



Analytical Methods

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Mobile mass spectrometry for water quality monitoring of organic species present in nuclear waste ponds

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This work uses a portable mass spectrometer (MS) for lab-based water quality monitoring of organic compounds, which are present in highly toxic nuclear waste ponds. This is due to a number of effects that such species have on storage of radioactive waste. The MS system that was used for the tests consists of a quadrupole mass spectrometer (QMS) housed in a mobile vacuum system with dual sample inlet options. The QMS uses a triple filter analyser for high performance and sensitivity to ppb levels in water. Mass spectra were obtained using a membrane sample inlet for the following organic substances: acetone, acetophenone, cyclohexanone, isophorone, 1-pentanol, 1-heptanol, propionaldehyde, ethyl acetate, ethyl propionate and odourless kerosene. Calibration curves were obtained for selected mass fragments for each of the compounds tested and showed excellent linearity ($R^2 \geq 0.9835$ in all cases). Spectra were also obtained for compound mixtures for acetone, cyclohexanone, acetophenone and isophorone as well as for 1-pentanol and 1-heptanol. All the tested substances were successfully detected with their spectral peaks clearly distinguished. Rise and fall membrane response times are given for specific compounds including their limits of detection (LOD), which are within the current demands of the nuclear industry.

Introduction

In recent years, the UK nuclear industry has started with programmed activities in retrieval and decommissioning its legacy ponds and silos to remove hazards and wastes for long-term storage. Such wastes have been generated and stored since 1950s, particularly at the Sellafield's Magnox Swarf Storage Silo (MSSS) nuclear reprocessing site in Cumbria, England. The decommissioning work is planned for at least another 100 years with an estimated cost in the tens of billions of pounds. This work entails a number of uncertainties and possible unexpected events due to the major environmental, technical and operational questions. This is due to poor record keeping at old nuclear sites and prolonged limited access due to high radiation hazards.¹ During decommissioning, the main goal will be to protect the workforce and minimise radioactive pollution of the environment.

The high hazard reduction program in nuclear industry is expected to require dynamic characterization of gases and organic species as part of post-operative clean out (POCO).² This procedure is typically carried out when a nuclear power plant reaches the end of its operating life. The main benefit of POCO is that it makes power plants radiologically clean and cost effective by removing their nuclear inventory. The nuclear industry is becoming increasingly aware of the importance of the effects of organic

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species during POCO and decommissioning. The behaviour and characterisation needs of the industry for monitoring organic species in nuclear fuel ponds are illustrated in the following paragraph using several examples.

Grout/cement that are used for encapsulating nuclear waste are very sensitive to the presence of organic materials in terms of both the concentrations and structure of the materials.³ The potential effects include:

- a. Impact on setting characteristics,
- b. Retardation, leading to throughput and bleed liquor issues,
- c. Acceleration, leading to cracking and other problems,
- d. Foaming.

Likewise, life-time product quality has the following impact on radioactive waste management (RWM) disposal in geological disposal facility (GDF):

- i. Hydrolysis and microbial degradation of organic species leads to gaseous problems and swelling/pressurization of containers such as ductile cast iron containers (DCIC).
- ii. Ongoing degradation of organic materials leads to acidification / HCl and corrosion of the product box / liner.
- iii. Organic complex formation with radionuclides leads to faster transport of activity into the environment, which can cause harmful effects such as radioactive contamination.

Limited sensing technology with real-time, in-situ chemical analysis capabilities is currently available for monitoring radioactive environments. Recently, Xylem Analytics UK Ltd. introduced a remote multi-sensing platform (EXO2) to measure conductivity, temperature, dissolved oxygen, pH, depth, total algae, fluorescent dissolved organic matter and turbidity within nuclear waste ponds.⁴ These factors are important to be continuously monitored to allow a clear overview of the overall condition of the water and to maintain stable radioactive waste storage conditions. An underwater mobile sensor network has been also designed to perform spatial sampling of depth, temperature, pH and radioactivity.⁵ Moreover, piezoelectric wafer active sensors have been suggested for structural health monitoring (SHM) including pipe and vessels applications (PVP) of nuclear dry cask storage systems.^{6,7}

The behaviour of organic material and radionuclides in nuclear ponds represents a complex and under study system.⁸ Water samples are routinely collected from the ponds for laboratory analysis using analytical instruments. Typical concentration range required by the nuclear industry is from ppb to ppm with 400-500 ppm concentrations measured at MSSS. Due to physical restrictions, water samples can only be taken from specific locations around the edge of the pond. Sample collection from the ponds is a complicated and time-consuming process where two persons are required. Personnel are required to wear PVC protective suits, facemasks and waterproof gloves, and can only stay at the pond for a limited time. Therefore, there is a need for portable analytical instruments that will provide remote, sensitive, non-destructive and continuous on-site water monitoring without human presence at the pond.

This paper presents a portable membrane inlet mass spectrometer (MIMS)⁹ with m/z 200 mass range that can potentially be used for remote monitoring of volatile organic compounds (VOCs) in water within nuclear waste ponds. Previous work has already shown the potential of MIMS for continuous on-site oil-in-

water/VOC monitoring at the Flotta Oil Terminal (Orkney, UK).¹⁰ Therefore, a similar configuration can be made in nuclear waste ponds. Experimental results are shown for a number of highly relevant hydrocarbon species present in the ponds, which were recommended by the National Nuclear Laboratory (Preston, UK). The individual samples and their mixtures were injected into water and tested at different concentrations. The experiments were performed in the lab with acetone, acetophenone, cyclohexanone, isophorone, 1-pentanol, 1-heptanol, propionaldehyde, ethyl acetate, ethyl propionate, methyl butyrate and odourless kerosene. Mixtures of acetone, cyclohexanone, acetophenone and isophorone in water as well as a mixture of 1-pentanol and 1-heptanol were also tested. Calibration curves were obtained for characteristic mass fragments and showed excellent linearity allowing determination of concentration down to ppb levels.

Experimental

The setup of the system is illustrated in the diagram of Figure 1. The system consists of a quadrupole mass spectrometer (QMS) with a triple filter analyser inside a vacuum chamber connected to the vacuum system and the electronic control unit (ECU). Samples were introduced through the inlet based on a thin hydrophobic flat sheet polydimethylsiloxane (PDMS) membrane. The PDMS material allows passage of non-polar volatile organic compounds (VOCs) from individual substances and mixtures using the pervaporation process, illustrated in Figure 2. The membrane sampling probe was inserted inside a 1.2 L flask (Sigma Aldrich Co. LLC., U.K.) with water and the injected sample. The flask was placed on a magnetic stirrer set at medium speed with a hot plate to maintain the water temperature at 50 °C. Samples were injected using a micro-pipetter (Brand GmbH, Germany).

QMS

The QMS (analyser + electronics) was supplied by Q-Technologies Ltd. It has a total weight of 1.2 kg with all of its parts assembled on a CF38 vacuum flange. It consists of a hot filament electron impact (EI) ion source, a triple filter quadrupole mass analyser, and a dual mode detector. The EI source is an open type with a twin thoriated iridium filament that requires 1.8 A filament current for 1.6 mA electron emission. The sensitivity of the EI source is set by the ion cage and electron repeller. The ion cage is held at positive dc voltage (7 V for optimal sensitivity) to attract electrons from the filament into the ionization region and to extract newly created ions into the mass filter. The electron repeller is held at negative dc voltage (-110 V for optimal sensitivity) to keep majority of emitted electrons in the ionization region. The EI source also has a lens system with ion extraction lens physically connected to the ion cage, ion focusing lens at negative dc voltage (-110 V for optimal sensitivity) and ion deceleration lens at 0 V for slowing down ions and improving resolution.

The mass analyser provides m/z 200 mass range with better than unit resolution across the entire range. It consists of a 25 mm long pre-filter, 125 mm long main filter and 25 mm long post-filter with circular rods of 6.35 mm diameter. The pre- and post-filters are used to provide enhanced ion focus and sensitivity with rf-only

voltages applied to them. The main filter has rf+dc scanning for non-magnetic selective isolation of ion masses. All filter rods were made from

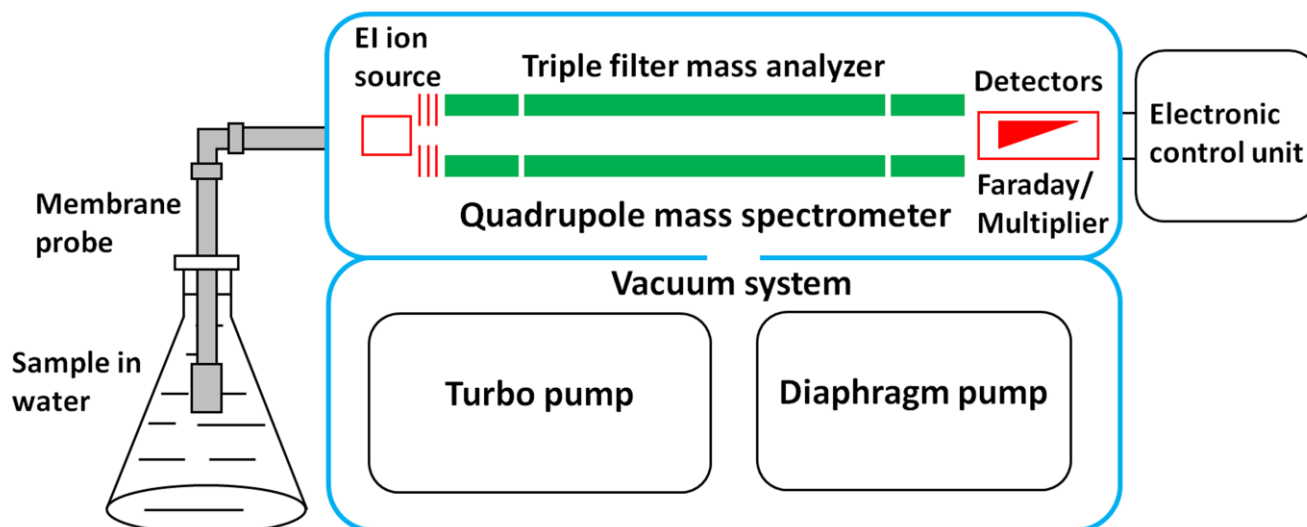


Fig. 1. Experimental lab setup for testing of organic species from in water using a portable membrane inlet mass spectrometer with a triple filter quadrupole analyser.

stainless steel and precision-aligned with grooves in alumina housing to better than 5 μm accuracy. Sensitivity of the analyser is 1×10^{-4} A/mbar with high ppt detection limit for dimethyl methylphosphonate DMMP and 2-chloroethyl ethyl sulphide (CES).¹¹ The detector is placed behind the analyser. It has a combined Faraday plate for small currents and Channeltron electron multiplier for very small currents (less than 1×10^{-10} A). Bias voltage on the multiplier can be varied between -600 and -2500 V depending on the output current from the analyser.

ECU

Electronic control unit (ECU) is used to provide voltage and frequency signals to the key parts of the QMS analyser and to collect values on the output current. It has weight of 4 kg and power consumption of 55 W at 24 V DC. The ECU has autotuned rf frequency in range between 1.8 to 2.2 MHz and maximum rf amplitude to 1600 Vp-p. The operating temperature range of the ECU is between 0 and 40 °C with up to maximum 90% relative humidity which allows it to operate in harsh environments at different weather conditions.

System assembly

The QMS is mounted inside the vacuum chamber with the ECU close coupled to the QMS flange. QMS vacuum chamber is coupled and mounted to a portable vacuum system box. The whole system weighs approximately 18 kg and it has been used in previous work.^{11,12} Vacuum system consists of a diaphragm pump (Oerlikon oil-free DIVAC 0.8 T) and a turbomolecular pump (TURBOVAC SL 80) purchased from Oerlikon Leybold Vacuum Ltd (Cheshington, UK). It provides base pressure of 7.5×10^{-8} Torr, which is monitored with a digital cold cathode

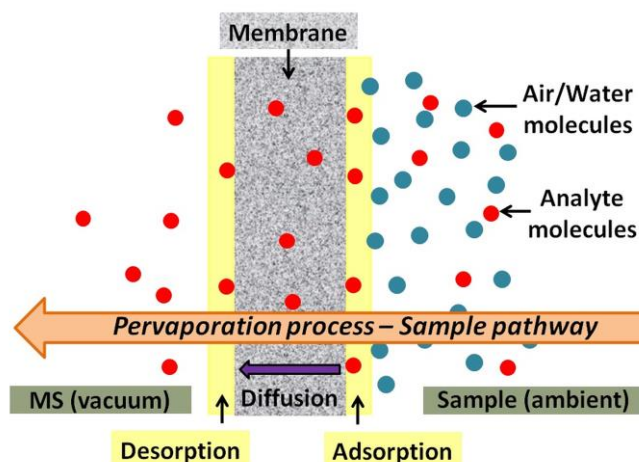


Fig. 2 Schematic diagram of the pervaporation process during VOC sample filtering including adsorption, diffusion and desorption through the polymer membrane.

pressure gauge (model: MPT 100) supplied by Pfeiffer Vacuum Ltd, Newport Pagnell, UK. The system also contains a membrane sample inlet that allows near real-time monitoring of VOCs and semi-VOCs in air and water. The membrane is a PDMS sheet of 0.12 mm thickness and 32 mm² area. It is mounted inside a Swagelok vacuum fitting union as described by Giannoukos et al.¹³ The length of the membrane sampling tube was kept at minimum with approximately 15 cm separation between the membrane and the EI source.

Sample analysis

Analysis of individual substances in pure water has been done for four concentrations: 0.5, 1, 5 and 10 ppm. Pure water was used for health and safety reasons which require such analysis to be done only on nuclear site or authorised laboratories. The substances were purchased from Sigma Aldrich except for odourless kerosene which was supplied by the National Nuclear Laboratory (Preston, UK). Operational pressure during analysis was 1×10^{-5} Torr. The substances that were tested include: acetone, acetophenone, cyclohexanone, isophorone, 1-pentanol, 1-heptanol, propionaldehyde, ethyl acetate, ethyl propionate, methyl butyrate and odourless kerosene. The two mixtures of substances in water were also analysed. Mixture 1 includes acetone, cyclohexanone, acetophenone and isophorone at 5 ppm each. Mixture 2 includes 1-pentanol and 1-heptanol at 5 ppm each.

Results and Discussion

The assembled portable MS system was tested in the laboratory for the key organic substances present in nuclear waste ponds. All the

samples were tested using a membrane inlet and ionized at 70 eV with an EI source. The triple filter analyser was driven at 2.2 MHz for all mass analysis experiments. Figures 3a-d show mass spectra for 10 ppm of acetone, acetophenone, cyclohexanone and isophorone respectively, which are all part of the ketone class. Characteristic mass fragments are visible for all the four compounds: acetone (m/z 43, 58), acetophenone (m/z 51, 77, 105, 120), cyclohexanone (m/z 55, 69, 98) and isophorone (m/z 55, 82, 95). Calibration curves are also shown for single mass fragments of acetone (m/z 58), acetophenone (m/z 120), cyclohexanone (m/z 98) and isophorone (m/z 82). Mass spectra for 10 ppm of 1-pentanol (alcohol), 1-heptanol (alcohol), propionaldehyde (aldehyde) and ethyl acetate (ester) are given in Figures 4a-d. Their characteristic mass fragments can be seen: 1-pentanol (m/z 55, 70), 1-heptanol (m/z 55, 70, 81), propionaldehyde (m/z 58) and ethyl acetate (61, 70, 73, 88). The corresponding calibration curves are included for single mass fragments of 1-pentanol (m/z 70), 1-heptanol (m/z 81), propionaldehyde (m/z 58) and ethyl acetate (m/z 88). Figures 5a-d show mass spectra for ethyl propionate (ester), methyl butyrate

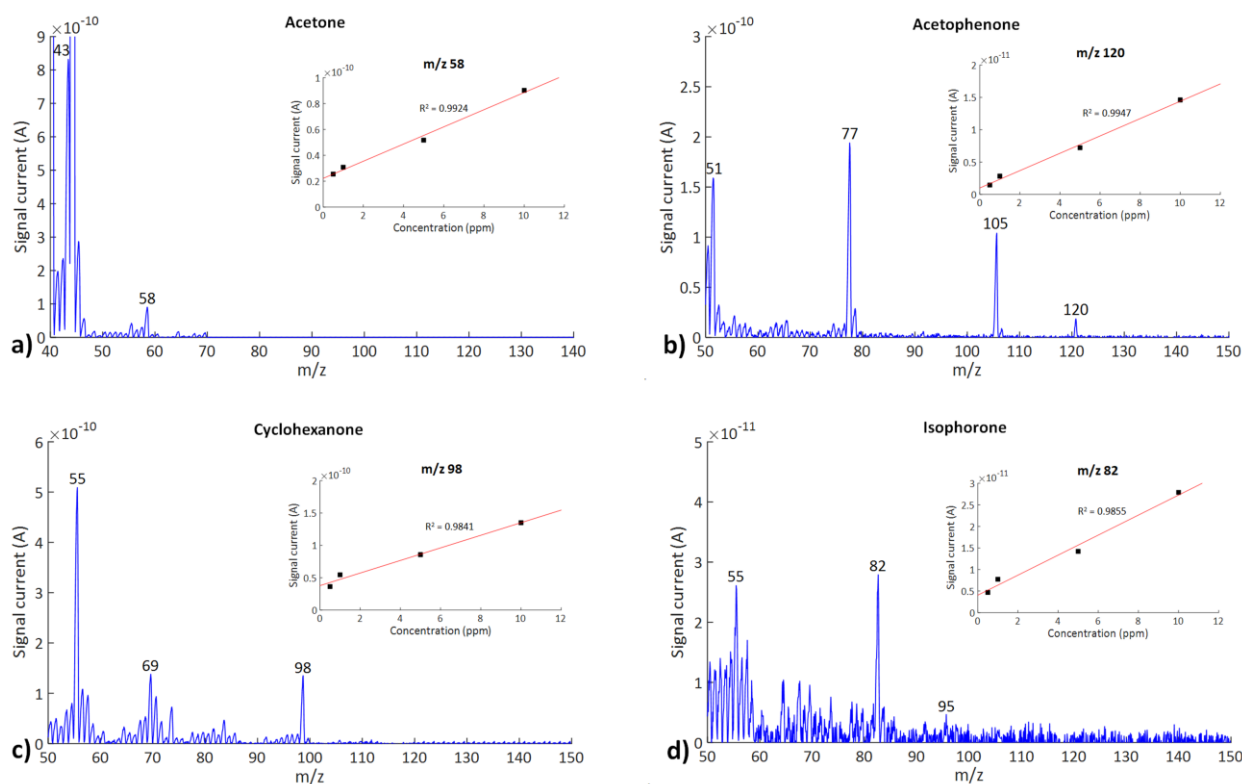


Fig. 3 Mass spectra and calibration curves obtained from a portable MS for a) 10 ppm acetone in water and its m/z 58 mass fragment, b) 10 ppm acetophenone and its m/z 120 mass fragment, c) 10 ppm cyclohexanone and its m/z 98 mass fragment, d) 10 ppm isophorone and its m/z 82 mass fragment.

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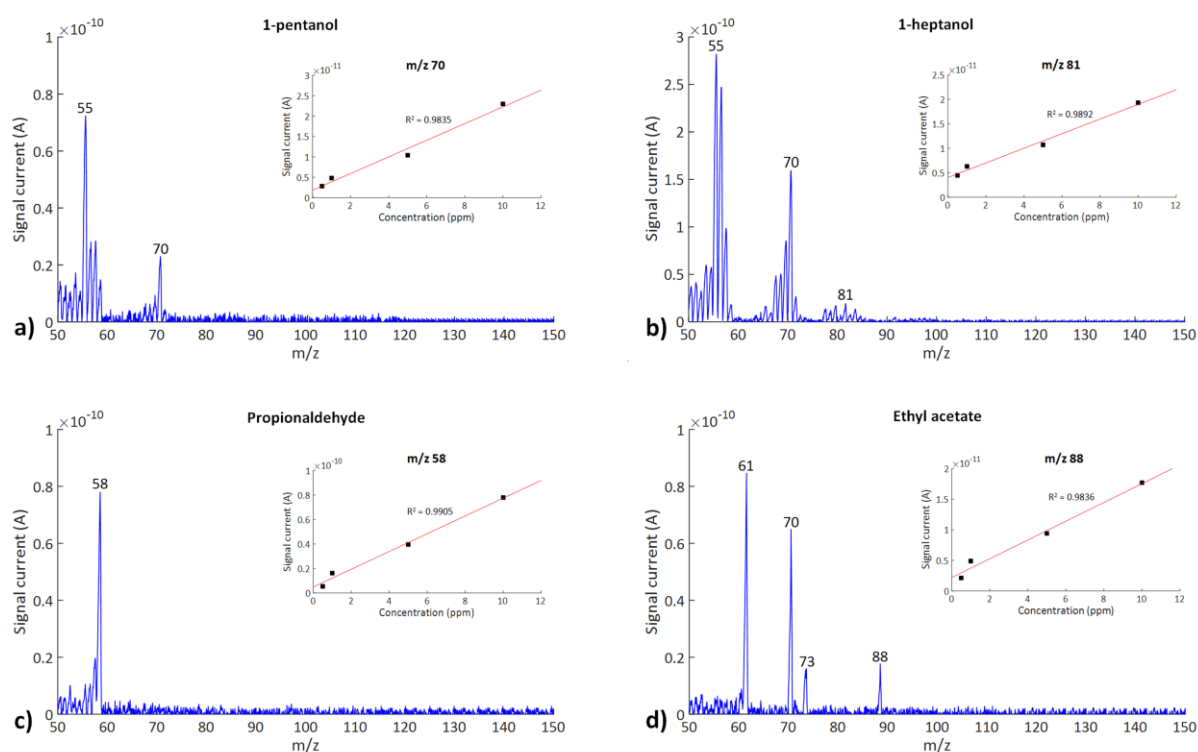


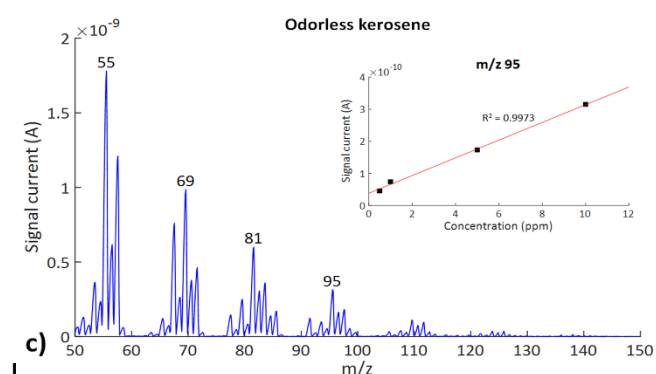
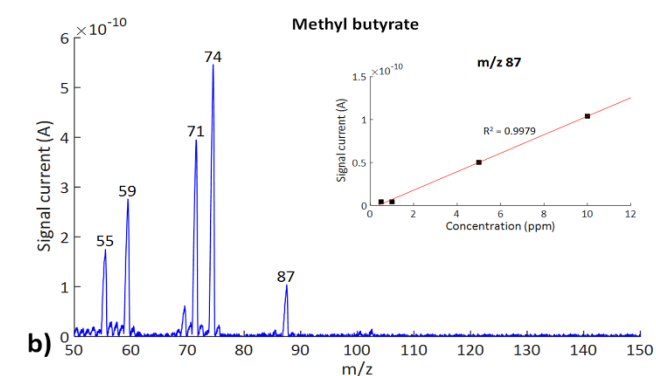
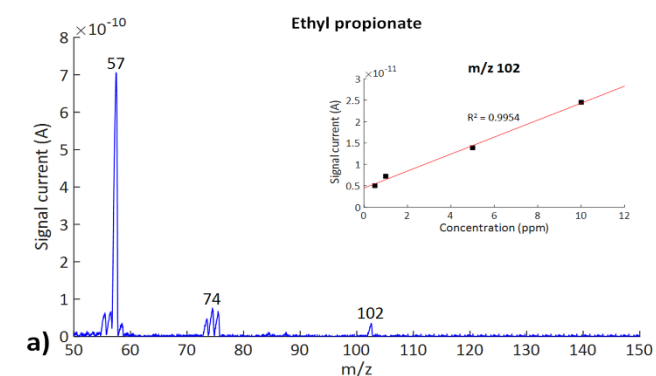
Fig. 4 Mass spectra and calibration curves obtained from a portable MS for a) 10 ppm 1-pentanol in water and its m/z 70 mass fragment, b) 10 ppm 1-heptanol and its m/z 81 mass fragment, c) 10 ppm propionaldehyde and its m/z 58 mass fragment, d) 10 ppm ethyl acetate and its m/z 88 mass fragment.

(ester) and odourless kerosene (hydrocarbon mixture). The characteristic mass fragments are visible for ethyl propionate (m/z 57, 74, 102) and methyl butyrate (m/z 55, 59, 71, 74, 87). Odourless kerosene does not have defined spectral peaks in the NIST library as it is a mixture of compounds, but the most distinguished fragments that were recorded during mass scanning are shown in Figure 5c (m/z 55, 69, 81, 95). The single fragment calibration curves can be seen in Figures 5a and b for ethyl propionate (m/z 102) and methyl butyrate (m/z 87). A calibration curve for the selected fragment for odourless kerosene (m/z 95) is given in Figure 5c to demonstrate linearity at different concentrations. As can be seen from Figures 3 to 5, excellent linearity was achieved for calibration curves of all the selected mass fragments with R^2 ranging from 0.9835 to 0.9979.

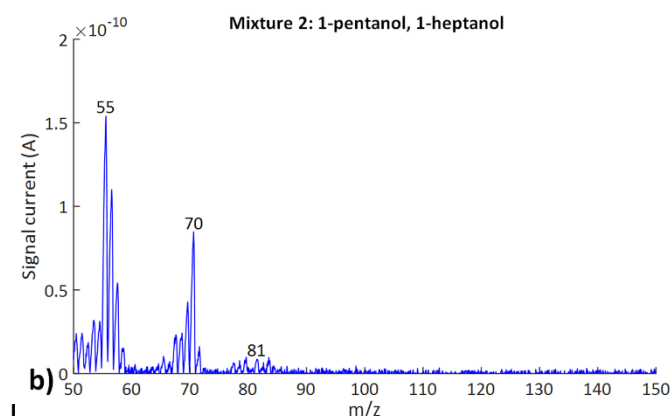
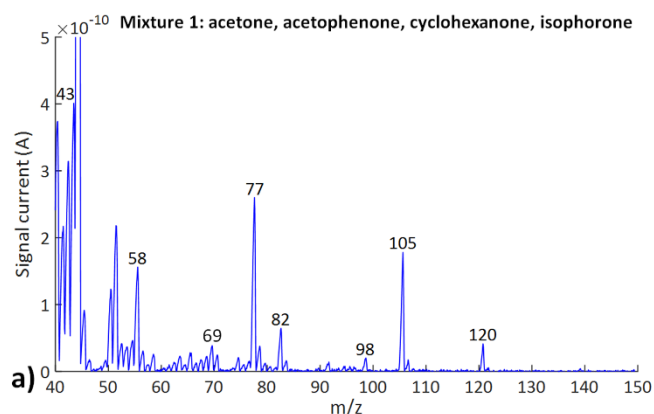
Figure 6a shows an experimentally obtained mass spectrum for a mixture of acetone, acetophenone, cyclohexanone and isophorone at 5 ppm each. As can be seen, all the key fragments for each of the four compounds can clearly be differentiated from the mixture spectrum. The mass fragment m/z 43 and 58 corresponds to acetone, the m/z 77, 105 and 120 corresponds to acetophenone,

the m/z 69 and 98 corresponds to cyclohexanone and the m/z 82 corresponds to isophorone. The second mixture spectrum is given in Figure 6b for 1-pentanol and 1-heptanol at 5 ppm each. Due to the number of overlapping mass peaks in each of the substances, it is more difficult to differentiate the components in this mixture than the previous one. 1-heptanol fragment at m/z 81 that is not present in 1-pentanol can help to differentiate the two species. The demands from nuclear industry will determine how precisely individual organic substances will have to be differentiated in nuclear waste legacy storage ponds. For better identification of mixed substances in water, a temperature-programmed desorption (TPD) unit may be used. It has been reported that TPD-MIMS can completely separate a number of similar VOCs in air,¹⁴ however there are currently no published results available for TPD-MIMS in water. Table 1 presents a summary of all the organic species from the NIST library that were tested in water with our mobile mass spectrometer. Apart from the key data, the table shows membrane rise and fall times for each of the compounds including limits of detection (LOD) with the existing setup. Rise time of the

compounds is important as this is when the spectral signal stabilizes, and concentration can reliably be measured. If necessary, lower detection limits in water may be achieved by using a thinner membrane and performing pre-filtering of water vapours before the MIMS selection. This is because reduced presence of water molecules will improve the ionization efficiency of sample VOCs. A simplified version of the triple filter analyser system is a recently made dual filter quadrupole system¹⁵, which will be used for future field tests with pond water with a new set of experiments. The system weighs 17 kg with dimensions of 61.6 × 49.3 × 22 cm. It represents the final version of a fully integrated and protected in-field system and a more compact option with greater portability and higher mass range (m/z 1-500).



MS for a) 10 ppm ethyl propionate in water and its m/z 102 mass fragment, b) 10 ppm methyl butyrate and its m/z 87 mass fragment, c) 10 ppm odourless kerosene and its m/z 95 mass fragment.



MS for a) 5 ppm acetone, 5 ppm acetophenone, 5 ppm cyclohexanone, 5 ppm isophorone, b) 5 ppm 1-pentanol, 5 ppm 1-heptanol. Characteristic mass fragments for each of the compounds are clearly visible from the spectra.

Future research

The assembled portable MS system has successfully been tested in the lab for detection of key organic substances present in nuclear waste legacy storage ponds that affect storage of radioactive waste. It has been demonstrated that concentrations of the target compounds can be determined from the levels of their characteristic mass fragments. Individual substances could also be differentiated from the mixtures.

Future work will involve field tests in a nuclear power plant with analysis of pond water in real time conditions. The screening will not only be done for the target organic compounds, but also for dissolved gases. The mass screening will be done across the entire range from m/z 1 to 500 to identify hitherto unrecognized chemicals by the nuclear industry. Such work will have importance for nuclear waste decommissioning. This will allow remote sensing of pond water using reliable analytical tools without human presence near ponds and silos.

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Compounds	Class	CAS number	Molecular weight	Key masses (m/z)	Rise time (sec)	Fall time (sec)	R ²	LOD (ppb)
Acetone (m/z 58)	Ketone (symmetrical)	67-64-1	58.0791	43, 58	42	63	0.9924	147
Acetophenone (m/z 120)	Ketone (asymmetrical)	98-86-2	120.1485	51, 77, 105, 120	198	242	0.9947	260
Cyclohexanone (m/z 98)	Ketone (cyclic)	108-94-1	98.1430	55, 69, 98	97	126	0.9841	103
Isophorone (m/z 82)	Ketone (cyclic)	78-59-1	138.2069	55, 82, 95	270	360	0.9855	160
1-pentanol (m/z 70)	Alcohol	71-41-0	88.1482	55, 70	185	240	0.9835	132
1-heptanol (m/z 70)	Alcohol	111-70-6	116.2013	55, 70, 81	210	300	0.9921	149
Propionaldehyde (m/z 58)	Aldehyde	123-38-6	58.0791	57, 58	144	176	0.9905	69
Ethyl acetate (m/z 88)	Ester	141-78-6	88.1051	61, 70, 73, 88	49	69	0.9836	177
Ethyl propionate (m/z 102)	Ester	105-37-3	102.1317	57, 74, 102	72	85	0.9954	375
Methyl butyrate (m/z 87)	Ester	623-42-7	102.1317	55, 59, 71, 74, 87	150	180	0.9979	89

Table 1: Performance summary of the portable MS for detection of organic compounds present in nuclear waste ponds.

Conflicts of interest

There are no conflicts to declare.

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