

Direct analysis and monitoring of organosulphur compounds in the gaseous phase using portable mass spectrometry.

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Short Title: Analysis of organosulphur compounds using portable MS.

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ABSTRACT

Organosulphides are ubiquitous in the natural world and are important in the agriculture, pharmaceuticals and petrochemical sectors. For the first time a lightweight (12 kg), man-portable membrane inlet mass spectrometer (MIMS) has been employed to analyse volatile organosulphur compounds (VOSCs) in the gaseous phase. Monitoring of such compounds in field conditions (outside the chemical laboratory). Representative compounds tested include: 2-methyl-2-propanethiol, 1-propanethiol, diethyl disulphide, 1-butanethiol, ethanethiol, thiophene, methyl ethyl sulphide and dimethyl disulphide. Experiments in the gas phase were performed at low parts-per-billion (ppb) analyte levels. The results obtained showed low limits of detection (high parts-per-trillion - ppt), very good linear regression within the examined concentration range, fast membrane response times and good repeatability with relative standard deviation, $RSD < 4\%$. Analysis of a complex multi-component gaseous mixture of organosulphur compounds was also demonstrated.

Keywords: *field chemical analysis, portable mass spectrometry, organosulphur compounds, environmental monitoring, gas analysis.*

1. INTRODUCTION

The continuous increase of air and water pollution poses a major concern for public health as well as contributing to climate change. The extensive use of volatile organic compounds (VOCs) is well known to contribute to environmental pollution [1-10]. Volatile organosulphur compounds (VOSCs), a subclass of VOCs, are mainly released into the atmosphere from industrial waste, waste management facilities and from natural sources (e.g. volcanoes, wildfires, vegetation, fossil fuels, oceans) [11]. The removal of organosulphides is also a major activity in the petrochemical sector and monitoring of organosulphide compounds is important in the pharmaceutical sector and in agriculture. VOSCs have been previously investigated in the gaseous phase using headspace gas chromatography (GC) with flame ionisation detection (FID) and/or GC coupled with an electrolytic conductivity detector (ELCD) [12]. Benchtop MIMS [13, 14] and proton-transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) have also been utilised [15].

Sample collection of sulphur compounds in the gas phase is a complicated procedure as organosulphur compounds are highly reactive, can be adsorbed onto surfaces, reacting with them. They may also undergo photooxidation reactions and are prone to catalytic oxidation [16, 17]. Thus, special containers (e.g. glass or stainless steel sorbent tubes, glass canisters, or gas sample bags) are required for their collection and transportation to the chemical laboratory, to avoid absorption phenomena or any type of chemical reactions. To prevent photochemical reactions, transparent glass canisters or sampling bags can be covered with light preventing surfaces e.g. aluminium foil. The complex reactive nature of the organosulphur compounds alongside with the time-consuming collection, transportation and storage of the samples demonstrate the need for *in-situ* and real-time chemical analysis using reliable systems with high sensitivity.

Portable MS and more specifically field-deployable MIMS [18-41] could be a possible solution for VOCs detection and monitoring. MIMS has been previously utilised in the detection and on-line monitoring of VOCs and semi-VOCs for various applications; i.e. homeland security, forensics, environmental monitoring (air quality and water analysis), industrial processes, health and life science, molecular communications, etc. MIMS is a well investigated analytical methodology which employs a membrane interface to introduce sample molecules into the vacuum system of a mass spectrometer for analysis. It is based on a three-stage pervaporation process. Sample molecules (from the gaseous, liquid or solid phase) absorb onto the surface of a membrane, diffuse through it and finally desorb into the vacuum system. MIMS is a selective technique, property which depends on the membrane material (e.g. silicone, polytetrafluoroethylene - PTFE, polyethersulfone - PES, nylon, etc.), its characteristics (e.g. hydrophobic, hydrophilic, thickness, porosity, etc.) and the operational conditions (e.g. sample flow, suction flow, applied temperature, etc.). A widely used membrane material is polydimethylsiloxane (PDMS) which allows non-polar or medium polarity molecules to pass through it.

Portable MS based systems for on-site VOCs analysis are still limited in the market for various reasons (operational or technical). The MS-200 (Kore Technology Ltd.) [42] is a portable time-of-flight MS weighting 20kg with a mass range of 1-1000 amu and limits of detection in the low ppb concentration area. It can analyse 1 spectrum every 5 minutes. The Torion T-9 Portable GC-MS (PerkinElmer Corporation) [43] is a toroidal ion trap mass spectrometer that weighs 14.5 kg. It can scan molecules with molecular weight from 50 to 500 amu. Sample collection and introduction into the vacuum chamber is done using a solid phase micro extraction (SPME) fibre. Griffin™ 400 (FLIR Systems Inc.) [44] is a transportable GC-MS that weighs 37 kg and consumes 600W of power when it is in operation. It has a mass range between 40 and 425 amu. The IonCam (OI Analytical Inc.)

[45] weighs 19 kg and has a power consumption of 150 W. It can scan masses below 210 amu. The EcoSys-P (European Spectrometry Services Ltd. UK) [46] weighs 23 kg, consumes 200 W of power when is in full operation and can scan masses up to 200-300 amu. The Dq1000™ (Fluid Inclusion technologies Inc.) [47] is a quadrupole mass spectrometer used in the detection and analysis of hydrocarbons and other species in oil-based drilling operations. It weighs 23kg, consumes 390W of power and can analyse light molecules (up to 140 amu). Mini 10, Mini 11 and Mini 12 are all portable MS systems based on ion trap technology developed in Aston Labs (Purdue University) [48] weighting 10, 4 and 25 kg respectively. These systems utilise various ambient environment ionisation techniques e.g. paper spray (PS), electrospray ionisation (ESI), etc. allowing the analysis of chemical analytes with different physical and chemical properties. Inficon (Syracuse, NY) [49] in collaboration with the University of North Texas have also developed a mobile QMS system for VOC screening.

In this work, a portable system based on triple filter quadrupole mass spectrometry (QMS) provided by Q-Technologies Ltd. UK [50] was utilised. The chemical sensor weighs less than 12 kg and has power consumption of 75 W. It can detect compounds with mass range m/z 1 – 200 amu, and its limits of detections are in the ppt range. The triple filter QMS has several advantages over single QMS. It offers enhanced ion focusing, high sensitivity and resistance to contamination. In this study, we focus on the analysis (detection and monitoring) of low molecular weight VOSCs in the gas phase with potential focus in industrial systems and environmental applications.

2. EXPERIMENTAL PART

2.1 Motivation

The motivation behind this study is to investigate the direct chemical analysis of volatile organosulphur compounds in the gas phase using a lightweight portable MS system. The target of this study is to provide a complete user-friendly analytical solution that will enable the measurement (detection, monitoring, alarming, etc.) of environmental pollutants and toxic industrial compounds in field applications. Selected chemicals for analysis are presented in Table 1, whereas Table 2 gives an overview of their main uses and possible health effects. The high toxicity of the investigated compounds and the human exposure to them may lead to severe health issues [1, 2, 4, 6, 7, 8, 9, 10].

Table 1. Summary of the volatile organosulphur compounds analysed by our MIMS system.

Compound	CAS Number	Molecular weight (g/mol)	Vapour pressure (kPa) at 25°C	log octanol/water partition coefficient (log K_{ow})	Odour threshold (ppb)
2-methyl-2-propanethiol	75-66-1	90.187	24.13	2.14	0.33
1-propanethiol	107-03-9	76.157	20.56	1.81	0.75
diethyl disulphide	110-81-6	122.244	0.57	3.17	N.A.
1-butanethiol	109-79-5	90.187	5.93	2.28	0.1-1
ethanethiol	75-08-1	62.134	70.53	1.27	0.76
thiophene	110-02-1	84.140	10.63	1.81	N.A.
methyl ethyl sulphide	624-89-5	76.161	24.7	1.54	N.A.
dimethyl disulphide	624-92-0	94.19	3.83	1.77	0.029

Table 2. Summary of common uses and potential health effects of the volatile organosulphur compounds tested in this work [6, 7, 8, 9, 10].

Compound	Main uses	Possible health effects
2-methyl-2-propanethiol	<ol style="list-style-type: none"> Natural gas odorant Flavour additive 	<ol style="list-style-type: none"> Depressant Muscular weakness Headache, dizziness, nausea,

		<p>confusion</p> <p>4. Lung damage (in high concentrations)</p> <p>5. Neurologic effects e.g. narcosis and paralysis</p>
1-propanethiol	<ol style="list-style-type: none"> 1. Agricultural uses 2. Feedstock for insecticides 	<ol style="list-style-type: none"> 1. Muscular weakness 2. Headache, nausea 3. Pulmonary irritation 4. Respiratory issues, e.g. paralysis 5. Unconsciousness
diethyl disulphide	<ol style="list-style-type: none"> 1. Petrochemical industry 2. Agricultural pesticide 3. Flavour constituent 	<ol style="list-style-type: none"> 1. Respiratory irritation 2. Skin irritation 3. Gastrointestinal irritation 4. Pulmonary edema 5. Cyanosis
1-butanethiol	<ol style="list-style-type: none"> 1. Food flavour 2. Natural gas odorant 3. Industrial solvent 4. Intermediate in cotton processing 	<ol style="list-style-type: none"> 1. Musculoskeletal abnormalities 2. Craniofacial abnormalities 3. Respiratory stimulation 4. Weakness, headache, dizziness, nausea 5. Visual disorders, confusion
ethanethiol	<ol style="list-style-type: none"> 1. Natural gas odorant 2. Stabiliser for adhesives 3. Mining industry 	<ol style="list-style-type: none"> 1. Dizziness, headache 2. Death 3. Liver and kidney disorder 4. Anaemia
thiophene	<ol style="list-style-type: none"> 1. Agrochemical industry 2. Pharmaceuticals 3. Petrochemical industry 	<ol style="list-style-type: none"> 1. Skin and eye irritation 2. Skin allergies 3. Liver damage 4. Headache, nausea, vomiting 5. Respiratory problems

methyl ethyl sulphide	<ol style="list-style-type: none"> 1. Natural gas odorant 2. Corrosion inhibitor for zinc 3. Food additive 	<ol style="list-style-type: none"> 1. Skin irritation and eye damage
dimethyl disulphide	<ol style="list-style-type: none"> 1. Pulp and paper facilities 2. Food additive 3. Industrial processes, e.g. petrochemicals, in refineries, 4. Agricultural pesticide 5. Soil fumigant 	<ol style="list-style-type: none"> 1. Toxic 2. Headache and nausea 3. Liver damage 4. Pulmonary irritation 5. Neurologic symptoms, e.g. coma 6. Gastrointestinal effects 7. Dermatological effects e.g. dermatitis 8. Hemolytic anemia

2.2 Reagents.

The following chemical analytes: 2-methyl-2-propanethiol (99% purity), 1-propanethiol (99% purity), diethyl disulphide (99% purity), 1-butanethiol (99% purity), ethanethiol (97% purity), thiophene (99% purity), methyl ethyl sulphide (96% purity) and dimethyl disulphide were purchased from Sigma Aldrich Co. LLC., U.K. Standard stock solutions of the above reagents were prepared in methanol at concentrations of 200 µg/mL and 1000 µg/mL. Methanol (HPLC grade, purity >99.9 %) was also provided by Sigma Aldrich Co. LLC., UK. All reagents were provided in the liquid phase and the stock solutions were stored in the fridge at 4°C until their use.

2.3 Experimental Procedure.

Experiments were done using a hand-portable (12 kg) membrane inlet mass spectrometer (Figure 1) supplied by Q-Technologies Ltd., Liverpool, UK. The MIMS system is based on quadrupole mass spectrometry and its technical characteristics have been previously

described in detail. Briefly, it consists of a triple filter quadrupole mass analyser (QMA) hosted in a stainless steel vacuum chamber continuously pumped down by a diaphragm and a turbomolecular pump (Agilent Varian Mini-TASK AG 81 pumping system). The pumping speed of the vacuum system is 38 L/m for N₂, whereas, the base pressure of the system with the sampling valve fully closed is 1 x 10⁻⁷ Torr. Sample introduction is achieved by a membrane inlet sampling probe connected to the side of the vacuum chamber. The technical characteristics of the probe can be found in the literature [35-38]. For our experiments, the sampling probe was kept at ambient temperature. Sample molecules pass through the membrane interface into the vacuum chamber where they are being ionised by an electron impact (EI) ion source. The generated ion fragments travel through a triple filter QMA, they are being separated according to their mass-to-charge ratio and they finally reach the detector that is a multiplier. The detected signals are being recorded and displayed on a laptop computer for further analysis. During data acquisition, 10 acquisition points per unit mass and 20 scans throughout the mass range *m/z* 40-150 amu were recorded.

To generate gas standards, we used the technique of the static dilution bottles. Details can be found in the literature [51, 52]. Appropriate quantities of the liquid stock solution were injected in clean 1.2 L glass flasks (Sigma Aldrich Co. LLC., U.K.) filled with zero grade nitrogen (purchased from BOC UK Ltd.). The flasks were covered with silicone caps and several layers of parafilm M. They were left then in ambient conditions for 8 hours to evaporate and to reach the thermodynamic equilibrium. Gas standards of the selected chemical analytes (Table 1) were prepared at the following concentrations: blank, 5 ppb, 10 ppb, 25 ppb, 50 ppb, 75 ppb and 100 ppb. All experiments were triplicated, to allow us to perform statistical analysis, to check the repeatability of the tests and the stability of our system.

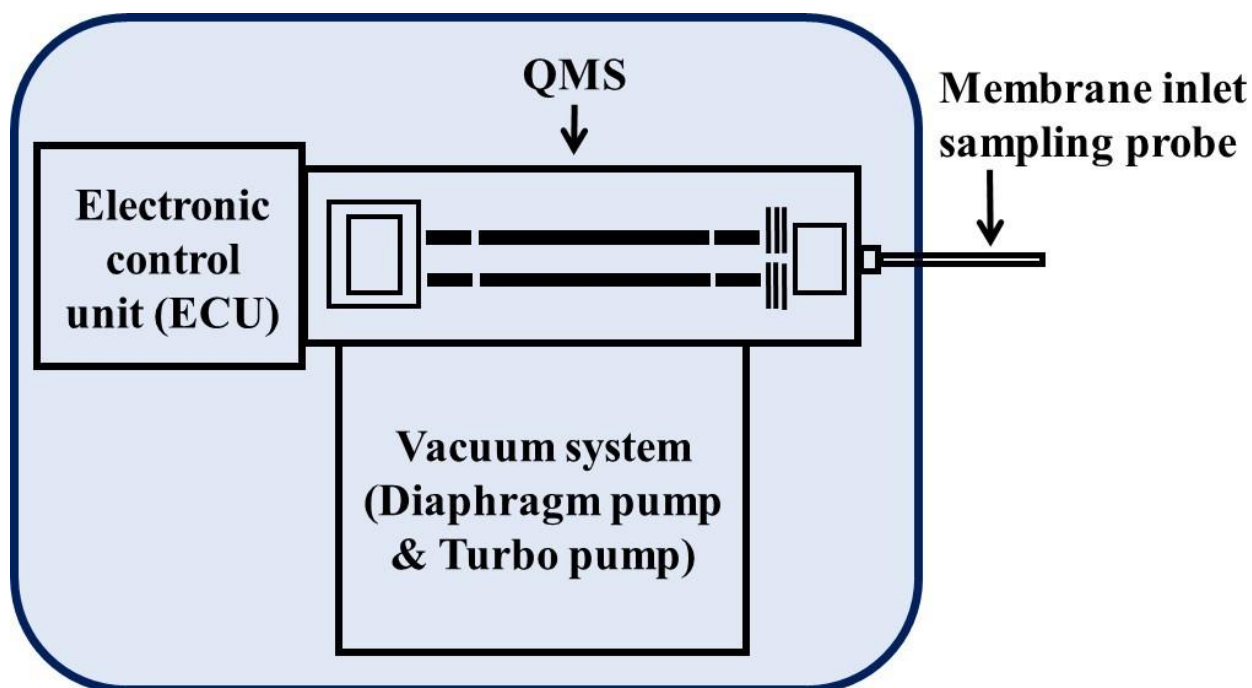


Figure 1. Schematic representation of the MIMS system used in our experiments.

3. RESULTS AND DISCUSSION

3.1 Organosulphur compound experiments

This experimental series was done to investigate the mass spectrometric detection and monitoring of volatile organosulphur compounds in the gas phase using our portable MS system. A membrane sampling probe was inserted into the individual flasks containing gaseous samples at standard concentrations (described above). The sequence of testing was done starting with the flask with the lowest concentration and ending with the flask containing the gas standard with the highest concentration to eliminate memory effects and/or carry over phenomena. Between individual concentration samples, a purging phase of 5 minutes was allowed. This included sampling of ambient air and cleanse of the spectrum area from any observed peaks. Representative mass spectra (at the maximum signal intensity value – at the point when detection reaches a steady state condition) for 2-methyl-2-propanethiol, 1-propanethiol, diethyl disulphide, 1-butanethiol, ethanethiol, thiophene, methyl ethyl sulphide and dimethyl disulphide corresponding to 100 ppb distinct gas

standards are presented in Figure 2 and 3. The relative intensities of the detected ion fragments of the experimentally obtained EI mass spectra match well with the reference mass spectra from the NIST Chemistry Webbook.

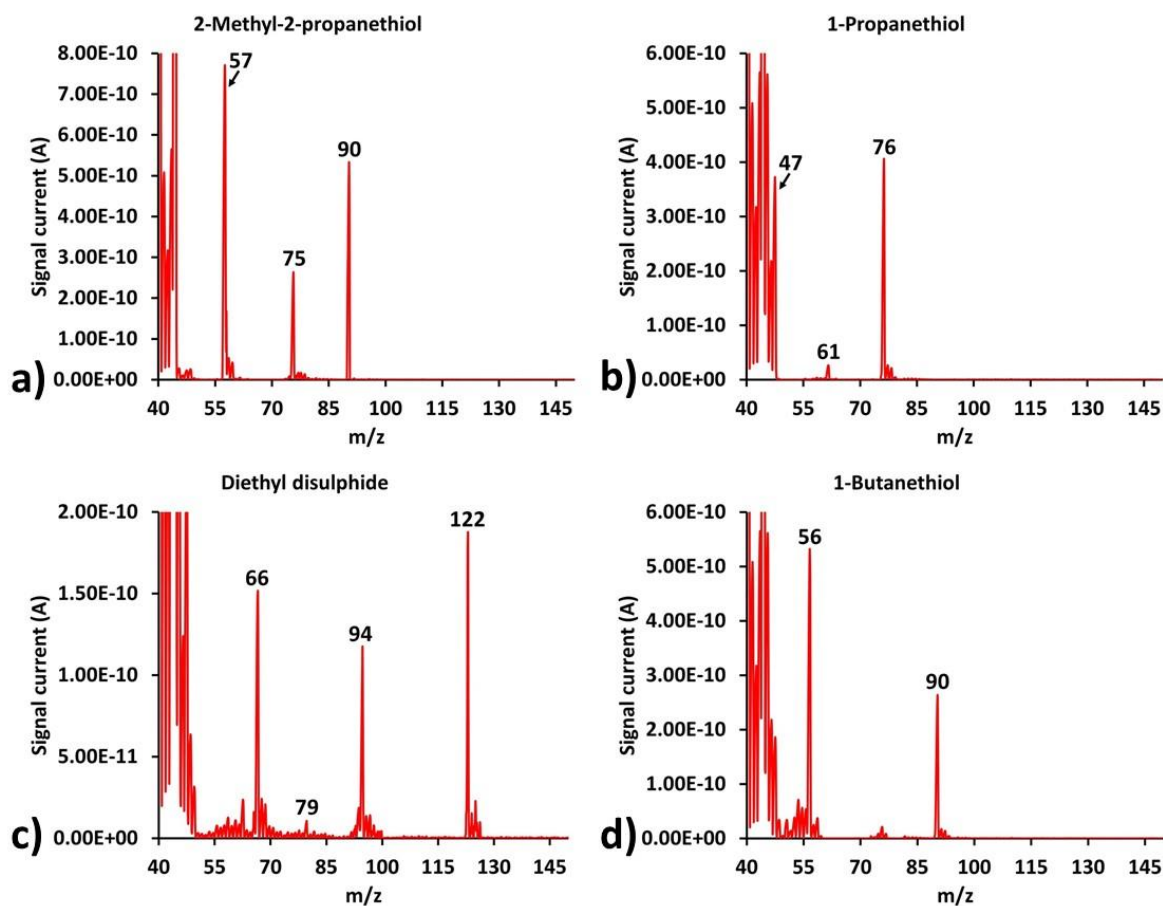


Figure 2. Representative experimental mass spectra at 100 ppb for a) 2-methyl-2-propanethiol, b) 1-propanethiol, c) diethyl disulphide and d) 1-butanethiol obtained with our MIMS system.

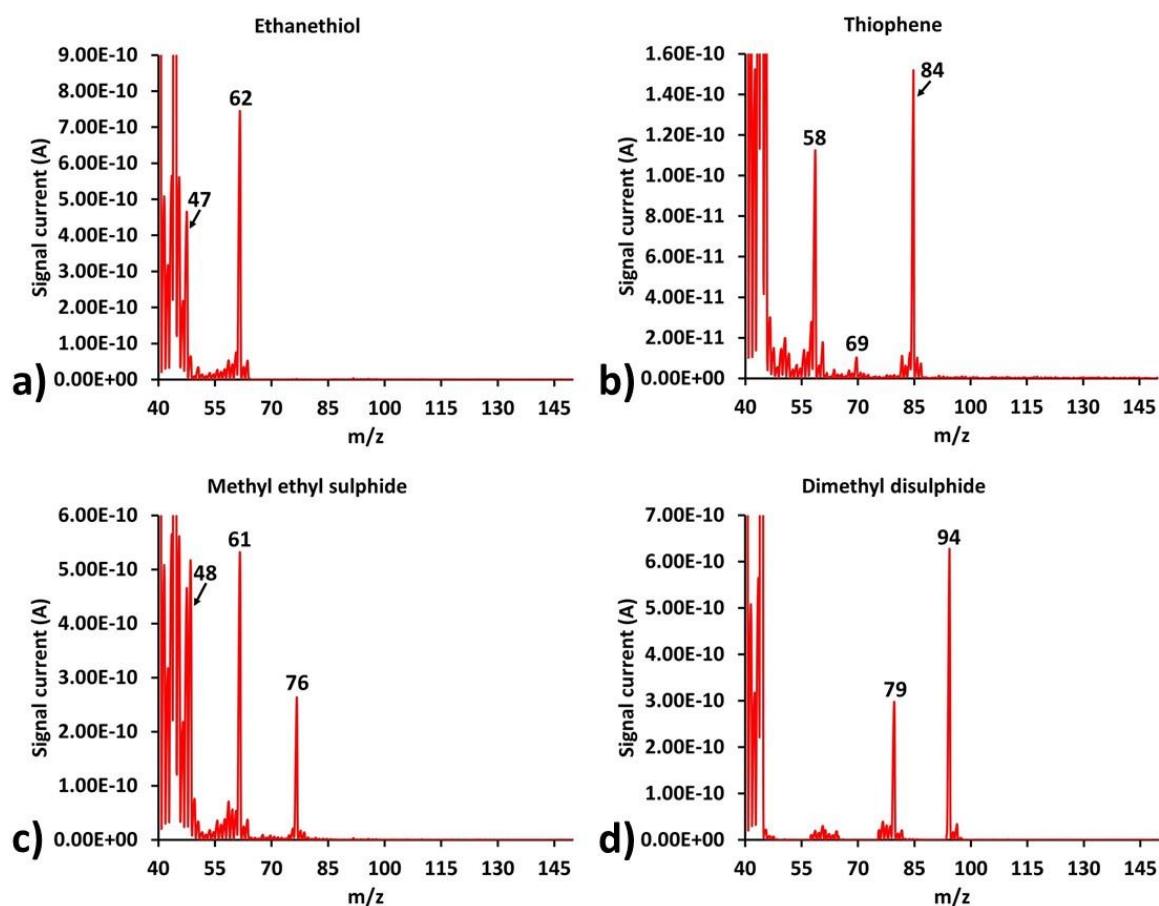


Figure 3. Representative experimental mass spectra at 100 ppb for a) ethanethiol, b) thiophene, c) methyl ethyl sulphide and d) dimethyl disulphide obtained with our MIMS system.

3.2 Multi-compound experiment

In order to examine that our system can operate reliably with complicated samples (which commonly occur in practice), we generated a gas mixture of 5 compounds: 1-butanethiol, 2-methyl-2-propanethiol, thiophene, dimethyl disulphide and methyl ethyl sulphide at 100 ppb each. Sample preparation was done within a stainless-steel mixing chamber connected with five pieces of Teflon tubing (150 mm length with 6.35 mm ID) to five 1.2 L glass flasks (one compound per flask) containing the gas standards. Gaseous samples were prepared following the same process as discussed above. A representative mass spectrum of a multi-compound

mixture is shown in Figure 4. Characteristic mass fragments of the examined compounds are clearly shown. There is an overlapping peak (m/z 90) common in the mass spectrum of 1-butanethiol and 2-methyl-2-propanethiol, which can be deconvoluted to the individual components by calculating the contribution of individual compound components to the peak intensity.

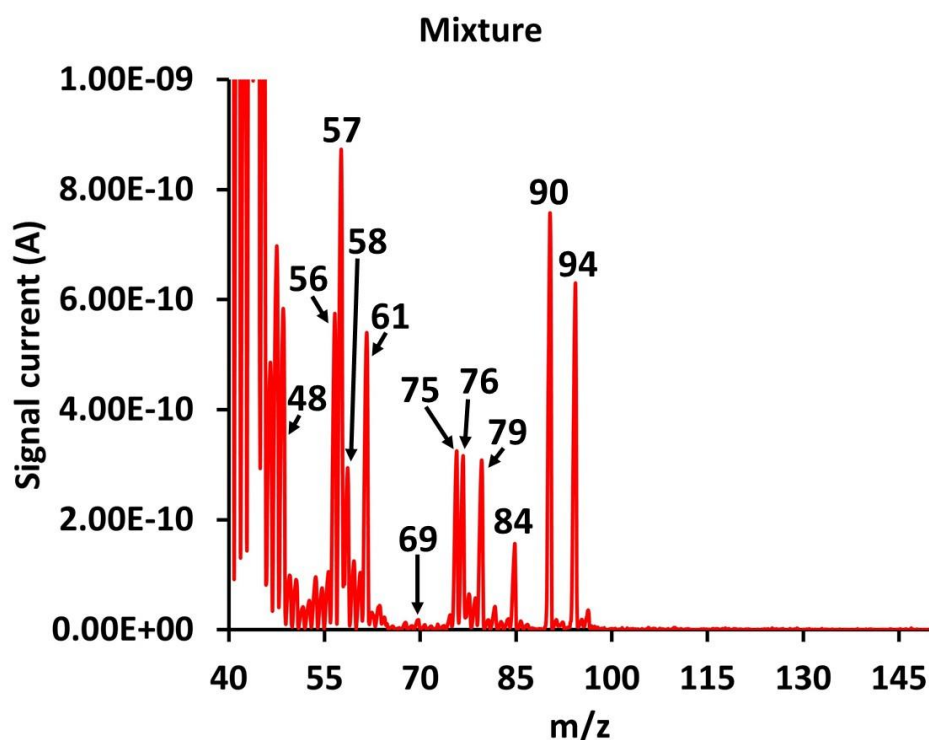


Figure 4. Experimental mass spectrum of a mixture of 1-butanethiol (m/z 56, 90), 2-methyl-2-propanethiol (m/z 57, 75, 90), thiophene (m/z 58, 69, 84), dimethyl disulphide (m/z 79, 94) and methyl ethyl sulphide (m/z 48, 61, 76) at 100 ppb each obtained with our MIMS.

3.3 Evaluation of the method

This section summarises the analytical characteristics of Liverpool MIMS system. We examine the following analytical criteria: a) membrane response, b) linearity of the data, c) limits of detection (LoD), d) repeatability and stability of the results obtained. Table 3 gives an overview of these characteristics. The calibration curves generated by the gas standards may allow us to run quantification measurements with confidence. The average linear

regression coefficient is 0.9947 whereas the LoD were found to be in low ppb concentration area. LoD values were calculated based on experimentally obtained signal current values of the characteristic peak of each compound. LoD were calculated to be five times above the baseline. The average rise time (the time required for the signal to reach its maximum signal intensity) for the compounds tested is 17.6 sec whereas the average fall time (the time required for the signal of a compound to return to the baseline levels) is 23 sec. The measurements obtained showed a good repeatability with relative standard deviation (RSD) equal to 3.9 %. The stability of our data was confirmed by monitoring selected ions for the compounds e.g. 1-propanethiol (m/z 76) and diethyl disulphide (m/z 122). Figure 5a presents four representative pulses of increasing concentration (25ppb, 50 ppb, 100 ppb and 200 ppb) of 1-propanethiol. Each step has a duration of 360 sec. **The response of the MIMS in regards to the increased concentrations is linear with an R^2 at 0.9966.** In addition, figure 5b shows an increase-decrease profile of 1-propanethiol with seven repeated steps at 50 ppb each. As it can be seen, even the short step times, Liverpool MIMS system provides repeatable data with an RSD equal to 4 %.

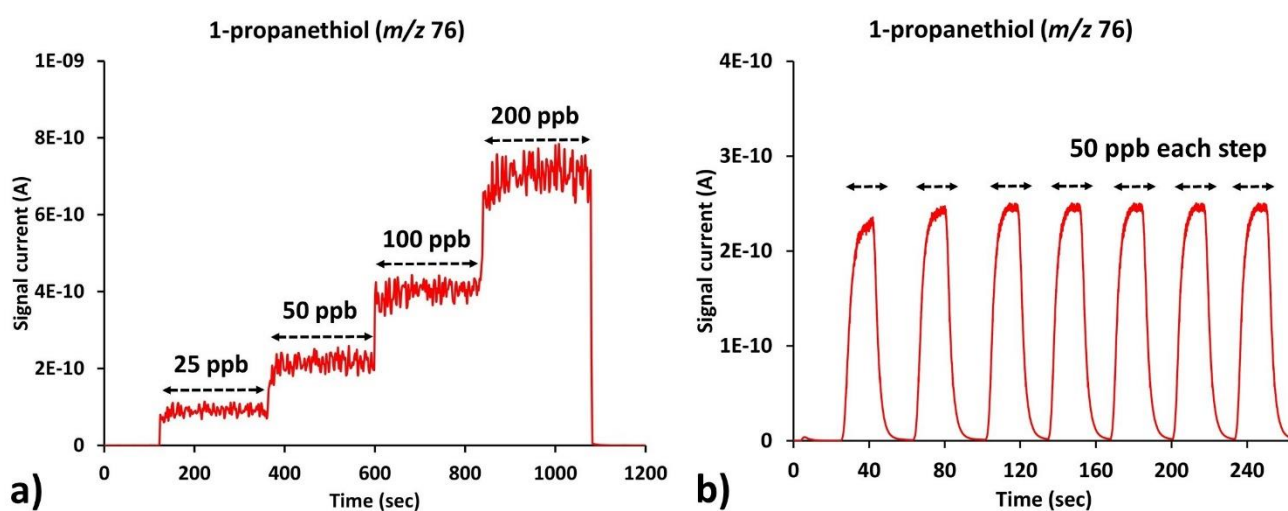


Figure 5. a) Stepwise increase profile for the mass fragment m/z 76 of 1-propanethiol, b) increase-decrease profile of the mass fragment m/z 76 of 1-propanethiol.

Table 3. Summary of the analytical characteristics (response time, R^2 values and LODs) of our MIMS approach in the analysis of organosulphur compounds that were tested.

Compound	characteristic mass fragments (m/z)	rise time (sec)	fall time (sec)	R^2	LOD (ppb) in air (calculated)
2-methyl-2-propanethiol (m/z 57)	57, 75, 90	14	19	0.9952	0.506
1-propanethiol (m/z 76)	47, 61, 76	15	22	0.9966	0.974
diethyl disulphide (m/z 122)	66, 79, 94, 122	22	33	0.9953	0.982
1-butanethiol (m/z 56)	56, 90	24	28	0.9841	0.740
Ethanethiol (m/z 62)	47, 62	26	31	0.9998	0.513
Thiophene (m/z 84)	58, 69, 84	12	17	0.9922	1.257
Methyl ethyl sulphide (m/z 61)	48, 61, 76	16	13	0.9987	0.769
Dimethyl disulphide (m/z 94)	79, 94	12	21	0.9956	0.635

3.4 Validation experiments

To validate the performance of our system, we run simulation experiments in a test chamber with a volume of 16 m³ to simulate an indoor environment [38]. The test chamber was purged overnight and filled with synthetic air (BOC Ltd. UK) before the start of the experiment. A vapour generator [53-56] was used to produce a mixture of 2-methyl-2-propanethiol, thiophene and dimethyl disulphide at 100 ppb each in a controllable way. The vapour generator (based on controlled evaporation of liquid analytes and their diffusion in a carrier gas stream) was connected with the test chamber and vapour samples were introduced by a sidewall hole with diameter of 6.35 mm. Injection time was 10 sec. In another sidewall, our MIMS system was sampling continuously the chamber air (as described above). A fan inside the chamber was providing a homogeneous distribution of the sample mixture. A representative mass spectrum of the injected mixture, 2 minutes after sample injection, is presented in Figure 6. At this time, the detected concentrations of 2-methyl-2-propanethiol,

thiophene and dimethyl disulphide were calculated (based on the calibration curves) to be 2.26, 3.01 and 2.05 ppb respectively.

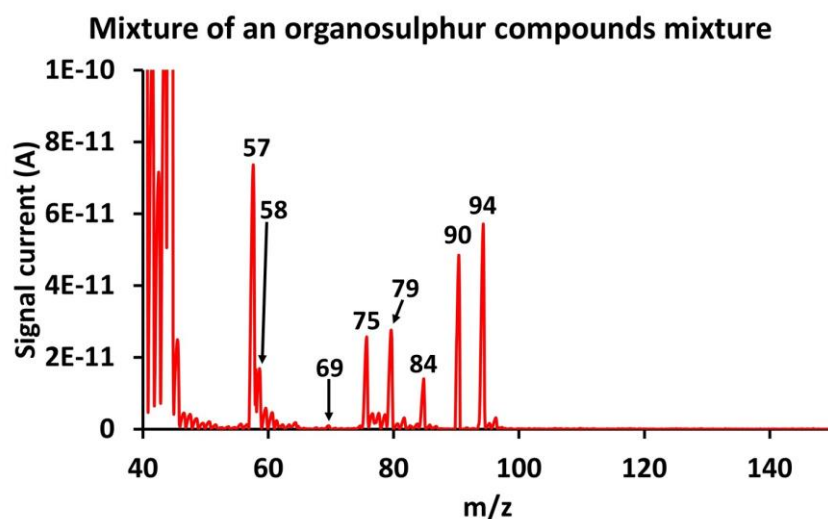


Figure 6. Representative mass spectrum of a mixture of 2-methyl-2-propanethiol (m/z 57, 75, 90), thiophene (m/z 58, 69, 84), dimethyl disulphide (m/z 79, 94) obtained from a test chamber using Liverpool MIMS system.

4. CONCLUSIONS

In this paper we report a lightweight (12 kg) portable MS is able to detect and monitor both qualitatively and quantitatively organosulphur compounds in the gaseous phase for air quality monitoring purposes and/or industrial emissions. Proof-of-principle for trace detection of low molecular weight VOSCs using MIMS was demonstrated. During measurements, fast membrane response times (few seconds) were observed, whereas we got good linear calibration curves for the compounds tested and repeatability with RSD calculated to be 3.9%. Good peak discrimination and separation were also obtained when a complex mixture of organosulphide compounds was tested. **Detection experiments within a test chamber with a**

volume of 16 m³ were also performed. These positive results allow future exploitation of this technology for example in environmental monitoring.

Future work includes field testing and validation of the technique described above. We also plan to further miniaturize our sensor using a lighter vacuum system (e.g. Pfeiffer HiPace 10 Turbo Pump and MVP-006 Diaphragm) and to improve its technical characteristics for higher pressure operation. Characteristically, for field testing, we plan to utilize a quadrupole mass analyser with mass range up to 500 amu in order to expand the range of the VOCs which we can detect on-site. A heated membrane sampling probe could allow detection of compounds at lower concentrations levels compared to the current LoD with faster response times (e.g. by a factor of 5), whereas integration of signal processing algorithms in our data analysis software would boost sensitivity. We also plan to benefit from machine learning and advanced chemometrics to allow our system to interpret data itself, generate alarms and make decisions autonomously. The later in combination with our additional miniaturization plans will enhance the capabilities of the system and will allow us to integrate it on autonomous robotic platforms for remote chemical sensing in various application areas.

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