of the device as a sampling unit was determined by two factors: (i) the diffusion process on the membrane; and (ii) temperature control on the unit. The physics of the process has been described previously for a single analyte [38]. The adsorption studies investigated competitive adsorption when a matrix containing two analytes with different diffusion coefficient was introduced onto the membrane.

Fig. 3 shows typical responses at different concentrations for the two analytes that were chosen to investigate competitive adsorption effects on the membrane. The study of competitive adsorption effects of 2-chlorophenol in water in the presence of o-xylene revealed some level of interaction for the mixed permeates according to the data. For e.g., the mean FID responses of o-xylene at 4.4 μg cm^{-3} when mixed with 5.5, 18, 182, 274, and 456 ng cm^{-3} of 2-chlorophenol were 647, 699, 721, 1129, and 730 mV, respectively. It was clear that the response of 4.4 μg cm^{-3} o-xylene when mixed with 274 ng cm^{-3} 2-chlorophenol gave the highest response. The change that was demonstrated for 4.4 μg cm^{-3} o-xylene mixture with 2-chlorophenol indicates a variation of 33–35% for the responses on the membrane. The mean FID response for 274 ng cm^{-3} 2-chlorophenol when mixed with 0.9, 4.4, 9, 18, and 27 μg cm^{-3} of o-xylene were 730, 778, 998, 608, and 1112 mV, respectively. The highest response for 274 ng cm^{-3} 2-chlorophenol occurred with the mixture with 27 μg cm^{-3} o-xylene. The data demonstrated a variation of 10–45% variation on the membrane for 274 ng cm^{-3} 2-chlorophenol responses. Similar variations in responses were observed for the other concentrations studied. As indicated previously, concentration of o-xylene chosen for this study were a 1000 fold greater than those of 2-chlorophenol. This was because 2-chlorophenol has a higher diffusion coefficient than o-xylene. Nevertheless, if competitive adsorption were absent, deviations of responses from the different mixture profiles would have been minimal.

To further investigate the variation in responses observed, a calibration was conducted for the same concentration profiles of o-xylene and 2-chlorophenol as single components analytes. These calibration responses were overlaid with the responses from the competitive adsorption studies. Fig. 4 shows the calibrated responses of both o-xylene and 2-chlorophenol overlaid with the responses from the competitive adsorption studies. The deviations from the individual calibration data were minimal at low concentrations for both analytes. However at higher concentrations, levels of fluctuations were significant. These deviations from our calibration responses enabled us to apply multiple linear regressions (MLR) to our data. The goal was to correct for the wide variation in responses observed within the data. Two models were used, one with no interaction term, and the second making use of a multiplicative interaction term between the concentrations of o-xylene and 2-chlorophenol, Eqs. (1) and (2).

$$Y_{x_1,x_2} = B_0 + B_1X_1 + B_2X_2 \quad (1)$$

$$Y_{x_1,x_2,x_1x_2} = B_0 + B_1X_1 + B_2X_2 + B_3X_1X_2 \quad (2)$$

where X_1 represents concentration of o-xylene, X_2 represents concentration of 2-chlorophenol and B_0, B_1, B_2, B_3 are constants.

The predicted responses from Eqs. (1) and (2) were initially plotted against the observed responses and the slope, intercept and correlation coefficients seem to correlate well. Regression line

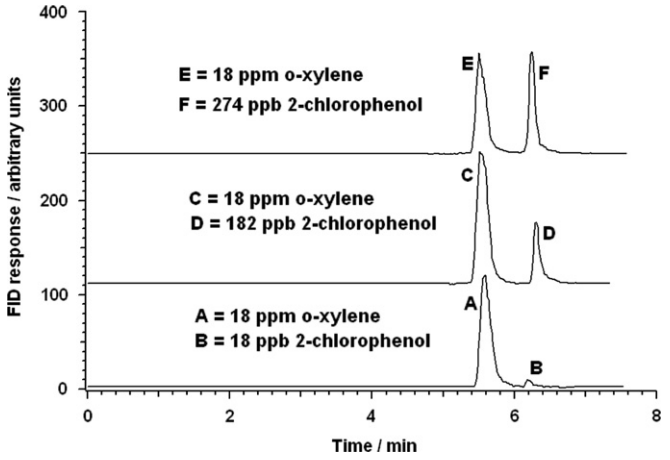

Fig. 3. Example responses for o-xylene and 2-chlorophenol from the competitive adsorption studies (On graph, ppm = μg cm^{-3}; and ppb = ng cm^{-3}).

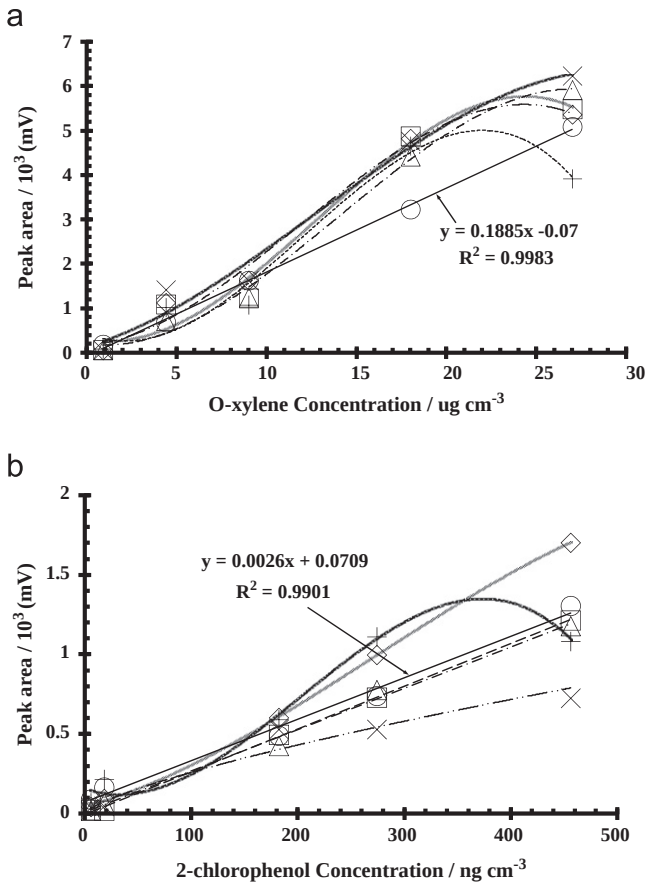

Fig. 4. Plot showing the individual calibrated response of o-xylene overlaid with responses of o-xylene from the competitive adsorption studies (a) and individual calibrated responses of 2-chlorophenol overlaid with responses of 2-chlorophenol from the competitive adsorption studies (b). In plot (a), the circles represent the single component calibration of o-xylene and squares, triangles, cross, diamond and positive cross represent o-xylene studied in a mixture with 5.5, 18, 182, 274 and 456 ng cm^{-3} of 2-chlorophenol, respectively. In plot (b), the circles represent the single component calibration of 2-chlorophenol and squares, triangles, cross, diamond and positive cross represent 2-chlorophenol studied with 0.9, 4.4, 9, 18 and 27 μg cm^{-3} of o-xylene, respectively. The result showed that at higher concentrations of both o-xylene and 2-chlorophenol, high level of deviations was apparent.

Table 2
Summary of multiple linear regression analyses on responses of 2-chlorophenol and o-xylene for the competitive adsorption studies. These regression summaries are the lines shown in Fig. 4 (model 1) and Fig. 5 (model 2). The first 4 rows in the table is the regression line summary for the plot of observed response vs. predicted response.

Description	Slope	Intercept	R^2
Model 1: o-xylene	0.9996	0.006	0.9165
Model 1: 2-chlorophenol	1.0003	−0.0003	0.8792
Model 2: o-xylene	0.9996	0.0009	0.9252
Model 2: 2-chlorophenol	1.1100	0.0049	0.8709
o-xylene individual calibration response	0.1885	−0.07	0.9983
o-xylene in a mixture with 5.5 ng cm^{-3} 2-chlorophenol (model 1)	0.2169	0.0655	1
o-xylene in a mixture with 18 ng cm^{-3} 2-chlorophenol (model 1)	0.2169	0.0574	1
o-xylene in a mixture with 182 ng cm^{-3} 2-chlorophenol (model 1)	0.2169	0.0481	1
o-xylene in a mixture with 274 ng cm^{-3} 2-chlorophenol (model 1)	0.2169	0.1073	1
o-xylene in a mixture with 456 ng cm^{-3} 2-chlorophenol (model 1)	0.2169	0.2245	1
o-xylene in a mixture with 5.5 ng cm^{-3} 2-chlorophenol (model 2)	0.2397	−0.2053	1
o-xylene in a mixture with 18 ng cm^{-3} 2-chlorophenol (model 2)	0.2381	−0.1984	1
o-xylene in a mixture with 182 ng cm^{-3} 2-chlorophenol (model 2)	0.2175	−0.056	1
o-xylene in a mixture with 274 ng cm^{-3} 2-chlorophenol (model 2)	0.206	0.0219	1
o-xylene in a mixture with 456 ng cm^{-3} 2-chlorophenol (model 2)	0.1831	0.1759	1
2-chlorophenol individual calibration response	0.0026	0.0709	0.9901
2-chlorpphenol in a mixture with 0.9 μg cm^{-3} o-xylene (model 1)	0.0026	−0.0285	1
2-chlorpphenol in a mixture with 4.4 μg cm^{-3} o-xylene (model 1)	0.0026	−0.003	1
2-chlorpphenol in a mixture with 9 μg cm^{-3} o-xylene (model 1)	0.0026	0.0304	1
2-chlorpphenol in a mixture with 18 μg cm^{-3} o-xylene (model 1)	0.0026	−0.0957	1
2-chlorpphenol in a mixture with 27 μg cm^{-3} o-xylene (model 1)	0.0026	−0.1611	1
2-chlorpphenol in a mixture with 0.9 μg cm^{-3} o-xylene (model 2)	0.0024	−0.0157	1
2-chlorpphenol in a mixture with 4.4 μg cm^{-3} o-xylene (model 2)	0.0024	0.0157	1
2-chlorpphenol in a mixture with 9 μg cm^{-3} o-xylene (model 2)	0.0024	0.0323	1
2-chlorpphenol in a mixture with 18 μg cm^{-3} o-xylene (model 2)	0.0023	0.0856	1
2-chlorpphenol in a mixture with 27 μg cm^{-3} o-xylene (model 2)	0.0022	0.1389	1

summary for the plot of observed response vs. predicted response are summarized in the first 4 rows of Table 2. Lines 5 and 16 were the data for the single component calibration of o-xylene and 2-chlorophenol, respectively. The predicted response data was then overlaid with the original calibration curves and Fig. 5a shows the MLR lines generated from Eq. (1), without the interaction term for o-xylene. Fig. 5b shows the MLR lines from Eq. (2), with the interaction for 2-chlorophenol. Similar results were obtained for the 2-chlorophenol model 1 data and the o-xylene model 2 data. In all cases, model 1 and 2 yield correlation coefficient of 1 (see Table 2). The data that showed levels of deviation for both o-xylene and 2-chlorophenol in Fig. 4 was fitted with high accuracy. Based on the data, the models thus reveal there were some levels of interaction for the analytes studied at high concentrations. Thus for the membrane used in this study, the adsorption and diffusion effect of an analyte can be affected when a second analyte is present. Table 2 gives a summary of the respective slopes and intercepts of the fitted lines for all the data accompanied with their respective correlation coefficients.

4.2. Sampling time and addition of salt

Fig. 6 shows plots for the two component sampling time studies. In Fig. 6a, the responses are for a 64 and 128 ng cm^{-3} pentanol standard. The plot show pentanol responses in the following mixture compositions: (i) 64 ng cm^{-3} pentanol vs. 1.02 μg cm^{-3} propylbenzene (triangles); (ii) 64 ng cm^{-3} pentanol vs. 2.03 μg cm^{-3} propylbenzene (circles); (iii) 128 ng cm^{-3} pentanol vs. 1.02 μg cm^{-3} propylbenzene (cross); and (iv) 128 ng cm^{-3} pentanol vs. 2.03 μg cm^{-3} propylbenzene (squares). In Fig. 6b, the responses are for a 1.02 and 2.03 μg cm^{-3} propylbenzene standard. The plot show propylbenzene responses in the following mixture compositions: (i) 1.02 μg cm^{-3} propylbenzene vs. 64 ng cm^{-3}pentanol (triangles); (ii) 1.02 μg cm^{-3} propylbenzene vs. 128 ng cm^{-3}pentanol (circles); (iii) 2.03 μg cm^{-3} propylbenzene vs. 64 ng cm^{-3}pentanol (cross); and (iv) 2.03 μg cm^{-3} propylbenzene vs. 128 ng cm^{-3}pentanol (squares). Fig. 7 shows some example spectra obtained from these studies at a sampling time of 4 min. The two component design sampling time studies revealed that analyte adsorption and diffusion has a linear dependence with concentration for up to 4 min sampling time. Furthermore, increasing the sampling time from 1 to 4 min increased sensitivity of the response by 77%. The response has shown to increase linearly up to 5 min sampling time where deviation occurred. At the concentrations studied for both analytes, the deviation from linearity was pronounced after 4 min sampling time. Inspection of the calibration data obtained for the single components of both pentanol and propylbenzene revealed that a reduce response was obtained when two analytes were sampled in a mixture on the membrane. This observation was in line with the competitive adsorption studies discussed above. This indicates that the deviation from linearity may not only be due to detector artefacts. To investigate this problem further a one-way ANOVA analysis was applied to the data at 1 and 5 min sampling times.

Table 3 shows a summary from the ANOVA analysis. For 1 min sampling time, $F_{3,8}=3.92$, and from statistical table $F_{3,8}=4.066$ at the 95% confidence level. Our calculated value was less than the value at 95% confidence limit, hence the null hypothesis was adopted for 1 min sampling time; we account that the samples were drawn from a population with mean μ and variance σ_0^2. The difference between the means for 1 min sampling time can thus be accounted for by random error. With the data for 5 min sampling time, $F_{3,8}=19.8$, and from statistical table $F_{3,8}=4.066$ at the 95% confidence level. The calculated value was greater than the value at 95% confidence limit, hence the null hypothesis is rejected; we account that the sample mean for 5 min sampling time do differ significantly. The ANOVA analysis reveals that there was a significant difference between the sample mean obtained at 5 min sampling time. It is important to note that the deviation from linearity was more pronounced at low concentrations for both analytes. It is not quite clear at this stage why this was the case and a logical explanation could be that for the longer sampling times some sort of interaction or reverse permeation has taken place leading to a loss of response. This effect was however minimized for the concentrated solutions. Nevertheless, the sampling unit used for these studies was impressive in the sense that even 1 min of sampling on the membrane was enough to perform an analysis for aqueous samples.

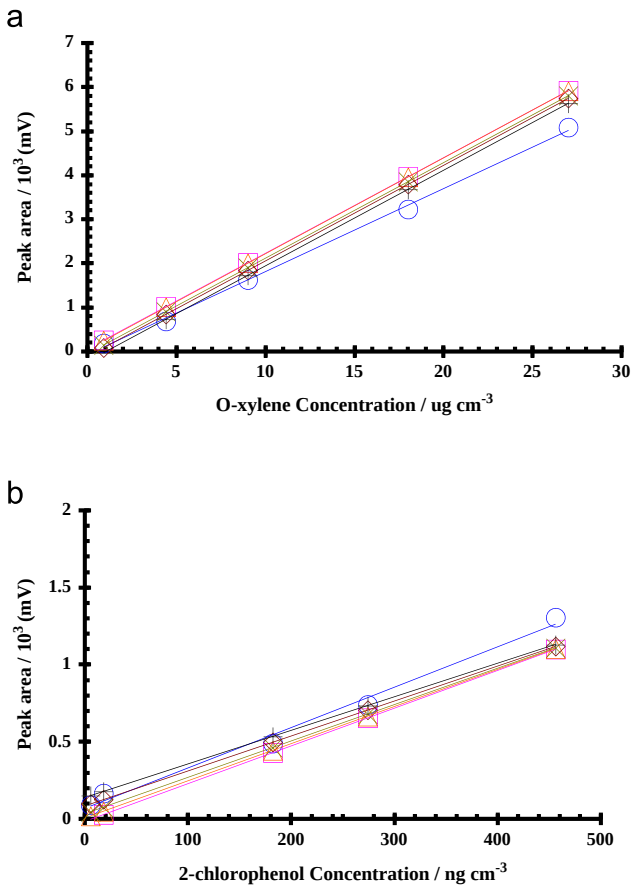

Fig. 5. Multiple linear regression data generated for o-xylene (a) in the absence of the interaction term using Eq. (1), and 2-chlorophenol (b) in the presence of the interaction term using Eq. (2). In plot (a), the circles represent the single component calibration of o-xylene and squares, triangles, cross, diamond and positive cross represent o-xylene studied with 5.5, 18, 182, 274 and 456 ng cm^{-3} of 2-chlorophenol, respectively. In plot (b), the circles represent the single component calibration of 2-chlorophenol and squares, triangles, cross, diamond and positive cross represent 2-chlorophenol studied with 0.9, 4.4, 9, 18 and 27 μg cm^{-3} of o-xylene, respectively.

Pentanol calibration was conducted with and without 0.02 g cm^{-3} sodium chloride solution added to the standards to prove whether increase extraction can be obtained with the addition of salt to the aqueous standard. The addition of salt to a hydrophilic compound such as pentanol is expected to increase the hydrophobicity of the compound resulting in better extraction [3]. Increasing the sampling time from 1 to 5 min increased sensitivity by 71% whether salt was added to standards or not. However, there was no significant difference for the same sampling time when these results were compared to standards with no added salt. Detection limits were estimated at 0.52 and 0.47 ng cm^{-3} for 1 and 5 min sampling time when salt was added to the pentanol standard. This may indicate that transport across the membrane into the instrumental system is restricted to molecules that can adsorb and diffuse through the membrane polymer structure. In the case of silicone membrane, transport is limited to relatively non-polar, relatively low molecular weight (<350 amu) organic compounds. The NaCl concentration in the samples studied was about 25%. Because this high concentration showed no difference between samples with and without the addition of salt, it was unnecessary to study other concentrations. Previous research have also demonstrated that the presence of salts, acids, bases, metals, suspended solids, and biological materials have no effect on the quality of membrane inlet mass spectrometry analysis [19,20].

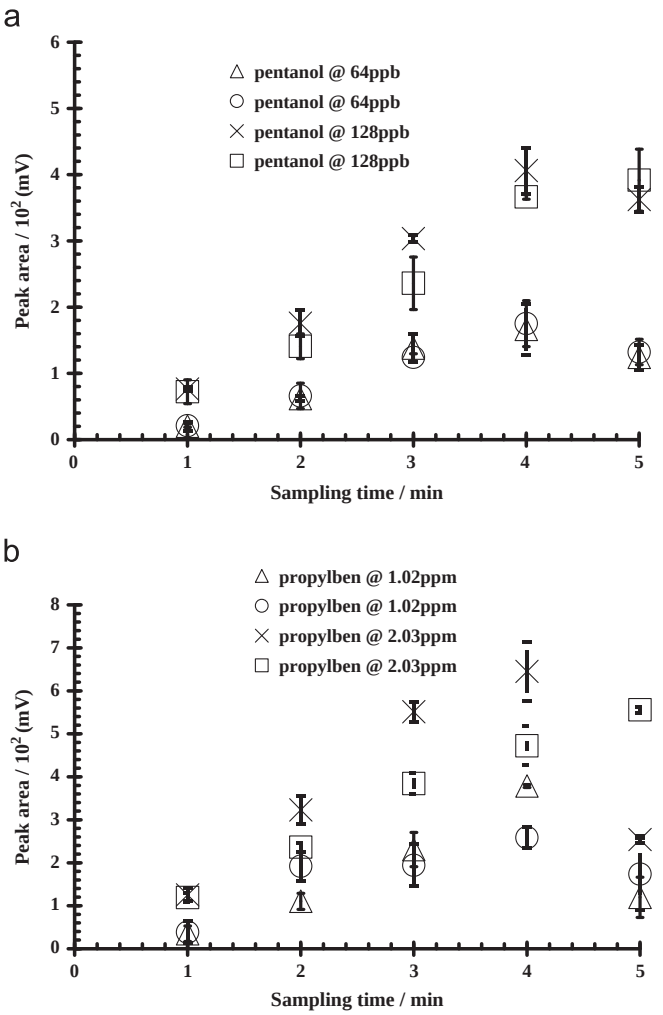

Fig. 6. A plot showing the change in response of pentanol in a mixture with propylbenzene (a), and propylbenzene in a mixture with pentanol (b). In plot (a), responses for (i) 64 ng cm^{-3} pentanol vs. 1.02 μg cm^{-3} propylbenzene (triangles); (ii) 64 ng cm^{-3} pentanol vs. 2.03 μg cm^{-3} propylbenzene (circles); (iii) 128 ng cm^{-3} pentanol vs. 1.02 μg cm^{-3} propylbenzene (cross); and (iv) 128 ng cm^{-3} pentanol vs. 2.03 μg cm^{-3} propylbenzene (squares), respectively are shown. In plot (b), responses for (i) 1.02 μg cm^{-3} propylbenzene vs. 64 ng cm^{-3}pentanol (triangles); (ii) 1.02 μg cm^{-3} propylbenzene vs. 128 ng cm^{-3} pentanol (circles); (iii) 2.03 μg cm^{-3} propylbenzene vs. 64 ng cm^{-3} pentanol (cross); and (iv) 2.03 μg cm^{-3} propylbenzene vs. 128 ng cm^{-3} pentanol (squares), respectively are shown. The results show a linear response from 1 to 4 min sampling time with deviation from linearity occurring at 5 min sampling time.

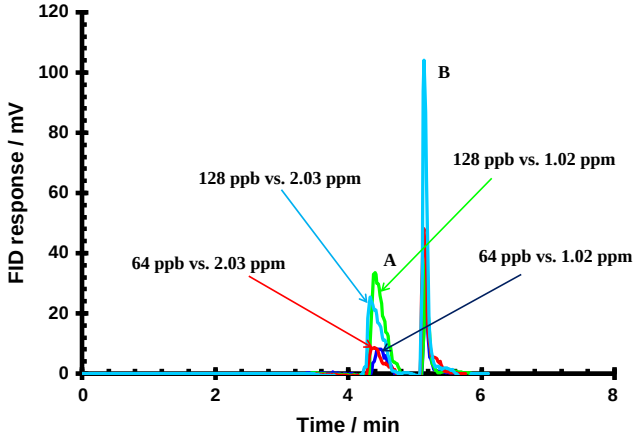

Fig. 7. Example chromatogram showing a two-component mixture for (A) pentanol and (B) propylbenzene at a sampling time of 4 min.

Table 3
Summary of the one-way ANOVA analyses for 1 and 5 min sampling time with data from the two component study involving pentanol and propylbenzene.

Source of variation	Sum of squares	Degrees of freedom	Mean square
1 min sampling time			
Between sample	2.94	3	0.98
Within sample	0.76	8	0.25
Total	3.7	11	
5 min sampling time			
Between sample	83.07	3	27.69
Within sample	11.18	8	1.4
Total	94.25	11	

Table 4
Summary of internal standard calibration study for mixtures of alcohols and aromatics. The internal standard used for the alcohols was octanol and that used for the aromatics was o-xylene.

Analyte	B_1/ μg^{-1} cm^3	B_0	R^2	LOD/ ng cm^{-3}	LOQ/ μg cm^{-3}
Pentanol	0.11±0.01	−0.11±0.02	0.996	0.5±0.2	12±2.0
Heptanol	0.07±0.01	−0.09±0.01	0.995	194±4.6	36±3.1
2-chlorophenol	0.02±0.01	0.17±0.02	0.994	1.2±0.1	0.4±0.01
Benzene	0.02±0.01	0.02±0.01	0.996	100±3.2	31±1.2
Propylbenzene	0.06±0.02	0.0001±0.00	0.992	33±1.7	124±1.1

The calibration summary for each response is given by the following equation:

$$Ratio\ of\ peak\ area\ response = B_0 + B_1(\mu g^{-1})(cm^3) \times [concentration](\mu g\ cm^{-3})$$

where B_0 is the intercept and B_1 is the sensitivity or slope.

4.3. Internal standard calibration on mixtures

Internal standard calibration studies were conducted for 5 compounds using the internally heated membrane coupled with the GC-FID. The internal standards were chosen carefully to reflect the chemical behavior of the compounds studied. The approach helps to compensate for sample-to-sample variations in extraction and desorption efficiency caused by the sample matrix. Table 4 summarizes the linear regression responses for the compounds studied. All sensitivities and intercepts are reported in Table 4. The regression lines for pentanol and heptanol gave a negative intercept. Using a t-test, these negative intercepts were shown to be statistically insignificant. Our first interpretation for the negative intercept was there may have been significant loss of material through the external walls of the membrane during the calibration process for the longer sampling times. Because the t-test demonstrated the negative intercepts to be statistically insignificant we conclude that losses through the membrane walls during the temperature programming stage was not significant.

The minimum limit of detection (LOD) based on three times the noise level, was reported for pentanol at 0.5±0.2 ng cm^{-3}, with a sensitivity of 0.11±0.01 μg^{-1} cm^3. The maximum LOD occurred with heptanol at 194±4.6 ng cm^{-3} with a sensitivity of 0.07±0.02 μg^{-1} cm^3. Table 4 also reports the limit of quantification (LOQ) for the 5 analytes studied. The data reported in Table 4 indicated that most of the analytes produced a linear response to the internal standard study with correlation coefficients >0.99.

5. Conclusion

A new sampling approach utilizing internally heated poly (dimethylsilicone) membranes has been constructed and interfaced with a capillary GC-FID. The sampling approach relies on temperature based modification of diffusion coefficients of different analytes and will probably pave the way for an effective sample interface for conventional analysis. The new sampling unit was evaluated for detecting key volatile organic compounds commonly found in water samples. The detection limit for key volatile organic compounds studied with internal standard calibration ranged from 0.5 to 194 ng cm^{-3}. The initial investigation for competitive adsorption effects revealed that analyte adsorption and diffusion into the membrane can be affected when mixtures were investigated. Analyte extraction was also affected by the diffusion coefficients of the analytes, the higher the diffusion coefficient the better the extraction. Nevertheless, the approach was impressive in that just 1 min of sampling time was enough to extract volatile analytes from aqueous matrices. Longer exposure of the sampling unit to the same analyte concentration was found to increase analyte uptake and the responses were linear for up to 4 min sampling time.

An important issue yet to be addressed is the reproducibility of responses for single and multiple component mixtures. Such data is yet to be fully documented; nevertheless, the sensitivity of the approach is promising for studying aqueous matrices. The next phase of this technology should also focus on the degradation performances of different types of membranes available in the market.

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References

[1] B. Vlaeminck, J. Harynuk, V. Fievez, P. Marriott, Eur. J. Lipid Sci. Technol. 109 (2007) 797.
[2] H. Lai, P. Guerra, M. Joshi, J.R. Almirall, J. Sep. Sci. 31 (2008) 402.
[3] A.B. Kanu, M. Dixon, Y. Yin Zu, J. Bailey, J.M. Gillies, J. Zweit, C.L.P. Thomas, Appl. Radiat. Isot. 58 (2003) 193.
[4] Y.-P. Pan, S.-W. Tsai, Anal. Chim. Acta 624 (2008) 247.
[5] J. Koziel, M. Jia, J. Pawliszyn, Anal. Chem. 72 (2000) 5178.
[6] H.J. Bestmann, L. Winkler, O. von Helverson, Phytochemistry 6 (1997) 1169.
[7] N.C. Yang, K.L. Hwang, C.H. Shen, H.F. Wang, W.M. Ho, J. Chromatogr. Biomed. Sci. Appl. 759 (2001) 307.
[8] L. Kovatsi, D. Giannakis, V. Arzoglou, V. Samanidou, J. Sep. Sci. 34 (2011) 1004.
[9] M. de, F.G. Meniconi, R. Parris, C.L.P. Thomas, Analyst 128 (2003) 1232.
[10] H. Schmidt, F. Tadjimukhamedov, I.V. Mohrenz, G.B. Smith, G.A. Eiceman, Anal. Chem. 76 (2004) 5208.
[11] M. Ishikawa, O. Ito, S. Ishizaki, Y. Kurobayashi, A. Fujita, Flavour Fragr. J. 19 (2004) 183.
[12] P. Dwivedi, L.M. Matz, D.A. Atkinson, H.H. Hill, Analyst 129 (2004) 139.
[13] C. Eckers, A.M-F. Laures, K. Giles, H. Major, S. Pringle, Rapid Commun. Mass Spectrom. 21 (2007) 1255.
[14] T.A. Fligge, K. Bruns, M. Przybylski, J. Chromatogr. B 706 (1998) 91.
[15] A.M. Munro, C.L.P. Thomas, M.L. Langford, Anal. Chim. Acta 375 (1996) 49.
[16] A.B. Kanu, H.H. Hill Jr., M. Gribb, R. Walters, J. Environ. Monit. 9 (2007) 51.
[17] C.L.P. Thomas, N.D. Rezgui, A.B. Kanu, A.M. Munro, IJIMS 5 (2002) 31.
[18] N. Ochiai, K. Sasamoto, H. Kanda, E. Pfannkoch, Gerstel Application Note, AN/2008/12/1-14, December 2008.
[19] G. Hoch, B. Kok, Arch. Biochem. Biophys. 101 (1963) 160.
[20] P. Llewelynn, D. Littlejohn, US Pat. 3429105, 1969.
[21] C.S. Creaser, J.W. Stygall, Anal. Proc. Commun. 32 (1995) 7.
[22] B.J. Harland, P.J. Nicholson, Sci. Total Environ. 135 (1993) 37.
[23] R.C. Johnson, N. Srinivasan, R.G. Cooks, D. Schell, Rapid Commun. Mass Spectrom. 11 (1997) 363.
[24] S. Bohatka, Rapid Commun. Mass Spectrom. 11 (1997) 656.
[25] K.F. Hansen, H. Degn, Biotechnol. Tech. 10 (1996) 485.
[26] P. Wong, N. Srinivasan, N. Kasthurikrishnan, R.G. Cooks, J.A. Pincock, J.S. Grossert, J. Org. Chem. 61 (1996) 6627.
[27] A.J. Maden, M.J. Hayward, Anal. Chem. 68 (1996) 1805.
[28] V. Stannett, J. Membrane Sci. 3 (1978) 97.
[29] C.S. Creaser, J.W. Stygall, D.J. Weston, Anal. Commun. 35 (1998) 9H.
[30] L.B. Westover, J.C. Tou, C.E. Enke, Anal. Chem. 46 (1974) 568.
[31] M.A. LaPack, J.C. Tou, C.E. Enke, Anal. Chem. 62 (1990) 1265.

[32] L.E. Sulvon, M.R. Bauer, J.S. Ho, W.L. Budde, Anal. Chem. 63 (1991) 1335.
[33] M.E. Bier, R.G. Cooks, Anal. Chem. 59 (1987) 597.
[34] M.E. Bier, R.G. Cooks, J.S. Brodbelt, J.C. Tou, L.B. Westover, US Pat. 4791292, 1989.
[35] M. Leth, F.R. Lauritsen, Rapid Commun. Mass Spectrom. 9 (1995) 591.
[36] F.R. Lauritsen, R.A. Ketola, Anal. Chem. 69 (1997) 4917.
[37] M.E. Cisper, P.H. Hemberger, Rapid Commun. Mass Spectrom. 11 (1997) 1449.
[38] N.D. Rezgui, A.B. Kanu, K.E. Waters, B.M.G. Grant, A.J. Reader, C.L.P. Thomas, Analyst 130 (2005) 755.
[39] A.B. Kanu, C.L.P. Thomas, Analyst 131 (2006) 990.