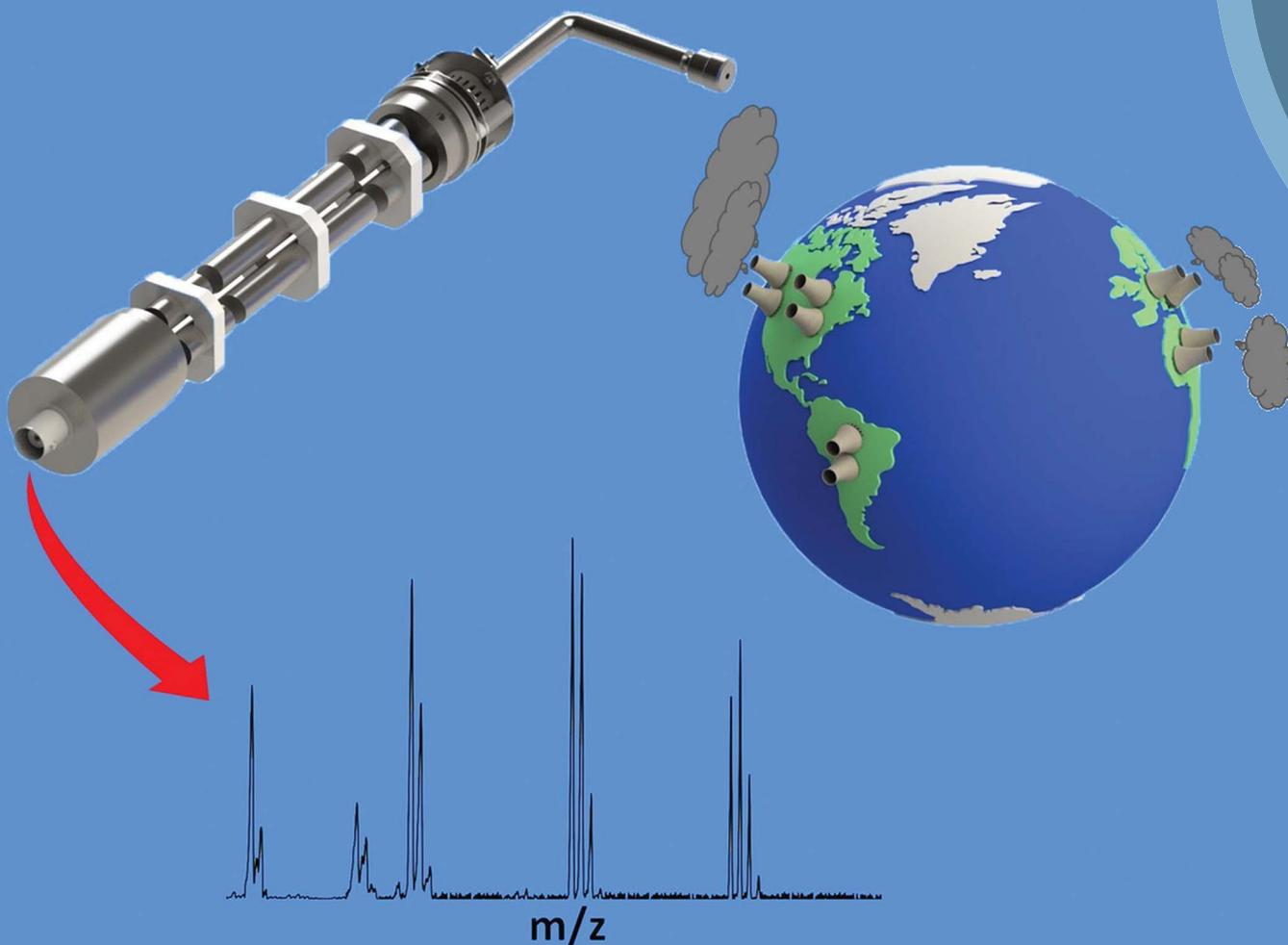


# Analytical Methods

[www.rsc.org/methods](http://www.rsc.org/methods)



Themed issue: Portable Instrumentation & Point of Care Technologies

ISSN 1759-9660



PAPER

Stephen Taylor *et al.*

Analysis of chlorinated hydrocarbons in gas phase using a portable membrane inlet mass spectrometer

**175** YEARS

Cite this: *Anal. Methods*, 2016, 8, 6607

# Analysis of chlorinated hydrocarbons in gas phase using a portable membrane inlet mass spectrometer

Stamatios Giannoukos,<sup>a</sup> Boris Brkić<sup>ab</sup> and Stephen Taylor<sup>\*ab</sup>

A compact portable membrane inlet mass spectrometer (MIMS) has been used for the first time to detect and monitor, both qualitatively and quantitatively, volatile chlorinated hydrocarbons in the gaseous phase. Continuous monitoring of such compounds in the field is of importance due to their wide industrial use and their potential negative impact on public health and the environment. Compounds tested include vinyl chloride, 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene. Gas phase experiments were performed at concentration levels from low ppb to low ppm. The results obtained showed very good linearity within the examined concentration range, ppb limits of detection and fast response (rise and fall) times. Mixture effects are also presented. The MIMS system was also investigated under periodic and dynamic experimental conditions and demonstrated stable and repeatable measurements.

Received 5th February 2016  
Accepted 23rd March 2016

DOI: 10.1039/c6ay00375c

[www.rsc.org/methods](http://www.rsc.org/methods)

## 1. Introduction

A slight modification of the quote “prevention is better than cure” into “pollution prevention is better than cure” means that it is always better to stop something bad or harmful for the environment from happening instead of dealing with the consequences. Air pollution is relevant to everyone and a topic of great concern worldwide.<sup>1–3</sup> The increase of industrial activity and the frequent infringements of environmental safety regulations have led to an increased number of uncontrolled pollutants released in the atmosphere. Air quality monitoring plays a major role in the control and management of air pollutants and subsequently in the general indoor or outdoor air pollution prevention. Air pollutants have been previously and are still being investigated scientifically, and it has been shown that some of them can be very harmful for public health and welfare. They are responsible for numerous health issues such as asthma, chronic bronchitis, *etc.* or they can, in some cases, cause death.<sup>2,3</sup>

Volatile organic compounds (VOCs) are a class of chemical compounds that partially contribute (directly or indirectly) towards ambient air pollution.<sup>2</sup> They can be found almost everywhere and they participate in both natural and manmade (*e.g.* industrial) activities. A subclass of VOCs, with a potential negative impact on the environmental status and on public health, is volatile chlorinated hydrocarbons (VCHs). These are organic compounds containing at least one covalently bonded chlorine atom in their structure.<sup>4</sup> VCHs such as vinyl chloride,

1,1-dichloroethylene, trichloroethylene and tetrachloroethylene are particularly of high environmental interest as they are dominant chemicals used widely.<sup>2,5</sup> Characteristically, vinyl chloride is the main chemical compound in many plastic manufacturing processes such as those used in making packaging materials, pipes, medical equipment, furniture, household products, *etc.* 1,1-dichloroethylene is used as an industrial solvent and as a component during plastic production (*e.g.* food packaging materials, flexible films, *etc.*). It is also used in the production of adhesives and refrigerants. Trichloroethylene is a general purpose industrial solvent and is also used for the production of particular types of textiles whereas tetrachloroethylene is widely used as a dry cleaning agent and as a metal degreasing agent. Research work on the above VCHs has shown that human exposure to them can result in toxic, genotoxic, mutagenic and carcinogenic effects.<sup>4,5</sup> Therefore, special care and strict regulations are needed during their production, distribution, use, storage and disposal stages.<sup>6</sup>

Current methodologies for the detection and lab analysis of VCHs in environmental gas samples employ hybrid gas chromatography (GC) techniques. In particular, for the detection of vinyl chloride, 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene in environmental gaseous samples the following techniques are commonly used: GC coupled with mass spectrometry (MS),<sup>7–11</sup> GC coupled with an electron capture detector (ECD)<sup>12</sup> and GC coupled with a flame ionization detector (FID).<sup>13</sup> The above analytical techniques have shown variable limits of detection in the concentration area from some parts per trillion (ppt) to low parts per million (ppm). However, a critical step during conventional VCH analysis is sample collection. So far, Tedlar bags have been used during air sample collection as well as stainless steel cartridges<sup>7</sup> filled with

<sup>a</sup>Department of Electrical Engineering and Electronics, University of Liverpool, Brownlow Hill, Liverpool, L69 3GJ, UK. E-mail: S.Taylor@liv.ac.uk

<sup>b</sup>Q Technologies Ltd, 100 Childwall Road, Liverpool, L15 6UX, UK

absorptive materials, or stainless steel canisters or solid phase microextraction (SPME) fibers.<sup>14</sup> These sample collection techniques, although they have many advantageous characteristics, do not allow rapid analysis, because samples need to be transferred from the point of measurement to the laboratory. Sample loss and/or contamination during transportation and storage are also possible. In addition, carriage and storage costs are relatively high. For these reasons, accurate and versatile analytical tools with real-time or near real-time chemical analysis capabilities are required to be developed and employed for direct on-site use.

Recent improvements in control electronics, miniaturisation of individual MS components (*e.g.* vacuum systems, mass analysers, *etc.*), and in the development of novel ionization techniques have allowed deployment of novel, portable MS based systems. Such systems offer more than adequate performance (sensitivity and/or resolution) for on-site chemical analysis.<sup>15,16</sup> According to the physical and chemical properties of the sample (simple or complex, gaseous, liquid or solid), different sample introduction and ionisation methodologies are required.<sup>17</sup> Typically for environmental applications, a direct leak and dual sorbent tube inlet is combined with a miniature cylindrical ion trap MS equipped with an internal ion source (glow discharge electron ionization (GDEI) source). This allows continuous sampling to identify and quantify toxic industrial gases.<sup>18</sup> The same compounds were also successfully tested with the Mini 10 (rectilinear ion trap mass analyser) from Purdue University.<sup>18</sup> Atmospheric pressure chemical ionization (APCI) was also used to externally generate ions from toxic chemicals in air and to introduce them in real-time into a portable tandem MS system. Analysis time was less than 5 s and detection limits were in the low ppb region.<sup>19</sup> Moreover, the Mini 10.5 handheld MS (Purdue University) coupled with an APCI interface was used to detect gaseous samples of benzene, toluene and ethylbenzene at trace levels.<sup>20</sup> A slightly modified version of Mini 10 with a flexible dual channel sampling probe and a discontinuous atmospheric pressure interface (DAPI) was successfully used to detect agrochemicals (*e.g.* PCP, and DNP) from three-dimensional surfaces in real-time.<sup>21</sup> Additionally, a Guardion-7 GC-TMS is a lightweight (13 kg) portable gas chromatograph (GC) instrument combined with a toroidal ion trap mass analyser able to perform VOC and toxic industrial chemical analysis on-site.<sup>22</sup> Sample introduction is done in this case using an SPME fibre. This instrument has near-real time chemical analysis capabilities with an integrated library of target analytes. The same GC-TMS system has also been used with a field vacuum extractor (FVE) and a SPME sample collection technique to analyse organophosphonate compounds from vinyl floor tiles.<sup>23</sup> Furthermore, a mobile laboratory equipped with fast response instrumentation (laser spectrometers, sampling devices, a modified proton transfer reaction mass spectrometer (PTR-MS) and an aerosol mass spectrometer (AMS)) was used to monitor air pollutants from vehicles in the urban environments of Mexico City and Boston.<sup>24</sup>

To overcome the limitations and portability issues of the existing analytical technology for *in situ* chemical analysis, portable membrane introduction mass spectrometry (MIMS)

can be used for both gaseous<sup>25–33</sup> and aqueous<sup>34,35</sup> analyses and monitoring in near-real time with no sample preparation requirements. The operating principle of MIMS is based on pervaporation separation through thin polymer membranes.<sup>26,27,31,36–38</sup> A membrane sampling inlet is connected with a MS system allowing selective permeation of organic compounds in the gas or liquid phase while blocking water or air molecules. In this way the instrument is protected from high humidity and high concentrations of inorganic gases. At the same time organic compounds may pass through the membrane to the ion source for ionization and then to the mass analyzer for spectral analysis. The rate of transfer of targeted compounds in the MS depends on the solubility and diffusivity properties of these compounds on the membrane material. Porosity and thickness of the membrane material have also been shown to play an important role in sensitivity maximization and detection of a wider range of VOCs and SVOCs<sup>29,33</sup> in complex matrices. The mass spectra produced can be subsequently processed for both qualitative and quantitative analyses.

A portable MIMS system integrated on a vehicle has been developed to spatially and temporally monitor VOCs and SVOCs around an industrial site.<sup>39</sup> In this way volatile emissions (both targeted and unexpected) from various sources and at different time points were recorded and quantified. Results for atmospheric benzene, toluene, xylenes and ethylbenzene at the oil and gas extraction facilities in Northern Alberta were presented. A portable (15 kg including a lithium battery) single photon ionization time-of-flight (ToF) MS with a membrane inlet was built for VOC monitoring in the environmental air and positively tested for toluene and xylene analysis in the sub-ppb concentration area.<sup>40</sup> A tandem MIMS was used to screen a wide range of toxic chemicals such as BTEX, naphthalene, pinenes, *etc.* at ppb concentration levels in urban air plumes. The same MIMS system was used for water analysis.<sup>41</sup> Furthermore, an underwater MS system integrated on a remotely controlled surface vehicle equipped with a global positioning system (GPS) was developed to spatially monitor dissolved gases and VOCs in aqueous environments.<sup>42</sup> Another lightweight transportable MIMS system was developed to monitor and distinguish two different types of North Sea crude oils in water. Field testing of the device was undertaken in the Flotta Oil Terminal (Orkney, UK).<sup>43</sup>

Compared to large size and weight laboratory MS based systems (*e.g.* GC-MS, *etc.*), portable MIMS offers very good sensitivity (low detection limits – ppt/ppb levels), rapid chemical analysis (within some seconds), accuracy, reliability, robustness, and user friendliness (small size and weight) with low maintenance costs. The utility of an entirely portable device with the above characteristics, addressing all the requirements raised during harsh environmental operations for harmful or toxic substance detection, is currently of great interest and attractive to environmental investigators for real-time decision-making at the point of analysis. The results in this paper demonstrate, for the first time, the detection and monitoring of VCHs in the gas phase from low ppb to low ppm concentration levels using an 18 kg portable MIMS system.

## 2. Experimental section

### 2.1 Motivation and concept

The motivation of this work is the chemical detection and the near real-time monitoring of low molecular weight (below 200 amu) volatile chlorinated hydrocarbons' emissions in ambient air using a portable MIMS. Target compounds that were selected for investigation in this work and their physical properties are presented in Table 1. These compounds constitute potential environmental organic threats, whereas human acute or chronic exposure hides adverse health effects or even a potential cause of death. They can affect the quality of life, environmental quality, and public health and have been classified as human carcinogens.<sup>4,44</sup> There are many cases (especially in occupational environments), where the legal exposure limits are usually being exceeded and employees' health is under potential risk. Moreover, the repercussions of those compounds during their life-cycle stages for human toxicity are relatively high. The aim of this work is to build, test and calibrate a portable analytical system for environmental (residential or occupational) air quality monitoring applications.

### 2.2 Reagents

Analytical standard solutions of vinyl chloride (2000  $\mu\text{g mL}^{-1}$  in methanol), 1,1-dichloroethene (1000  $\mu\text{g mL}^{-1}$  in methanol), trichloroethylene (5000  $\mu\text{g mL}^{-1}$  in methanol) and tetrachloroethylene (5000  $\mu\text{g mL}^{-1}$  in methanol) were purchased from Sigma Aldrich Co. LLC., U.K. All reagents were provided in the liquid phase.

### 2.3 Experimental setup

Experiments were performed using a portable membrane inlet quadrupole mass spectrometer (QMS) supplied by Q-Technologies Ltd., Liverpool, UK.<sup>25,26</sup> The MIMS system consists of four components: (a) a membrane sampling probe which allows the gas samples to penetrate through the membrane material into the vacuum chamber for ionisation and further mass spectrometric separation and analysis, (b) a triple filter QMS, (c) the vacuum system which maintains overall system's pressure stable in low levels and simultaneously offers a sufficient suction rate of the molecules absorbed onto the membrane material and (d) a laptop which is required for data acquisition and interpretation.

The triple filter QMS consists of the following main parts: (a) the electron impact (EI) ion source, (b) the mass analyzer and (c) the detector. The enclosed EI ion source has a twin thoria

filament assembly at about 1.68 mA electron emission current. The applied EI electron energy is 70 eV. The mass analyzer consists of a pre-filter (25 mm length), a main filter (125 mm length), and a post-filter (25 mm length) with rods of 6.3 mm diameter. It has a mass range of  $m/z = 1-200$  with a unit resolution over the entire mass range. The mass analyzer is set up so that the ratio of peak height to valley with adjoining peaks is 10%. The sensitivity of the quadrupole analyzer is  $1 \times 10^{-4} \text{ A mbar}^{-1}$ . The RF frequency is 2 MHz, whereas the DC/RF ratio is set to 8.6. The scan rate can vary according to the determined acquisition points and is typically within 10–15  $\text{amu s}^{-1}$ . The detector contains both a Faraday cup for detecting usual ion currents and a Channeltron type electron multiplier for detecting very low signal currents like those produced from low concentration level VOCs emitted from harsh chemical environments during, for *e.g.*, environmental quality monitoring applications. Since we were investigating compounds at very low concentration levels, the Channeltron multiplier was selected as the detector. During data acquisition, 10 acquisition points were recorded per unit mass with an average number of 20 scans per measurement throughout the mass range of  $m/z = 40-200$ . This mass range was selected for mass scanning to protect the multiplier from saturation (due to the high concentration air molecules *e.g.*  $\text{N}_2$ ,  $\text{O}_2$ , *etc.*) and to extend its lifetime. Data were recorded on a laptop computer, plotted, and compared with reference mass spectra, using the online open access NIST Chemistry Web-Book<sup>45</sup> as a reference database for spectral peaks of each compound.

The QMS was housed in a stainless steel chamber pumped by using a TURBOLAB 80 vacuum system (Oerlikon Leybold Vacuum Ltd., Chessington, UK) consisting of an Oerlikon dual-stage oil-free DIVAC 0.8 T diaphragm pump and a TURBOVAC SL 80 H turbomolecular pump. The diaphragm pump provides a pressure of down to  $1 \times 10^{-2}$  Torr while the turbomolecular pump gives a base pressure of  $7.5 \times 10^{-8}$  Torr. The system pressure was continuously being monitored by using a highly accurate digital pressure gauge (model: MRT 100) supplied by Pfeiffer Vacuum Ltd., Newport Pagnell, UK that uses a Pirani/cold cathode method of measurement. Operating pressure for mass analysis with the PDMS sheet membrane sampling probe attached and the sample inlet valve fully open was varied between  $2.5 \times 10^{-6}$  Torr and  $3.0 \times 10^{-5}$  Torr depending on the concentration of the under analysis standard gas sample and on the nature (chemical structure, vapour pressure, *etc.*) of the under examination component that affects permeability through the PDMS membrane.

**Table 1** Summary of the volatile organochlorine compounds used in the MIMS experiments

Compound	CAS number	Molecular weight	Vapor pressure (kPa) at 25 °C	log octanol/water partition coefficient (log $K_{ow}$ )	Odor threshold (ppm)
Vinyl chloride	75-01-4	62.498	346.64	1.36	3000
1,1-Dichloroethene	75-35-4	96.943	78.79	1.32	190
Trichloroethylene	79-01-6	131.388	9.86	2.42	28
Tetrachloroethylene	127-18-4	165.833	2.46	3.40	1

## 2.4 Sample preparation

MIMS linearity during online monitoring of the targeted VOCs was determined using gas standards produced by the technique of static dilution bottles. The procedure that was followed for gas standard production was based on the studies of McClenen *et al.*<sup>46</sup> and Naganowska-Nowak *et al.*<sup>47</sup> Liquid stock solutions of individual organochlorine compounds were bought at standard concentrations. Appropriate quantities of each liquid stock solution, corresponding to their analogous standard gas phase concentrations in a defined volume of air, were injected with high precision micropipettes (Mettler-Toledo Ltd., Leicester, UK) into 1.3 L and 2.8 L narrow-neck glass flasks (Sigma Aldrich Co. LLC., U.K.). The glass flasks were then filled with atmospheric air, carefully covered and left for 4 hours at room temperature (25 °C) to evaporate and reach thermodynamic equilibrium. To ensure avoidance of potential sample leakage, the flask tops were lidded with stoppers and covered with several layers of parafilm M wrapping film. Gas standards of vinyl chloride, 1,1-dichloroethene, trichloroethylene and tetrachloroethylene were prepared at the following concentrations: blank, 10 ppb, 50 ppb, 100 ppb, 250 ppb, 500 ppb, 750 ppb and 1 ppm. Before individual testing series, the glass flasks were carefully purged with an odor-free soap and water and rinsed with deionised water (ReAgent Chemical Services Ltd, Cheshire, UK) in order to remove and eliminate interferences with other volatile compounds. They were left overnight uncovered at 60 °C, so that the remaining water droplets would evaporate. The standard gases were tested with the following sequence: from the lowest concentration level to the highest. This was done to reduce potential memory effects between distinctive measurements and sample to sample carryover errors. Blank flasks containing only atmospheric air were also prepared following the above described process for examination of potential exogenous VOC contaminations prior to the start of the experimental series. Moreover, the covered parafilm flasks which contain the prepared gas standards were peripherally (outer surrounding area) tested with the MIMS system before the start of the experiments to examine any volatile leakage through the wrapping film. All the experiments were replicated three times to ensure reproducibility and consistency of the results. The experiments showed a repeatable degree of agreement and precision between the three experimental series.

## 2.5 Sample introduction

During tests, a flat polydimethylsiloxane (PDMS) membrane probe connected to the vacuum valve was directly inserted into the gas dilution bottles and was used for sampling the prepared standard gases. The membrane probe assembly consists of 10 cm stainless steel tubing coupled with a membrane sheet supported in the one end side with a 6.35 mm Swagelok stainless steel vacuum fitting union. The non-sterile PDMS membrane sheeting was provided by Technical Products, Inc. of Georgia, USA. The PDMS membrane sheet thickness was 0.12 mm whereas the sampling area was 33.2 mm<sup>2</sup>. The membrane was supported by a 0.8 mm thick stainless steel porous frit with 20 µm porosity. The membrane probe and subsequently the

membrane were kept at ambient temperature throughout the measurements. The sample was introduced directly into the vacuum system. No analyte enrichment procedures (*e.g.* carrier gas) were used.

# 3. Results and discussion

## 3.1 Organochlorine compound experiments

This experimental series was done to investigate the mass spectrometric detection and monitoring of volatile organochlorine compounds in the gaseous phase using portable MIMS. A PDMS membrane sampling probe was initially used to examine whether the targeted compounds, corresponding to our specific application, could be detected. Representative mass spectra (at the maximum signal intensity value) of vinyl chloride, 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene corresponding to 250 ppb distinct gas standards are presented in Fig. 1.

The mass spectra of vinyl chloride, 1,1-dichloroethylene and trichloroethylene agree well (agreement between compounds' mass fragments and their relative ion abundances) with the reference mass spectra obtained from NIST Chemistry Web-Book; mass peaks 164 and 166 of the tetrachloroethylene mass spectrum present a slightly weaker abundance compared to the reference spectrum. A possible explanation is that the sample introduction technique followed during the measurements has affected ion production in the source, and subsequent transmission and detection of those particular mass fragments. It is well known that PDMS membranes are highly sensitive to alkylbenzenes<sup>43</sup> (for *e.g.* benzene –  $m/z = 77$  and  $78$ , toluene –  $m/z = 91$  and  $92$ , xylene –  $m/z = 105$  and  $106$ , and ethylbenzene –  $m/z = 91$  and  $106$ ). However, within a complex real air mixture, volatile organochlorines can be distinguished from alkylbenzenes by selective ion monitoring and comparison of their relative abundances (*e.g.* from 3 and 4 main characteristic mass fragments) with the reference mass spectra to look for potential overlapping effects or other types of interactions. The same applies for VCHs with relatively low molecular weights such as chloromethane (CH<sub>3</sub>Cl) with a characteristic mass fragment of  $m/z = 50$  or methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) with characteristic mass fragments of  $m/z$  values of 49, 84, and 86.

After detection with the MIMS was confirmed, gas standards of the selected volatile compounds were prepared for on-line monitoring at the following concentration levels: blank, 10 ppb, 50 ppb, 100 ppb, 250 ppb, 500 ppb, 750 ppb and 1 ppm. Calibration curves (Fig. 2) of our MIMS instrument for the target organochlorine compounds gas standards in the concentration range from 10 ppb to 1 ppm exhibited very good linearity with  $R^2$  values in the range from 0.9946 to 0.999 as shown in Table 2.  $R^2$  values correspond to the characteristic mass fragment (mostly molecular weight) for each compound.

## 3.2 MIMS response experiments

In order to examine the MIMS response under various conditions (*e.g.* periodic and dynamic processes), two experimental scenarios were investigated. The first scenario is described in

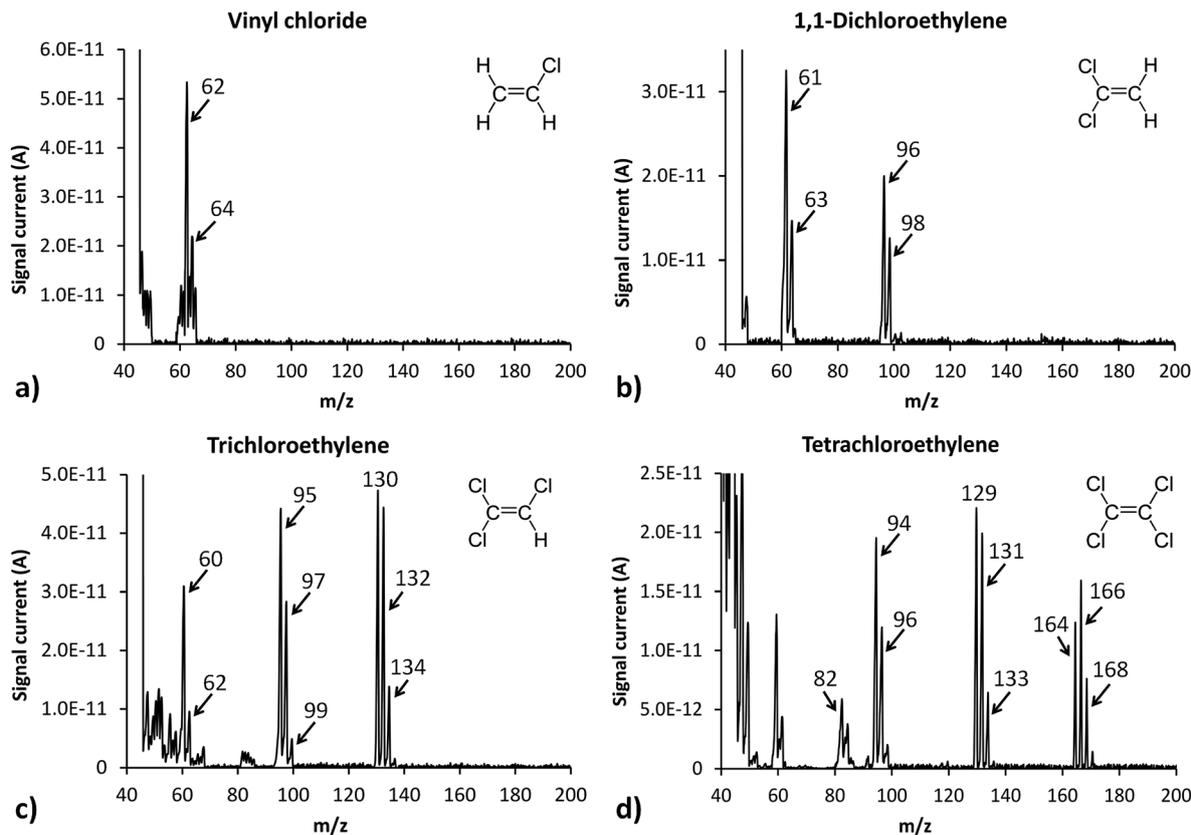


Fig. 1 Representative experimental mass spectra at 250 ppb for (a) vinyl chloride, (b) 1,1-dichloroethylene, (c) trichloroethylene and (d) tetrachloroethylene obtained with our MIMS.

Fig. 3a, where an increase–decrease profile of the mass fragment of  $m/z = 166$  of tetrachloroethylene is presented. For this experiment, three separate gas standards of tetrachloroethylene at 100 ppb each were prepared in glass flasks with the technique that was described above (Section 2.4). The total data collection time was 28 minutes and the measurement included three repetitions between 4 minute sampling periods of blank samples and 4 minute sampling periods of 100 ppb gas standard samples of tetrachloroethylene. The multiple ion monitoring mode was applied to monitor the ion mass of  $m/z = 166$ , where 30 acquisition points per minute were recorded. Mass fragments of  $m/z = 129$ , 131 and 164 were also continuously monitored, displaying the same increase–decrease profile as the mass fragment of  $m/z = 166$ . Repeatable [relative standard deviation (% RSD) was calculated to be 8.1%] and stable signal patterns were obtained with fast rise and fall response times (Table 2).

The second scenario is presented in Fig. 3b and shows a stepwise increase profile of the mass fragment of  $m/z = 166$  of tetrachloroethylene. Again, gas standards of tetrachloroethylene at the following concentrations: blank ( $\times 2$ ), 50 ppb, 100 ppb, 250 ppb, and 500 ppb were prepared. The sampling process lasted for 24 minutes and was split into six 4-minute steps with the following sequence: blank, 50 ppb, 100 ppb, 250 ppb, 500 ppb and blank. The multiple ion monitoring mode was applied to monitor ion masses of  $m/z$  129, 131, 164 and 166.

During data acquisition, for every single ion mass, 30 acquisition points per minute were recorded. The MIMS system showed a linearly increasing response and stable data recordings per step. Fast response times (both rise and fall) were also observed (<60 s).

Both scenarios correspond to simulation cases where non-continuous and non-stable chemical gaseous plumes of organochlorine compounds are released from a potential indoor or outdoor source (*e.g.* industrial facility) and transferred in the ambient air of, for *e.g.*, an indoor environment such as a workplace environment, a domestic residence, *etc.*

### 3.3 Multi-compound detection experiment

The aim of this experimental series was to confirm the simultaneous detection and analysis of a mixture of organochlorine compounds with the MIMS. For this purpose gas standards (1 of each) of vinyl chloride, 1,1-dichloroethylene, trichloroethylene and tetrachloroethylene at a concentration level of 100 ppb each were prepared in glass flasks. Four 6.35 mm Swagelok PFA flexible tubes with a total length of 20 cm each were imported into the flasks *via* small holes made on their lids. The other end sides of the PFA tubes were connected to a 6.35 mm stainless steel Swagelok cross-union and a 6.35 mm union tee. The membrane sampling probe was connected with the free end connection of the cross-union *via* a 10 cm stainless steel tube.

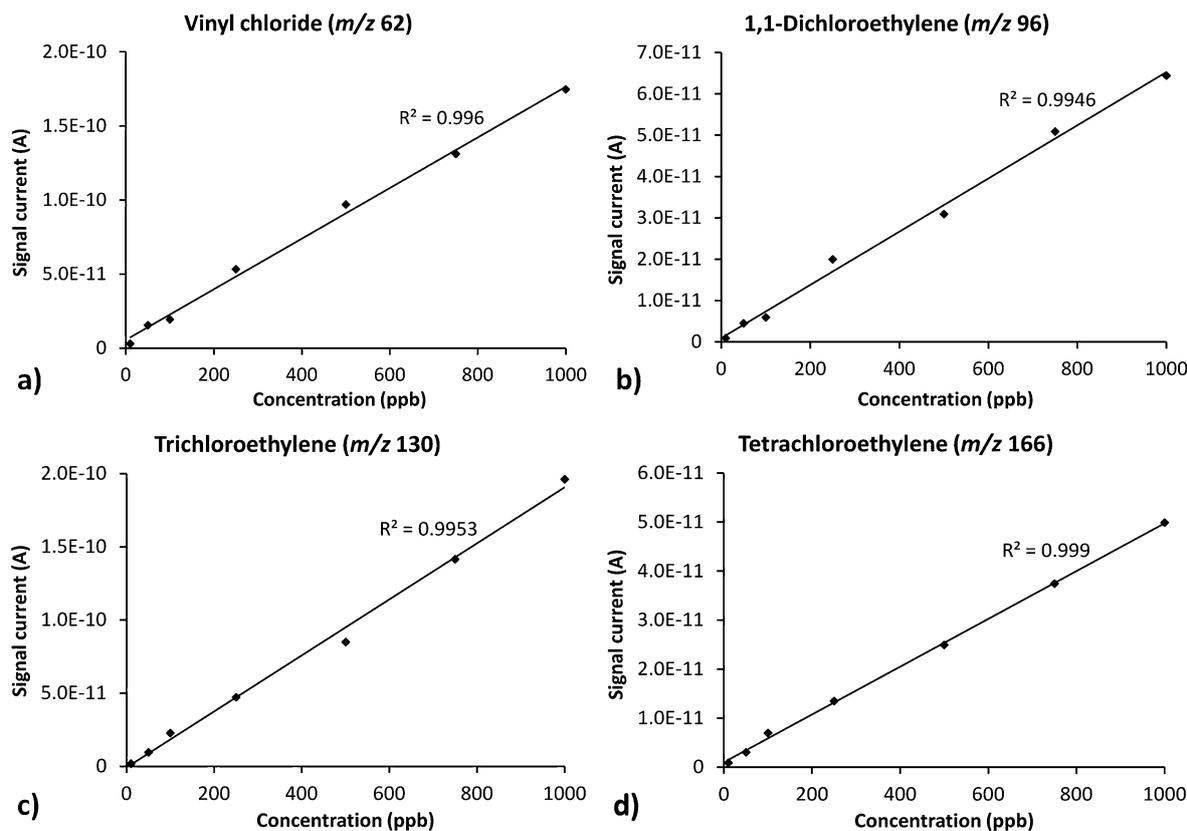


Fig. 2 Calibration curves of (a) vinyl chloride ( $m/z = 62$ ), (b) 1,1-dichloroethylene ( $m/z = 96$ ), (c) trichloroethylene ( $m/z = 130$ ) and (d) tetrachloroethylene ( $m/z = 166$ ) obtained from our portable MIMS system.

The mixing of the organochlorine compounds was performed in the centre of the cross-union that acted as a mini-mixing chamber. Fig. 4a presents schematically the experimental setup that was followed during multi-compound experiments. Fig. 4b shows a representative mass spectrum obtained from the described above gas mixture. Most of the characteristic mass fragments for every single organochlorine compound are easily and clearly distinguished. Peak overlapping is observed in few cases, *e.g.* a peak at  $m/z = 62$  which is present in both vinyl chloride and trichloroethylene mass spectra.

However, in a real case scenario (*e.g.* in the field), complex sample matrices (both qualitatively and quantitatively) require analysis and interpretation. Detection, monitoring and quantification strategies or steps (*e.g.* apparatus calibration in the lab, on-site calibration, *etc.*) need to be designed and properly applied to ensure the quality of the obtained information.

### 3.4 Evaluation of the method

The MIMS approach in the detection, analysis (both qualitative and quantitative) and on-line monitoring of volatile organochlorine compounds was evaluated by addressing the following criteria: (a) response times (rise and fall), (b) linear dynamic range within the examined concentration range, (c) repeatability and (d) detection limits (sensitivity).

For the targeted compounds tested, the average rise time was 32.5 s while the average fall time was 39.5 s (Table 2). The rise response time was the time required for the signal intensity to reach 90% of its maximum value (optimum sensitivity) after the membrane sampling probe was inserted into the flasks containing the gas standards. The fall time response represents the time required for the PDMS membrane to purge and peak signals to return to the base level (noise level). Rise and fall

Table 2 Summary of the PDMS membrane rise and fall times,  $R^2$  values and limits of detection (LODs) for the target compounds that were examined using our MIMS system

Compound name	Characteristic mass fragments ( $m/z$ )	Rise time (s)	Fall time (s)	$R^2$	LOD (ppb)
Vinyl chloride ( $m/z$ 62)	62, 64	15	28	0.996	2.41
1,1-Dichloroethene ( $m/z$ 96)	61, 63, 96, 98	18	33	0.9946	7.31
Trichloroethylene ( $m/z$ 131)	60, 62, 95, 97, 99, 130, 132, 134	25	45	0.9953	3.97
Tetrachloroethylene ( $m/z$ 166)	82, 94, 96, 129, 131, 133, 164, 166, 168	32	52	0.999	7.34

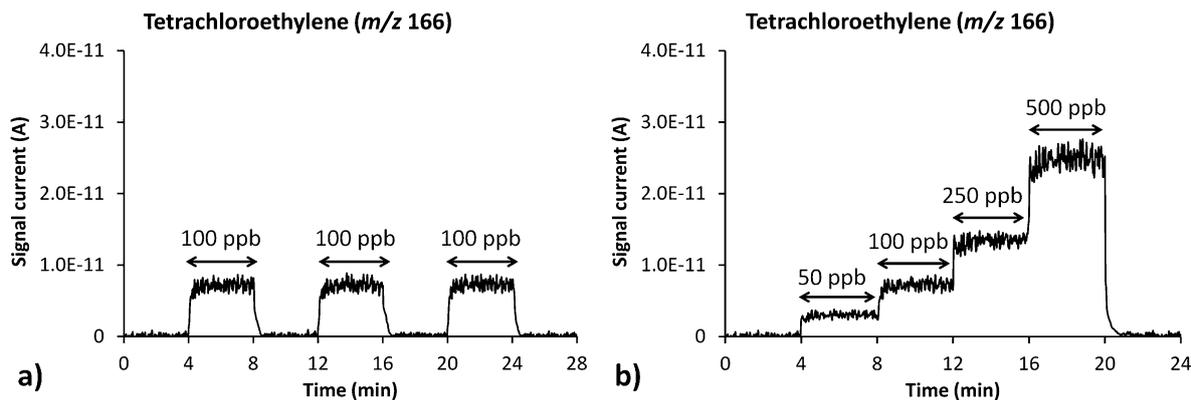


Fig. 3 (a) Increase–decrease profile of the mass fragment of  $m/z = 166$  of tetrachloroethylene, and (b) stepwise increase profile of the mass fragment of  $m/z = 166$  of tetrachloroethylene.

response times as well as sensitivity can be improved by heating the membrane sampling probe as heating affects the diffusion rate of molecules through the membrane material. Sensitivity can further be improved through analyte enrichment during sample introduction. The linear regression coefficient  $R^2$  and limits of detection obtained from the calibration curves produced from the experiments for each individual component are also summarized in Table 2.  $R^2$  values correspond to the characteristic mass fragment for each compound for the concentration range from 10 ppb to 1 ppm. Experimental results showed very good linearity *versus* concentration. The limit of detection (LOD) values were calculated from the calibration plots and are estimated at the low ppb levels (Table 2). The LOD estimates were based on signal current values obtained experimentally in our lab 10 ppb gas standards. The LOD values were based on the characteristic mass fragment of every single compound (as mentioned above) and were counted to be at least three times above the baseline. Repeatability of our technique is presented in Fig. 3a, where the same concentration gas standards present reproducible profiles with constant signal output values. Moreover, MIMS responses during periodic and dynamic phenomena (Fig. 3a and b) and for low-ppb

concentration levels are shown. Finally, our membrane approach was successfully tested in the detection of individual target organochlorines from multi-component mixtures (Fig. 4b).

In addition to the above performance criteria, it is essential to mention some of the technical characteristics of our apparatus such as simplicity (limited or no sample preparation requirements), selectivity (target compounds analysis), low power consumption (<150 watts) and portability (man or vehicle). Compared to commercial systems or those portable MS systems developed by others, our apparatus is both low cost and rugged. The membrane approach and assembly is long-lasting. For monitoring of low concentrations, (<1 ppm) a membrane seldom requires replacement. A PDMS membrane allows for selective permeability of sample molecules in the vacuum system whereas at the same time it protects the entire system from environmental contaminations (*e.g.* dust, and water molecules). The structure of our membrane sampling inlet makes the system totally safe for both liquid and gas analyses, offering the option for near real-time compound identification, screening and quantification. Our MIMS system is man-portable or it can be

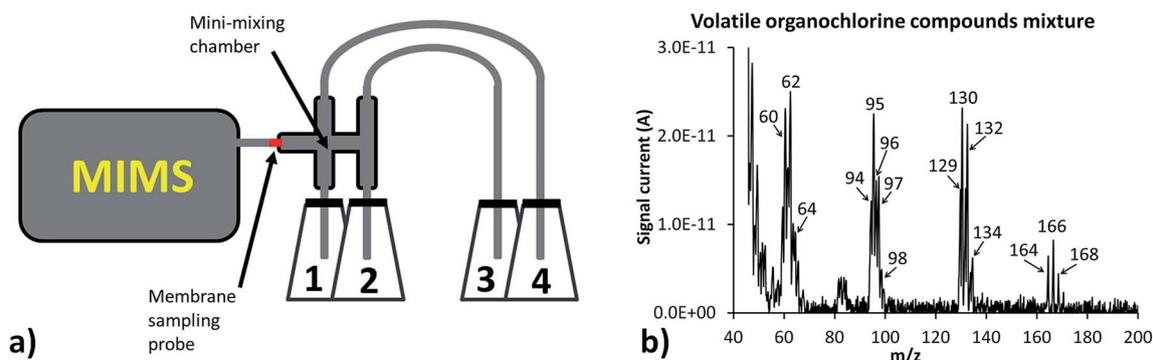


Fig. 4 (a) Schematic of our experimental setup (flasks 1, 2, 3 and 4 correspond to vinyl chloride, 1,1-dichloroethene, trichloroethylene and tetrachloroethylene, respectively, at 100 ppb each), (b) experimental mass spectrum of a mixture of vinyl chloride ( $m/z = 62$ , and  $64$ ), 1,1-dichloroethene ( $m/z = 96$ , and  $98$ ), trichloroethylene ( $m/z = 60$ ,  $95$ ,  $97$ ,  $130$ ,  $132$ , and  $134$ ) and tetrachloroethylene ( $m/z = 94$ ,  $96$ ,  $129$ ,  $164$ ,  $166$ , and  $168$ ) at 100 ppb each obtained with our MIMS.

integrated onto a vehicle (car or AUV). Such portable MIMS systems, potentially operated remotely, are suitable for in-field operations such as air quality monitoring, environmental monitoring and/or pollution screening in extremely hazardous environments.

## 4. Conclusions

A portable membrane inlet mass spectrometer has been used to detect, analyse (qualitatively and quantitatively) and screen potential pollutants and hazardous components in air quality monitoring applications. This paper demonstrates a proof of principle for trace detection (low ppb) and on-line monitoring of volatile chlorinated hydrocarbons in the gaseous phase using a portable MIMS. During measurements, minimum sample pre-treatment requirements were needed while fast detection response times (some seconds) were observed. The MIMS response in periodic and dynamic processes was also investigated, presenting repeatability and stability of our technique. Calibration curves of individual analytes demonstrated very good linear regression in the examined concentration range. Mixture effects were also examined.

Future work includes field validation of our MIMS system under real conditions *e.g.* in a polyvinyl chloride (PVC) production facility, a packaging material facility (food-packaging films production factory), hazardous waste sites, a metal degreasing facility, a dry cleaning industry, *etc.* Further sensitivity (achievement of even lower concentration analyzed) enhancement and response time improvement are planned by heating the membrane sampling inlet and analyte enrichment with a carrier gas. Heating of the sampling probe has significant suction effects on the molecules (both qualitative and quantitative) from the membrane material to the vacuum system. We will also try to increase the mass range of our mass analyzer (*e.g.* up to 300 or 400 Da) in order to expand the range of the potentially detectable analytes (such as organofluorine, organobromine, organoiodine compounds, *etc.*). Further weight reduction (*e.g.* below 10 kg) of our apparatus is also planned. This can be achieved by replacing the current vacuum system (which currently weights 14.5 kg) with a lighter one *e.g.* Mini-TASK AG81 from Agilent Technologies LDA UK Ltd. (weight approximately 7.5 kg) and by replacing the laptop computer with a tablet PC.

## Acknowledgements

The authors gratefully acknowledge Mr David McIntosh from the University of Liverpool, Dr Neil France and Mr Barry Smith from Q-Technologies Ltd., UK, and Dr Tom Hogan from Pathway Systems Ltd., UK for their technical assistance. Particular thanks are due to Q-Technologies Ltd., UK for the financial support of this work and to Da Vinci Laboratory Solutions B. V., NL for the fruitful technical discussions and the collaboration throughout the duration of the experimental work.

## References

- 1 World Health Organization, <http://www.who.int/en/>.
- 2 U.S. Environmental Protection Agency, <http://www.epa.gov/>.
- 3 European Parliament, <http://www.europarl.europa.eu/portal/en>.
- 4 U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, <http://www.atsdr.cdc.gov/>.
- 5 U.S. Department of Labor, Occupational Safety & Health Administration, <https://www.osha.gov/>.
- 6 S. Hellweg, E. Demou, M. Scheringer, T. E. Mckone and K. Hungerbuhler, *Environ. Sci. Technol.*, 2005, **39**, 7741–7748.
- 7 K. J. Krost, E. D. Pellizari, S. G. Walburn and S. A. Hubbard, *Anal. Chem.*, 1982, **54**, 810–817.
- 8 L. Zoccolillo, L. Amendola, S. Insogna and E. Pastorine, *J. Chromatogr. A*, 2010, **1217**, 3890–3895.
- 9 L. A. Wallace, E. D. Pellizzari, T. D. Hartwell, H. Zelon, C. Sparacino, R. Perritt and R. Whitmore, *J. Occup. Med.*, 1986, **28**, 603–608.
- 10 V. B. Stein, R. S. Narang, L. Wilson and K. M. Aldous, *J. Anal. Toxicol.*, 1986, **20**, 145–150.
- 11 R. Kroneld, *Bull. Environ. Contam. Toxicol.*, 1989, **42**, 868–872.
- 12 D. E. Harsch, D. R. Cronn and W. R. Slater, *J. Air Pollut. Control Assoc.*, 1979, **29**, 975–976.
- 13 CDC, The National Institute for Occupational Safety and Health (NIOSH), <http://www.cdc.gov/niosh/>, Method 1003.
- 14 M. Chai, C. L. Arthur, J. Pawliszyn, R. P. Belardi and K. F. Pratt, *Analyst*, 1993, **118**, 1501–1505.
- 15 Z. Ouyang, R. J. Noll and R. G. Cooks, *Anal. Chem.*, 2009, **81**, 2421–2425.
- 16 C.-H. Chen, T.-C. Chen, X. Zhou, R. Kline-Schoder, P. Sorensen, R. G. Cooks and Z. Ouyang, *J. Am. Soc. Mass Spectrom.*, 2014, **26**, 240–247.
- 17 S. Taylor and V. M. Bierbaum, *J. Am. Soc. Mass Spectrom.*, 2008, **19**, 1375–1376.
- 18 J. N. Smith, A. Keil, J. Likens, R. J. Noll and R. G. Cooks, *Analyst*, 2010, **135**, 994–1003.
- 19 C. C. Mulligan, D. R. Justes, R. J. Noll, N. L. Sanders, B. C. Laughlin and R. G. Cooks, *Analyst*, 2006, **131**, 556–567.
- 20 G. Huang, L. Gao, J. Duncan, J. D. Harper, N. L. Sanders, Z. Ouyang and R. G. Cooks, *J. Am. Soc. Mass Spectrom.*, 2010, **21**, 132–135.
- 21 C.-H. Chen, Z. Lin, R. Tian, R. Shi, R. G. Cooks and Z. Ouyang, *Anal. Chem.*, 2015, **87**, 8867–8873.
- 22 J. A. Contreras, J. A. Murray, S. E. Tolley, J. L. Oliphant, H. D. Tolley, S. A. Lammert, E. D. Lee, D. W. Later and M. L. Lee, *J. Am. Soc. Mass Spectrom.*, 2008, **19**, 1425–1434.
- 23 G. S. Groenewold, J. R. Scott, E. D. Lee and S. A. Lammert, *Anal. Methods*, 2013, **5**, 2227–2236.
- 24 S. Herndon, J. T. Jayne, M. S. Zahniser, D. R. Worsnop, B. Knighton, E. Alwine, B. K. Lamb, M. Zavala, D. D. Nelson, J. B. McManus, J. H. Shorter, M. R. Canagaratna, T. B. Onasch and C. E. Kolb, *Faraday Discuss.*, 2005, **130**, 327–339.

- 25 S. Giannoukos, B. Brkić, S. Taylor and N. France, *Anal. Chem.*, 2014, **86**, 1106–1114.
- 26 S. Giannoukos, B. Brkić, S. Taylor and N. France, *J. Am. Soc. Mass Spectrom.*, 2015, **26**, 231–239.
- 27 R. C. Johnson, R. G. Cooks, T. M. Allen, M. E. Cisper and P. H. Hemberger, *Mass Spectrom. Rev.*, 2000, **19**, 1–37.
- 28 E. Boscaini, M. L. Alexander, P. Prazeller and T. D. Mark, *Int. J. Mass Spectrom.*, 2004, **239**, 179–186.
- 29 A. J. Thompson, A. S. Creba, R. M. Ferguson, E. T. Krogh and C. G. Gill, *Rapid Commun. Mass Spectrom.*, 2006, **13**, 2000–2008.
- 30 L. S. Riter, B. C. Laughlin, E. Nikolaev and R. G. Cooks, *Rapid Commun. Mass Spectrom.*, 2002, **16**, 2370–2373.
- 31 R. A. Ketola, T. Kotiaho, M. E. Cisper and T. M. Allen, *J. Mass Spectrom.*, 2002, **37**, 457–476.
- 32 I. Cotte-Rodriguez, E. Handberg, R. J. Noll, D. P. A. Kilgour and R. G. Cooks, *Analyst*, 2005, **130**, 679–686.
- 33 L. S. Riter, Z. Takáts and R. G. Cooks, *Analyst*, 2001, **126**, 1980–1984.
- 34 P. Bocchini, R. Pozzi, C. Andalo and G. C. Galletti, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 2049–2053.
- 35 T. Kotiaho, S. Gylling, A. Lunding and F. R. Lauritsen, *J. Agric. Food Chem.*, 1995, **43**, 928–930.
- 36 F. J. Santos and M. T. Galceran, *Trends Anal. Chem.*, 2002, **21**, 672–685.
- 37 N. G. Davey, E. T. Krogh and C. G. Gill, *Trends Anal. Chem.*, 2011, **30**, 1477–1485.
- 38 R. A. Ketola, T. Kotiaho, M. E. Cisper and T. M. Allen, *J. Mass Spectrom.*, 2002, **37**, 457–476.
- 39 R. J. Bell, N. G. Davey, M. Martinsen, C. Collin-Hansen, E. T. Krogh and C. G. Gill, *J. Am. Soc. Mass Spectrom.*, 2015, **26**, 212–223.
- 40 W. Gao, G. Tan, Y. Hong, M. Li, H. Nian, C. Guo, Z. Huang, Z. Fu, J. Dong, X. Xu, P. Cheng and Z. Zhou, *Int. J. Mass Spectrom.*, 2013, **334**, 8–12.
- 41 J. M. Etzkorn, N. G. Davey, A. J. Thompson, A. S. Creba, C. W. LeBlanc, C. D. Simpson, E. T. Krogh and C. G. Gill, *J. Chromatogr. Sci.*, 2009, **47**, 57–66.
- 42 P. G. Wenner, R. J. Bell, F. H. W. van Amerom, S. K. Toler, J. E. Edkins, M. L. Hall, K. Koehn, R. T. Short and R. H. Byrne, *Trends Anal. Chem.*, 2004, **23**, 288–295.
- 43 B. Brkić, N. France and S. Taylor, *Anal. Chem.*, 2011, **83**, 6230–6236.
- 44 U.S National Library of Medicine, Toxicology Data Network, <http://toxnet.nlm.nih.gov/index.html>.
- 45 NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>.
- 46 W. H. McClennen, C. L. Vaughn, P. A. Cole, S. N. Sheya, D. J. Wager, T. J. Mott, J. P. Dworzanski, N. S. Arnold and H. L. C. Meuzelaar, *Field Anal. Chem. Technol.*, 1996, **1**, 109–116.
- 47 A. Naganowska-Nowak, P. Konieczka, A. Przyjazny and J. Namiesnik, *Crit. Rev. Anal. Chem.*, 2005, **35**, 31–55.