Investigating and monitoring of contaminated environmental water using portable real time, membrane introduction-mass spectrometry (MIMS).

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Keywords

Membrane introduction-mass spectrometry (MIMS), NIST chemistry web book, analytical chemistry, contaminated environmental water, real time, VOCs, parts per million (ppm).

Abstract

Membrane introduction-mass spectrometry (MIMS) for chemical analysis involves the use of a semi-permeable membrane that is coupled to a mass spectrometer. This technique allows the direct sampling of analytes in gaseous, and liquid samples. Our company Aspec investigated the use of our MIMS instrument in the monitoring of dissolved gases in environmental water, with the desire to isolate harmful chemical contaminates in real time, in the lab and the field. 3 common VOCs were used to demonstrate that the instrument is a suitable, accurate, stable and reliable analytical method of monitoring contaminates in a laboratory. The instrument was deployed in the field first for 24hrs unmanned, in a bore hole, to measure the water table. The data was analysed in order to identify and contaminates. Then a salt water analysis was carried out to demonstrate the instruments ability to analyse salt water. In the laboratory the MIMS instrument picked up all 3 VOC contaminates, as the mass spectrum matched that of the one on the NIST chemistry web book. All 3 had low standard errors demonstrating the stability of the instrument to monitor the concentration of the contaminant in real time. 2 of the VOCs had a significant linear relationship (ANOVA $F= (1,1)$ $P<0.05$) meaning the instrument picked up the 3 added concentrations of contaminant accurately, over 2 decades, without a recalibration. The instrument produced a mass spectrum for both the field tests, and the spectrum was compared to a control/reference, to identify differences and any contaminants.

Introduction

Membrane introduction-mass spectrometry (MIMS) for chemical analysis involves the use of a semi-permeable membrane that is coupled to a mass spectrometer. This technique allows the direct sampling of analytes in gaseous, and liquid samples. This method of analytical chemistry has an advantage over other well-known methods like liquid and gas chromatography-mass spectrometry, as it can it can yield analytical results in real time. Because the samples can be continuously passed over the membrane interface, allowing the continuous motoring, and data logging of the sample (Davey and Krogh *et al* 2011).

Figure 1. Aspec ltd MIMS system installed in the University of Milan. Measuring gas produced by the roasting process of coffee beans.

MIMS technology has many industrial uses including on line monitoring of chemical and biological reactors, analysis of volatile organic compounds (VOCs) in environmental systems including air, water and soil (Johnson and Cooks *et al* 2000). MIMS primary use currently is environmental monitoring of VOCs in liquids, however not many systems are used in the field due to

the size of the instrument. Tortell (2005) designed a smaller MIMS instrument that was used to analyse dissolved gasses in seawater in real time. The aim was to show that MIMS could provide gas measurements consistent with other standard techniques. Seawater could be passed across its semi-permeable membrane into the ion source of the mass spectrometer. The data gave insight into the gas cycling in a marine environment. Kristensen et al (2010) demonstrated how the MIMS system can be deployed and then monitor unsupervised in a matrix. A MIMS instrument was used in the monitoring of trihalomethane concentrations in a public swimming pool. The system could be monitored on site, or left unsupervised with off-site real time surveillance. Food production (Figure 1) and the fermentation industry is another example of where currently MIMS technology is being used. Further uses of MIMS are being devolved and the potential of MIMS technology is enormous. In vivo applications are being developed tested, for example direct real time analysis of human breath, which could prove valuable in the medical industry.

The main focus of research in our company Aspec ltd is investigating the use MIMS in the monitoring of dissolved gases in aquatic environments, with the desire to isolate harmful chemical contaminates (e.g. VOCs). Many industrial sites release these contaminates into the environment, and this needs close monitoring, to ensure that potential harmful amounts are not being released. Often factories near a natural water source like a river release chemical waste, however continues monitoring of this waste is time consuming and costly. These chemicals include organic or inorganic toxic chemicals (Table 1), also organic chemicals like sewage that can increase Eutrophication in water systems.

Table 1. Some common chemical waste realised mostly in industry, that are often found to contaminate environmental water systems. It includes both organic (usually contain carbon bound to hydrogen) and inorganic compounds (usually lack carbon). The type/group represents the chemicals classification in industry. The Molecular formula contains which atoms and how many of them the compound contains. Main uses are the most common uses in industry. A CAS registry number is a numerical identifier assigned by Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature (American chemical society 2009). Allowing quick searching of chemicals in chemical data bases such as NIST chemical web book.

Organic/ inorganic	**Type/group**	**Chemical/compound names**	**Molecular Formula**	**Main uses**	**CAS**
Organic	Petroleum hydrocarbons	Benzene	C_6H_6	Compound of Gasoline	71-43-2
		Ethylbenzene	C_8H_{10}	Chemical intermediate (polystyrene production)	100-41-4
		Toluene	C_7H_8	Precursor, solvent and fuel.	108-88-3
	Volatile Organic compounds (VOCs)	IPA (Isopropyl alcohol)	C_3H_8O	Chemical intermediate , solvent	67-63-0
		2-Butanone/MEK (Methyl ethyl ketone)	C_4H_80	Solvent, plastic welding agent	78-93-3

		BGE (2-Butoxyethanol)	C_6H_80	Solvent, Petroleum industry.	111-76-2
		Acetone	C_3H_60	Solvent, chemical intermediate	67-64-1
		MEG/1,2-ethanediol/mono ethylene glycol	C_2H_60	Precursor to polymers, Dehydrating agent. Antifreeze.	107-21-1
	Chlorinated solvents	Methylene chloride /Dichloromethane	CH_2CL_2	Solvent	75-09-2
		Trichloroethylene	CH_2HCL_2	Solvent	79-01-6
Inorganic	Acidity from industry	Sulphur dioxide	O_2S	Precursor, preservative, reagent, steel making.	7446-09-5
	Ammonia	Ammonium nitrate	$H_4N_20_3$	Fertilizers, explosives.	6484-52-2

These chemicals (Table 1) pose a risk to river ecosystems especially if the regulations of exposure are not followed. Petroleum hydrocarbons (Table 1) are a mixture of hydrocarbons and crude oil. Crude oil contains many other chemicals like benzene and toluene (Table 1). There are many methods of monitoring and identifying these chemicals in water systems including MIMS. Petroleum hydrocarbons most commonly enter water systems from industrial sites like petroleum processing. It can be from spillages, leaks and even purposeful release. Benzene released in water can be broken down by microorganisms reducing the contamination risk and danger to other organisms. However, in high concentrations benzene is toxic, and may therefore impact organisms like fish in the water system, but there is not much evidence of this (Agency for toxic substances and disease registry 1999). VOCs are another group of chemical compounds that pose a danger to aquatic water ecosystems because they are released from such a variety of applications in industry (Table 1). They have a high vapour pressure at normal room temperature, so they vaporize easily (turns into gas). Many VOCs are produced naturally in the environment for example plant signalling, however more harmful ones are released from anthropogenic sources. VOCs that end up in water systems usually vaporize before they can cause any long term damage to the ecosystem. Harmful effects are more likely in high concentration when exposure time increases, as a result of an accidental spillage for example. Ethylene glycol is an example of a VOC which at high concentrations is toxic, acting as a tetratogen (causing physical abnormality in development), so could therefore damage organisms in these systems (Heath Canada 2013).

Chlorinated solvents are widely used commercially and industrially as their chlorate structure helps them dissolve organic material (fats and grease). In industry they are commonly used as solvents (Table 1). Spillages into aquatic systems pose a danger because they do not easily dissolve in water, and are heavier than water, so sink making clean up difficult. Most of them are carcinogenic to animals therefore pose a hazard to aquatic ecosystems. Methylene chloride usually is broken down in water by other chemicals and bacteria to carbon dioxide, which is found naturally in the environment. However, it could reduce oxygen levels in water ecosystems posing a threat to fish (Agency of toxic substances and disease registry 2000). Sulphur dioxide gas (Table 1) has the potential to disrupt the natural pH levels in aquatic ecosystems which are very sensitive to pH change. It's mainly released from the combustion of fuels from factories into the atmosphere. One

main hazard to aquatic systems is that it causes acid rain- gas dissolves in water droplets in clouds then falls as acid rain. As a result, it can increase acidity levels in water ecosystems (lakes being the most susceptible as they are stagnant) which are normally around pH 6-8. At pH 5 or lower undesirable plankton and mosses grow acting as invasive species, reducing fish numbers and blocking out light (LENNTECH BV 2016). Corals calcium carbonate skeleton is very sensitive to pH drops as the skeleton starts dissolving.

One of the most significant chemical pollutants of aquatic ecosystems is ammonium nitrate (Table 1). It is a white crystallised solid that is highly soluble in water. Lots of nitrogenous pollutants like ammonium nitrate leach into aquatic ecosystems from farm land (fertilizers) and industrial waste. Stagnant water ecosystems like lakes are most at risk. Ammonium toxicity is thought to be a cause of many unexplained losses in fresh water fish stocks. Ammonium is an essential nutrient needed in organisms, but excess ammonia can accumulate in the organism and alter its metabolism, increase the body pH and increase the likelihood of mutations. High concentrations even in a short exposure time can lead to gill damage in fish, increased respiratory activity and increased heart rate (Oram 2014). Additionally, the increased nitrogen can lead to Eutrophication. Excess growth of undesirable plankton, algae, bacteria leading to reduced light and oxygen levels in the water ecosystem.

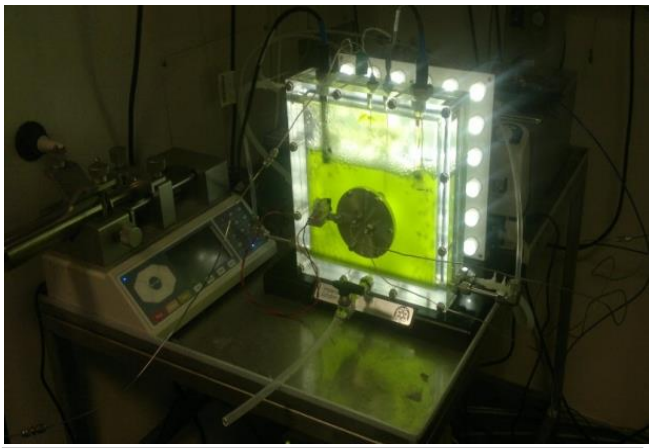

Figure 2. Aspec MIMS instrument measuring a range of VOCs evolved from genetically modified algae in Imperial college.

We have designed a process Quadrupole Mass Spectrometer that has been adapted on site with MIMS technology, allowing the detection of atmospheric and dissolved gas compounds in liquid matrices. It is capable of measuring direct concentrations in ppm % (parts per million) of many complex dissolved compounds in water. In particular low trace detection or data logging of solvents, complex VOCs (Volatile organic chemicals), glycol based compounds. Up to 64 separate compounds may be simultaneously trended in real time which provides more insight into changes and process monitoring. Because its portable and cheaper to build than its counterparts, it makes it a suitable *in-situ* environmental field based instrument (Davey and Krogh *et al* 2011). Assessment and monitoring programs of contaminates in many environmental companies use periodic grab sampling, which provides limited information, often with delay times. (Bell and Davey *et al* 2015). Our portable MIMS system will solve this problem allowing continues monitoring, saving time and reducing the chance of any contaminates being missed in systems or samples. The purpose of this study was to assess the accuracy and stability of the data produced by the MIMS instrument in the laboratory referring to NIST (Chemistry web book), and then trial it in a field environment. We would like to show that this instrument would be suitable for in field aquatic environmental monitoring programs (Figure 2) and identification of dissolved gasses and VOCs. For example, assessing the quality of a river systems over time. We would also like to show that the MIMS instrument can identify contaminant concentrations as low as 50ppm and stalely measure up to 500µl.

The key aims of this study were: to be able to identify and monitor a range of contaminants typically found in environmental waters, near industrial sites, using membrane introduction-mass spectrometry (MIMS). Demonstrate that MIMS is a suitable, accurate, stable and reliable analytical method of monitoring contaminates in a laboratory. To investigate environmental water in the field using a portable, real time, data logging MIMS in order to monitor water contaminates, and provide

qualitative time resolved data. Consider how the chemical contaminates identified could impact the river ecosystem. The hypothesis in this study was membrane introduction-mass spectrometry (MIMS) can accurately identify and monitor contaminates in environmental water, both in the laboratory, and in real time in the field.

Materials and method

Instrument design

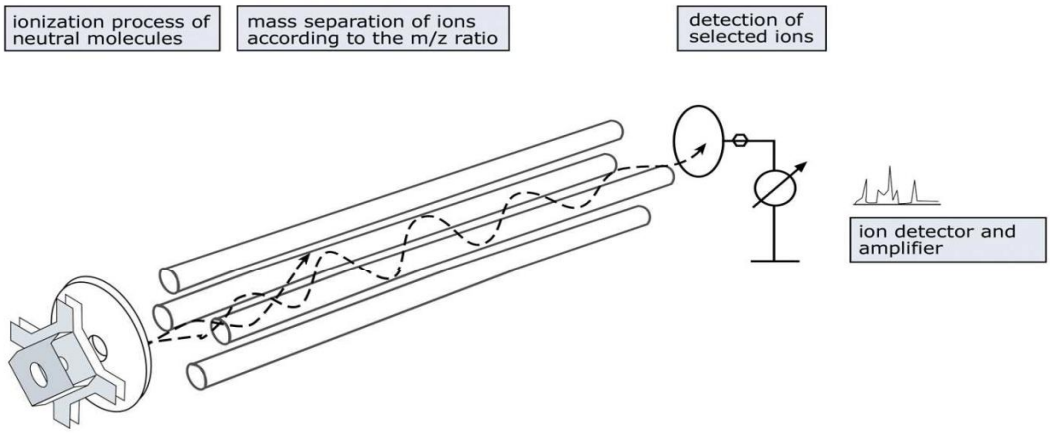

Figure 3. It was a Quadrupole Mass Spectrometer, consisting of an Ioniser, mass filter and detector. Ions produced by the Ioniser travel through a mass filter, which consists of 4 ground stainless steel rods. Once the ions enter the mass filter they are separated into their ion weights by the influence of both RF and DC voltages, that are applied to apposing rods to create an electrostatic field.

Ion Source

The ioniser was an electron ionisation/bombardment design. A hot filament in the ioniser produces electrons of around 56ev. These electrons are focused towards the molecule of gas they collide, thermally react and ionise the molecule (+ve charged). The sample ions are then re-focussed into the mass spectrometer where they are separated by mass.

Vacuum system

To achieve a vacuum of $1x10^{-6}$mbar, 2 pumps are used. A backing pump that provides pressure of 2mbar that allows the turbo molecular pump to become effective. This pumps at speeds between 70Litres/sec-250Litres/sec. All pressures are measured by the full range vacuum gauge. An additional heater helps remove water and background contamination from the analyser vacuum housing.

Interface construction

The interface of the machine can be changed for liquid (Figure 4) and gas analysis. Meaning it can switch from a MIMS design to a normal quadrupole mass spectrometer.

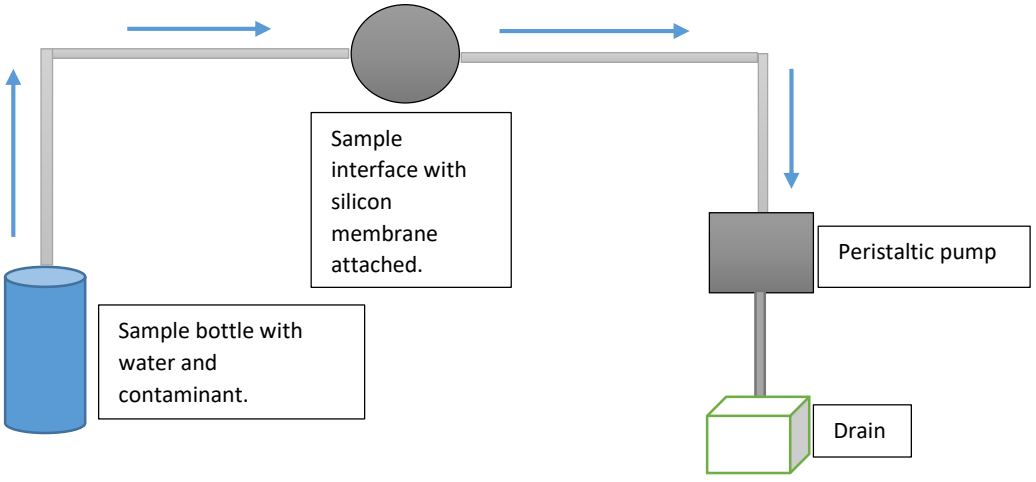

Figure 4. Interface of machine with the dialysis silicon membrane attached, for identifying molecules in liquid samples (MIMS). This is how the machine was configured for the lab experiment. In the field a Remote Membrane Sampler (RMS) was attached (Figure 5). The blue arrows indicate the flow of the sample through the system. Water flows through the membrane and the gas molecules are filtered out, and then enter the analyser. Any waste liquid was pumped out by the peristaltic pump (4litres/hr) into a drain which was disposed.

Analysis software

A windows 7 laptop is connected via USB/COMMS to the instrument (any windows is sufficient). The analysis operating system is loaded onto the laptop. The analysis program has 3 main modes. Raw mass scan mode: that scans the entire mass range of the instrument in less than 2 seconds, and produces a complete spectrum of any gas composition. Background process subtraction: which enables monitoring of a process for any changes that may occur. A difference in gas composition can be logged. The acquired spectrum may be interrogated and compared with a spectrum library (e.g. NIST) for identification of new, evolved gasses/isotopes. Full calibration data mode: calibrates and displays up to 64 gasses and measures in direct concentration. Each gas is calibrated and the instrument will measure data log and display the data in real time.

Lab experiment

Experimental design

The MIMS instrument was configured by fitting the dialysis silicon membrane (Figure 4). It was then switched on; the vacuum system pressure was allowed to reach better than $1x10^{-6}$. Then instrument emission was switched on and left to stabilize. Isopropyl alcohol (IPA), Methyl ethyl ketone (MEK) and Acetone were chosen from Table 1 to demonstrate the MIMS technique and the quality of our instrument. These are common chemical contaminates tested by Chemsol ltd, a commercial company that does water testing, looking for contaminates in environmental water systems.

Sample Bottles design

A sterilised sample bottle with 1 litre (1,000,000 µl) or 1,000,000ppm of distilled water was made up. 3 experimental tubes for each chemical contaminant was made up using a microliter syringe. These solutions contained 1,000,000 µl of distilled water in which 50µl (50ppm), 250 µl (250ppm) and 500 µl (500ppm) of the chemical contaminant (e.g. IPA) was added independently to each of the 3 bottles.

Experimental Procedure

Each chemical will be monitored using Full calibration data mode for 70 minutes, with the control being monitored at 10 minute intervals in-between the 3 different concentrations of the chemical contaminant (table 2). This was done to flush out contamination and to show the dynamic range of the instrument. To identify the chemical contaminant, we referred to NIST chemical web book to identify the mass spectrum, and compare it to the chemical being monitored. Before the experiment some tests were down with the chemical contaminates to test check the instrument was working correctly. It was then calibrated for the highest concentration of contaminant 500µl/500ppm.

Table 2. Experimental procedure showing how the different concentrations of chemical contaminants were monitored along with the control. This procedure was repeated for all the chemical contaminates: Isopropyl alcohol (IPA), Methyl ethyl ketone (MEK), and Acetone.

Time (minutes)	Sample being monitored by MIMS instrument
0-10	Control tube
10-20	50µl tube of chemical contaminant
20-30	Control tube
30-40	250µl of chemical contaminant
40-50	Control tube
50-60	500µl of chemical contaminant
60-70	Control tube

Data analysis

The mean was calculated from where the concentration of the contaminant plateaued. The standard deviation and standard error was calculated. A regression test was performed. If a significant linear regression was identified, it would help demonstrate the stability and accuracy of the instrument over 2 decades, without a recalibration.

Field Testing

Saltwater analysis: A 1 litre sample bottle of salt water was collected from and then analysed using raw mass scan mode. A 1 litre control sample of distilled water was analysed. Differences in the masses identified by the instrument, between the control/reference and experimental litre of saltwater were identified. NIST was used to help identify any contaminates in the salt water mass spectrum.

Figure 5. Aspec ltd MIMS instrument with RMS attachment (yellow instrument) deployed in bore hole. A 1 litre bottle of flush (water and detergent) and a 1 litre bottle of calibration fluid. (distilled water).

Contaminated water table: water was sampled from a 3-meter pre-established bore hole which penetrated the water table. The instrument was diploid unmanned using a Remote membrane sampler (RMS); this interface is the sampler to the instrument (Figure 5). It includes the same features as in Figure 4, but has been adapted to be portable. The instrument was then switched on and set to Raw mass scan mode. It was left for 12hrs and the spectrum was then analysed. NIST was used to help identify any contaminates seen in the mass spectrum of the bore hole water, and compared to a control/reference of distilled water.

Results

Lab experiment

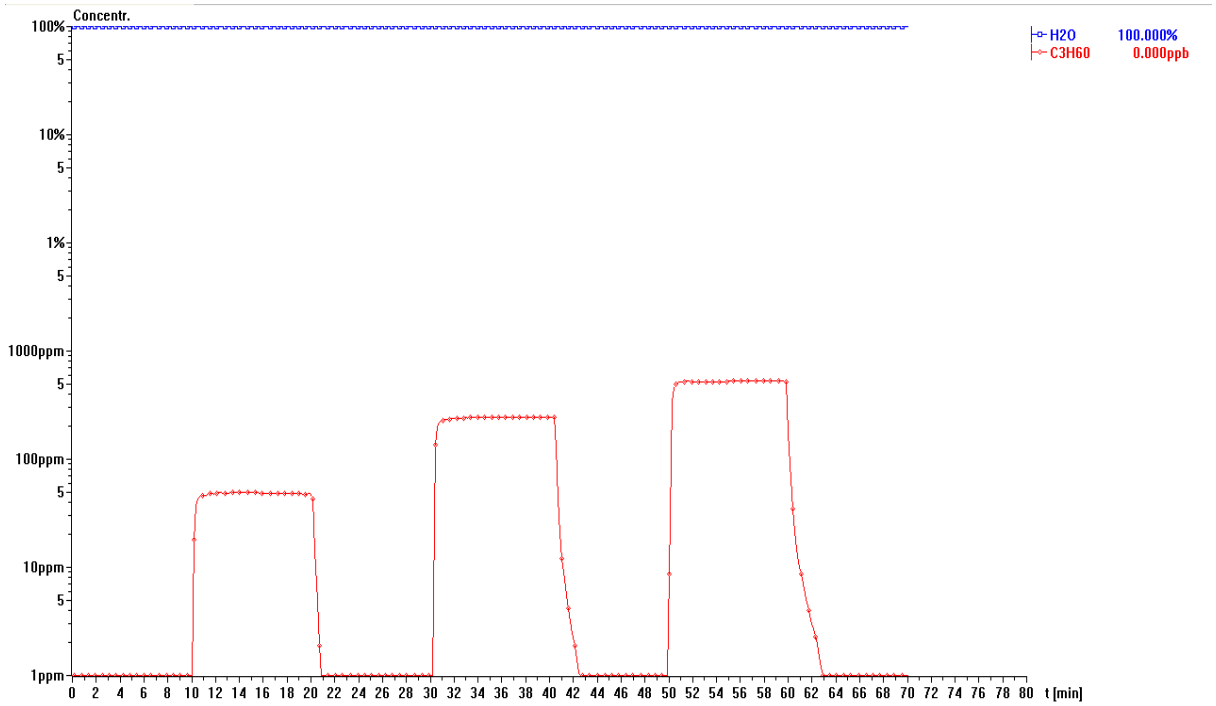

Figure 6. MIMS instrument data showing the concentration and ppm of Acetone (C_3H_60) in real time. H_2O was flushed through every 10 mins. The red peaks represent the 3 different concentrations of acetone added to H_2O (50,250,500µl).

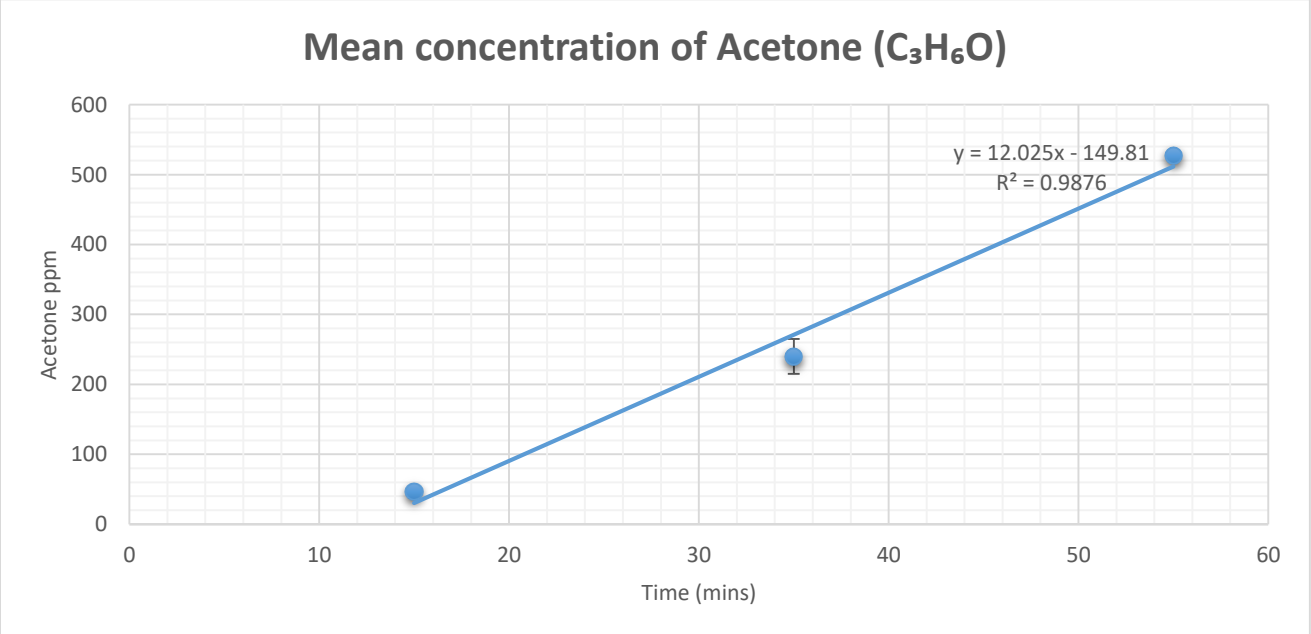

Figure 7. Mean ppm of Acetone over 70 mins (with standard deviation). The 3 points are 50, 250 and 500µl of Acetone. Sample size for each concentration: 50µl, N=31, 250µl, N=23 and 500µl, N=29. The regression line was to allow us to see the stability of the instrument at measuring the concentration of Acetone. At the 50µl concentration of Acetone (C_3H_60), 46ppm was the mean (N=31) with a SE ± 1.35. At the 250µl concentration of Acetone, 240 ppm was the mean (N=23) with a SE ± 5.47. At the 500µl concentration of Acetone, 527.1 ppm was the mean (N=29) with a SE ± 0.61. The R^2 value of

0.9876 shows that 98% of the values fell on the regression line. The regression was not significant (ANOVA F= (1,1) =79.906, p=0.07), as p>0.05.

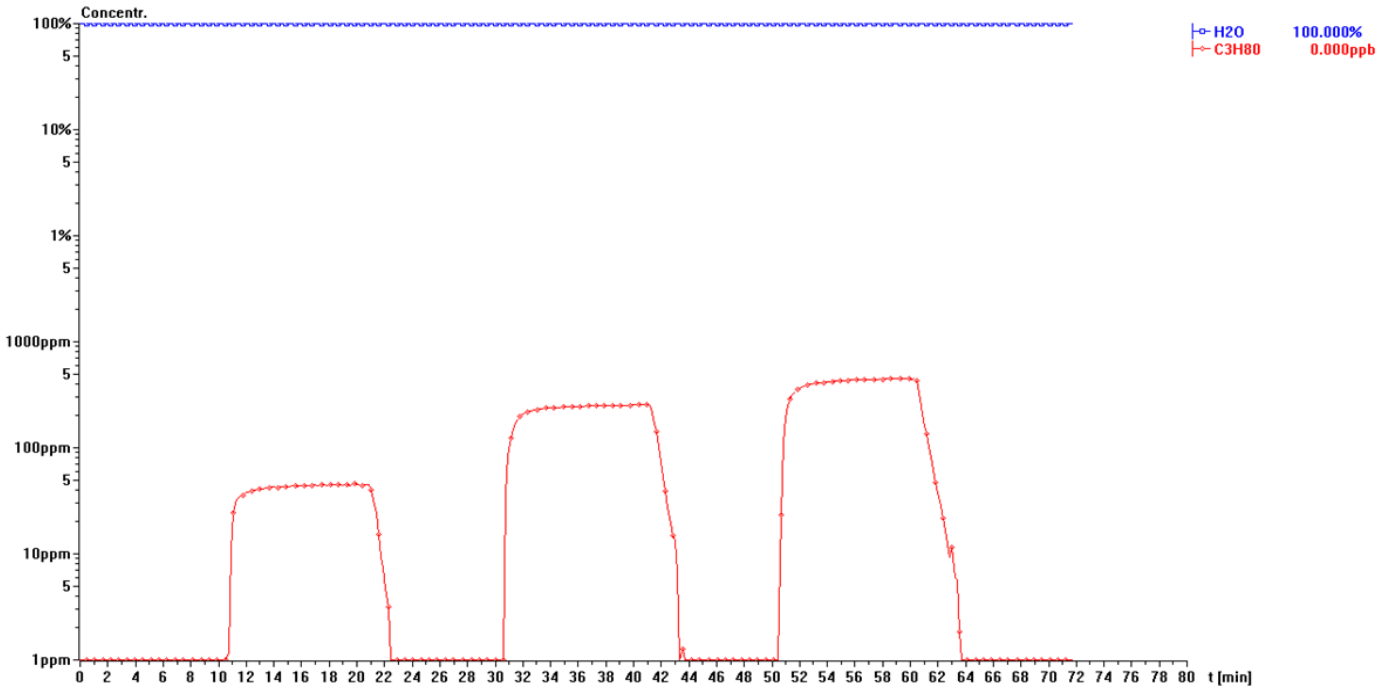

Figure 8. MIMS instrument data showing the concentration and ppm of MEK (C_4H_80) in real time. H_20 was flushed through every 10 mins. The red peaks represent the 3 different concentrations of MEK added to H_20 (50µl, 250µl and 500µl).

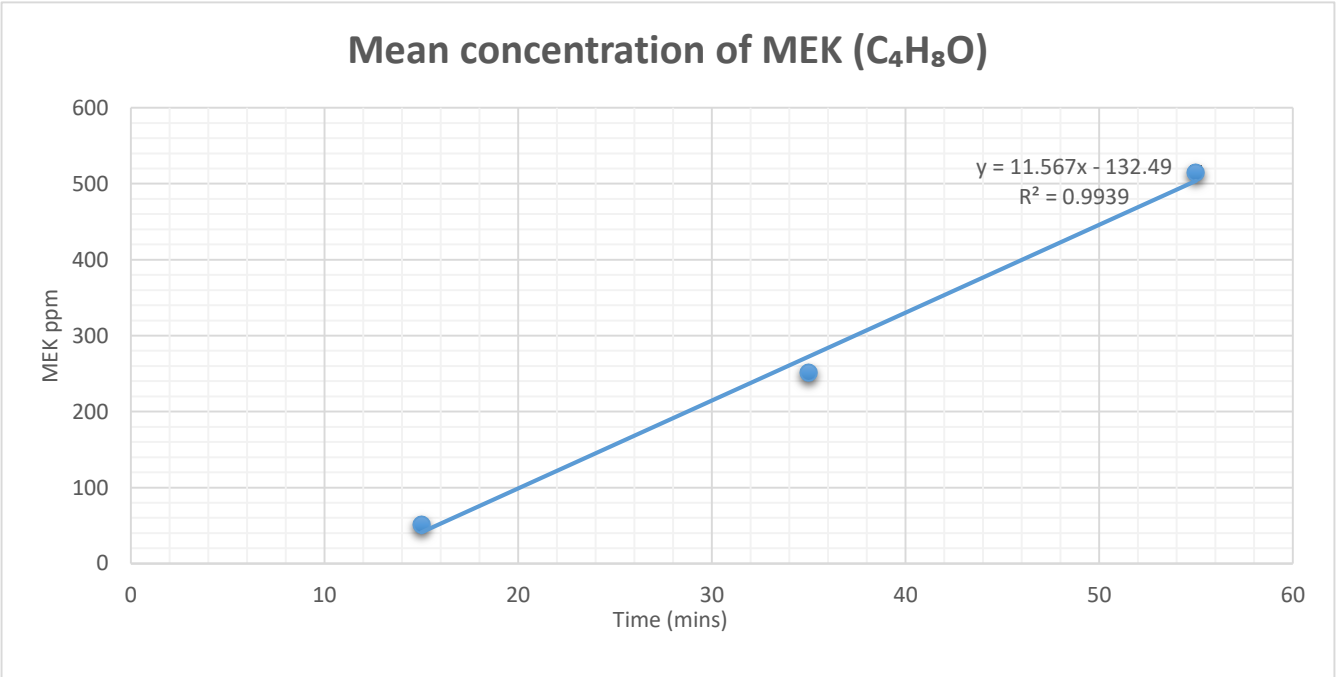

Figure 9. Mean ppm of MEK over 70 mins (with standard deviation). The 3 points are 50, 250 and 500µl of MEK. Sample size for each concentration: 50µl, N=39, 250µl, N=25 and at 500µl, N=43. The regression line was to allow us to see the stability of the instrument at measuring the concentration of MEK. At the 50µl concentration of MEK (C_4H_80), 51.5ppm was the mean (N=39) with a SE ± 0.28. At the 250µl concentration of MEK, 251.4 was the mean (N=25) with a SE ± 0.21. A 500µl concentration of MEK, 514.2 was the mean (N=43) with a SE ± 1.38. The R_2 value of 0.9939 shows

that 99% of the value fell on the regression line. The regression was significant (ANOVA F= (1,1) =161.98, p=0.04) as p<0.05.

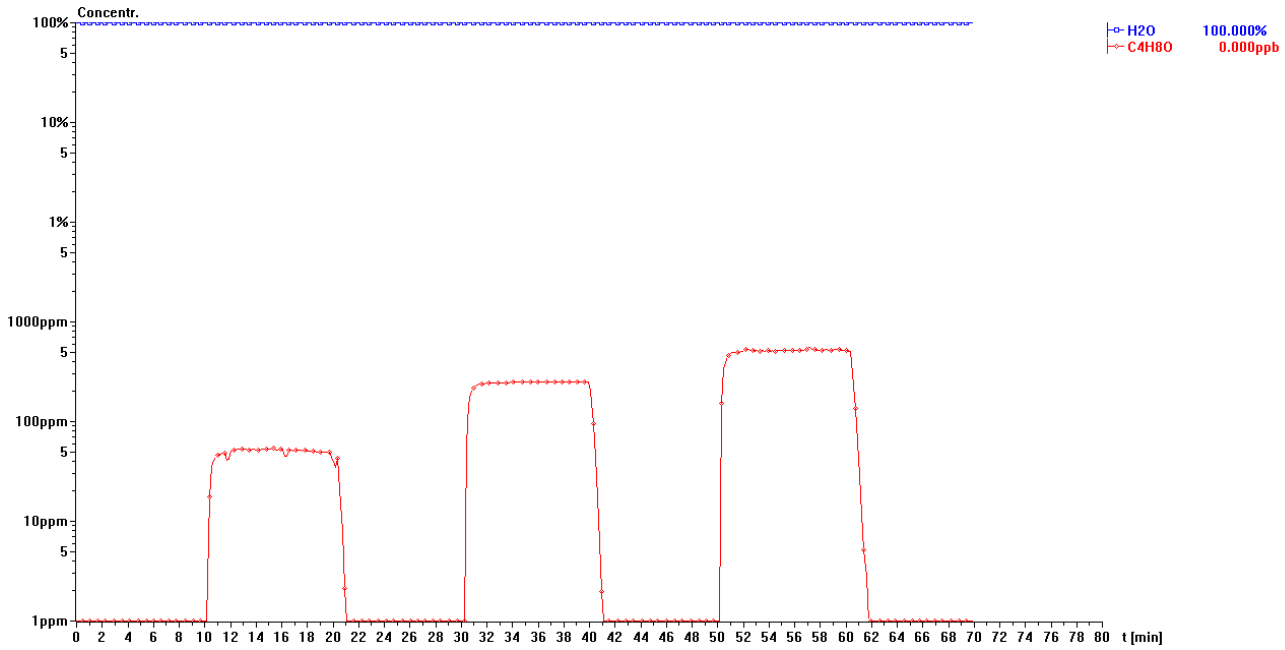

Figure 10. MIMS instrument data showing the concentration and ppm of IPA (C_3H_8O) in real time. H_2O was flushed through every 10 mins. The red peaks represent the 3 different concentrations of IPA added to H_2O (50,250,500µl).

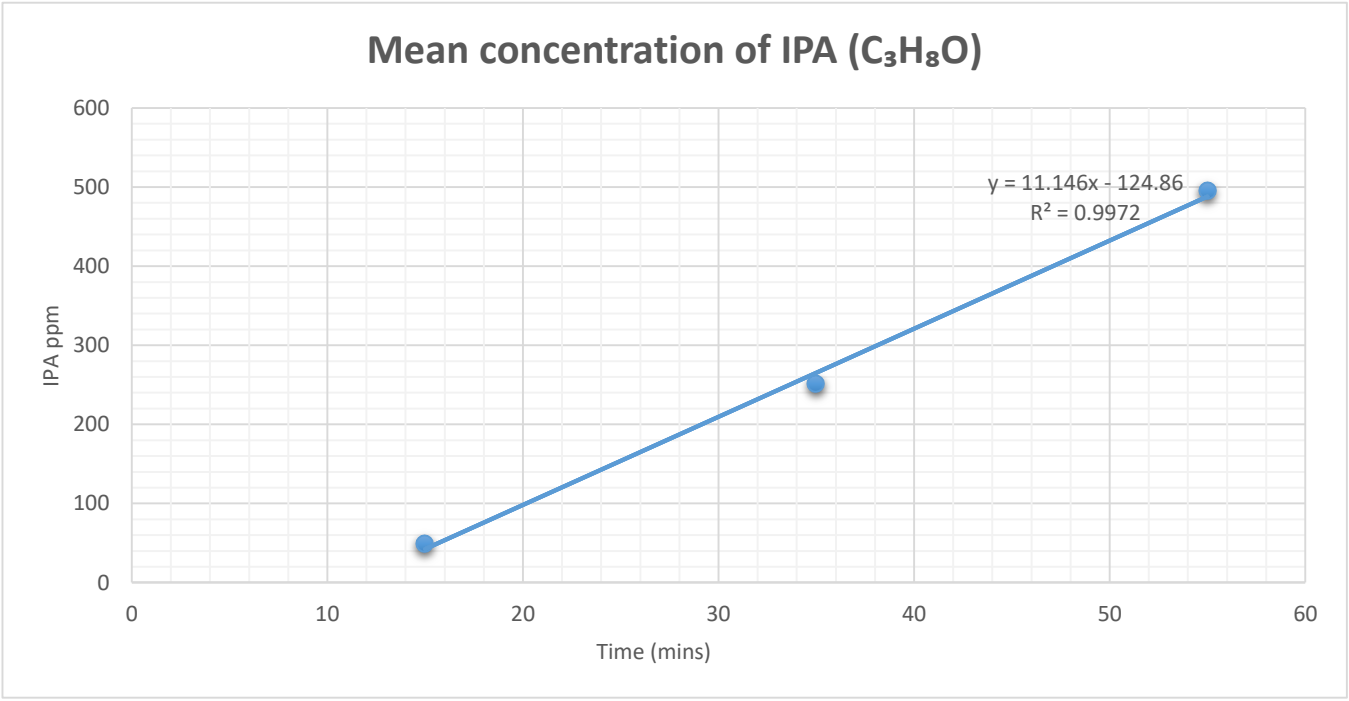

Figure 11. Mean ppm of IPA over 70 mins with standard deviation. The 3 points are 50, 250 and 500µl of IPA. Sample size for each concentration: 50µl, N=41, 250µl, N= 23 and at 500µl, N= 18. The regression line was to allow us to see the stability of the instrument at measuring the concentration of IPA. At the 50µl concentration of IPA, 49.2ppm was the mean (N=41) with a SE ± 0.08. At the 250µl concentration of IPA, 251.5ppm was the mean (N=23) with a SE ± 0.4. A the 500µl concentration of IPA, 495.0ppm was the mean (N=18) with a SE ± 0.27. The R^2 value of 0.9972 shows

that 99% of the values fell on the regression line. The regression was significant (ANOVA F= (1,1) =350.70, p=0.03) as p <0.05.

Field Testing

Contaminated water table, Bore hole:

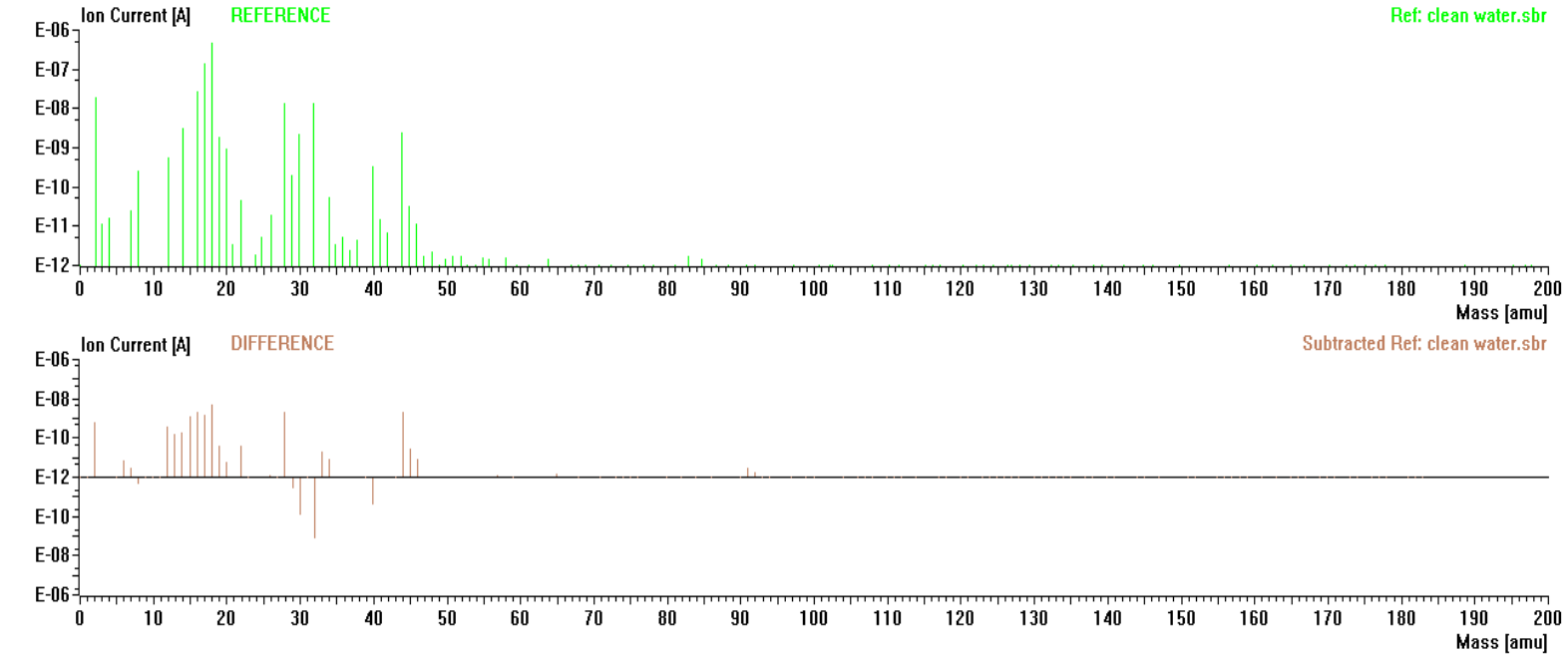

Figure 12. Graph 1: Mass spectrum of the control/reference sample of distilled water. Graph 2: Mass spectrum showing the difference between the reference sample (black line at E-12) and the bore hole contaminated water table sample. The taller the peak the more of that gas is present in the sample. The peaks lower than the black line indicate that there were less gasses of that mass in the bore hole water, compared to the reference sample. For example, there is less of mass 32 which is 0xygen. Peaks above the black line indicate that there were more gasses of that mass in the bore hole water, compared to the reference sample.

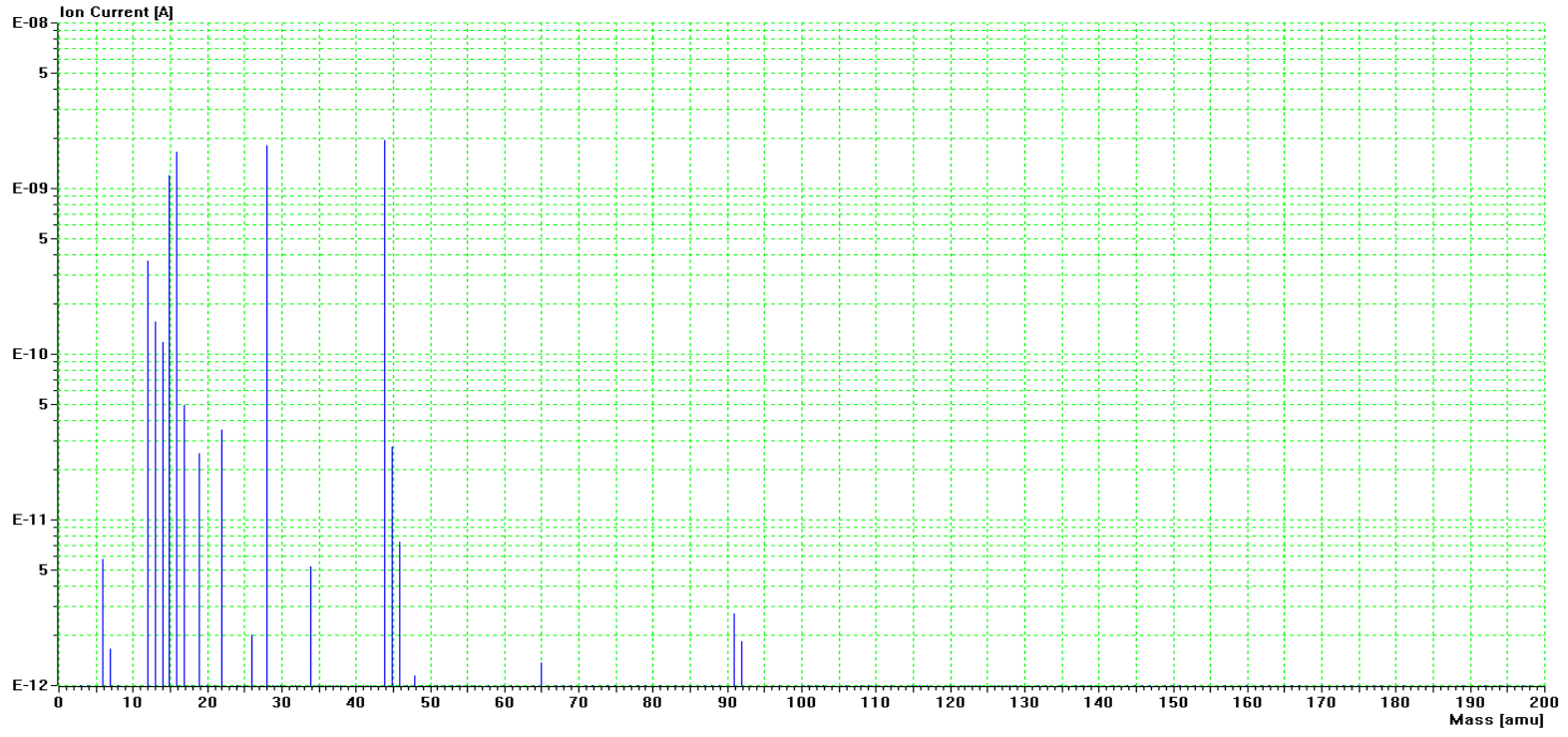

Figure 13. Mass spectrum of bore hole water difference graph (Figure 12, graph 2) showing peaks above the reference sample. The blue peaks indicate that there were more gasses of this mass present in the bore hole water compared to the reference sample. There is more of mass 17 (Ammonia) in the bore hole sample compared to normal water. There is also more Nitrogen (mass 28) and its isotope at mass 14. there is also more carbon dioxide (mass 44). The peaks at 91 and 92 where not present in normal water, and were thought to be contamination in the bore hole water.

Saltwater Test:

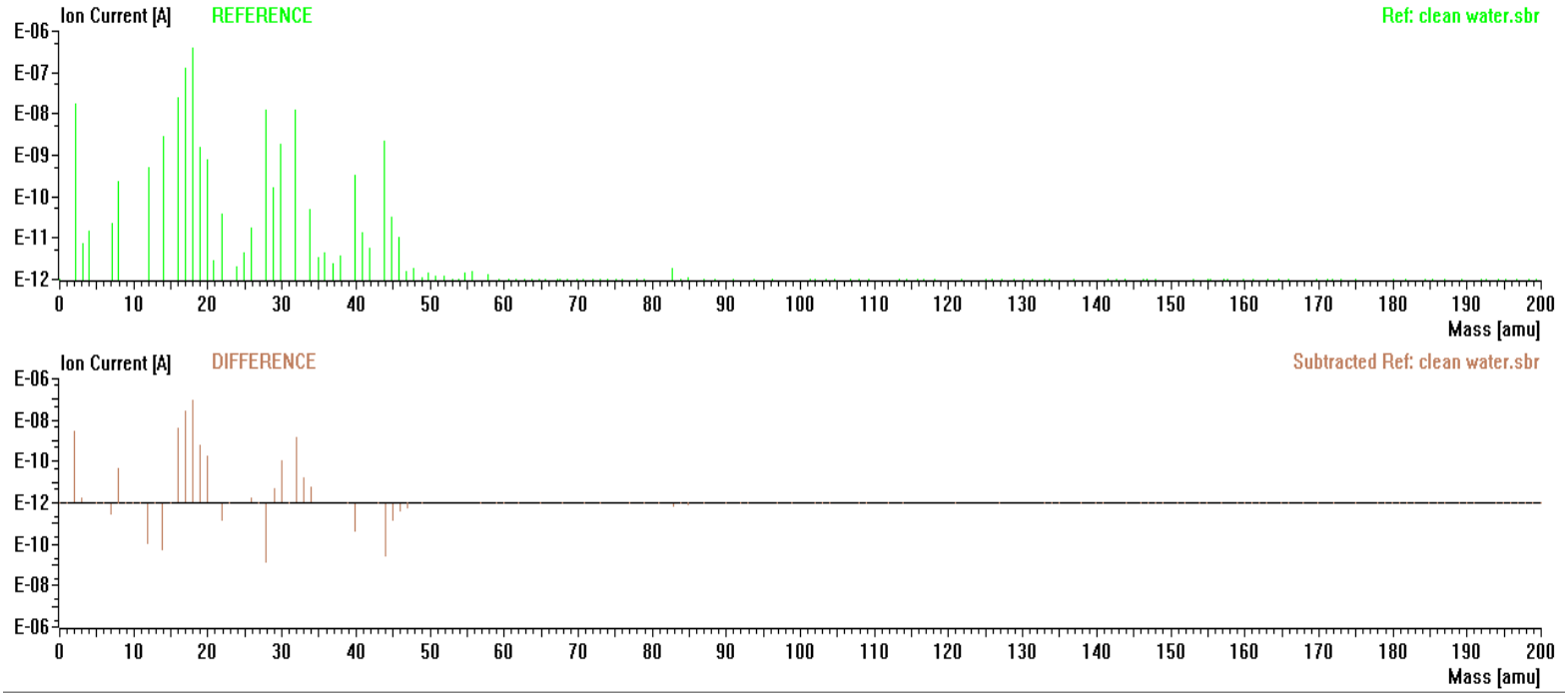

Figure 14. Graph 1: Mass spectrum of the control/reference sample of distilled water. Graph 2: Mass spectrum showing the difference between the reference sample (black line at E-12) and the salt water sample. The taller the peak the more of that gas there is in the sample. The peaks lower than the black line indicate that there was less gas of that mass in the saltwater, compared to the reference sample. At mass 44 (Carbon dioxide) the peak is lower than the reference line (E12), therefore there was less carbon dioxide in the saltwater sample compared to the normal water sample. This was also true of mass 28 (Nitrogen).

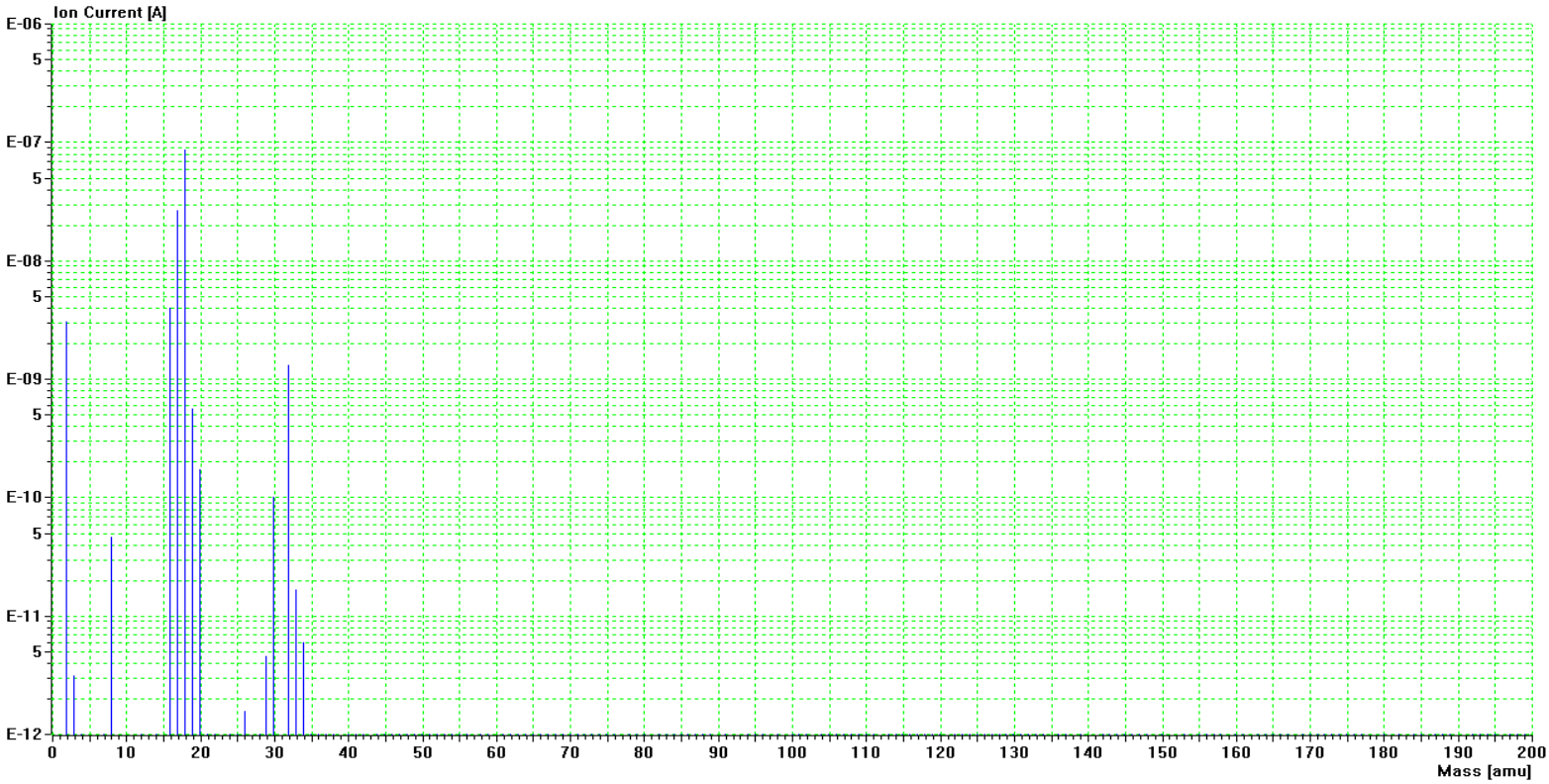

Figure 15. Mass spectrum of Saltwater difference graph (Figure 14, graph 2) showing peaks above the reference sample. The blue peaks indicate that there were more gasses of this mass present in the saltwater compared to the reference sample. There is more of mass 2 (Hydrogen), 32, 16, 8 (Oxygen and its isotopes) and mass 17 (Ammonia) in the saltwater sample compared to the reference sample.

Discussion

In the lab experiment the MIMS instrument was able to identify and monitor all 3 contaminates at a variety of concentrations, over a large dynamic range. A linear relationship was found for MEK (figure 9) and IPA (figure 11) demonstrating stability of the MIMS instrument in the lab. This shows that the MIMS instrument reached all 3 added concentrations (50,250,500µl) in a stable linear fashion for 70 mins. Also all 3 of the added contaminates had very small standard errors, at each concentration (figure 7,9,11), once they had plateaued off at the added concentration. This demonstrates the accuracy and stability of the instrument, as there was little variation from the mean concentration. The MIMS instrument was able to pick up the lowest concentration of 50µl accurately for all 3 contaminates, which is considered an extremely low concentration for most analytical instruments to detect accurately. It was also able to do this with only 1 calibration for each contaminant, making it an extremely easy analytical instrument to set up and use. For all 3 contaminates the instrument behaved roughly the same, with only 1 calibration for each, one silicon semi- permeable membrane and the same set up method, demonstrating the reliability of the instrument. The instrument behaved slightly differently for IPA (figure 10) as it took longer than 10 minutes for the instrument to reach the added concentration and stabilize. Therefore, we left it for a few minutes longer for each concentration to ensure it did reach the designated concentration accurately. Even though IPA did behave slightly differently it was still just as accurate once it plateaued off, showing that it can still perform reliably even with highly volatile chemicals. Acetone was the only contaminant that did not demonstrate a significant linear relationship (figure 7). The 250 µl concentration was an outlier with a larger SE ± 5.47, therefore it influenced the rest of the

data. It could have been caused by human error, for example an inaccuracy of the concentration added. Because the instrument read the other concentrations accurately.

In the Bore hole test in the field, the MIMS instrument demonstrated its ability to be deployed unmanned, continuously monitoring the environmental water in the bore hole. The spectrum (figure 12 and 13) shows the monitoring of the bore hole water over 12hrs compared to the reference sample. There was clear difference between the reference and the bore hole sample, proving the instruments accuracy to identify gasses in the field. The instrument was able to identify a range of gases in the bore hole including possible contamination. For example, in figure 13 mass 91 and 92 were identified as being contaminates. The masses can be looked up in the NIST database in order to identify them. Like the study done by Kristensen et al (2010), this MIMS instrument proved it could be deployed unmanned, with off-site real time surveillance, of contamination in a liquid matrix. It also demonstrated that it can monitor gasses in saltwater as well (figure 14 and 15). Like in the bore hole, the reference sample was different to the saltwater sample showing the instruments accuracy of gas identification in saltwater. For both field tests the instrument provided qualitative data, as the masses could be identified in NIST. It also provided us with identification of the gases and any possible contamination in the matrices.

The three VOC contaminants used in the lab experiment (IPA, MEK and Acetone) are not considered to be partially harmful in environmental water systems, unless they are in high concentrations. Low levels of VOCs that end up in water systems usually vaporize before they can cause any long term damage to the ecosystem. However, small traces that are from an anthropogenic source (industrial site), could lead to higher quantities being released in the future. Monitoring with the MIMS instrument would be an excellent way of discovering if this is occurring, and as a result help to protect the aquatic ecosystem from harm by contamination.

Overall we felt the experimental design of the study was reliable, repeatable and as accurate as we could make it. There is however the chance that overlapping isotopes could have made separation of the gas compounds difficult leading to inaccuracy. This is often a problem associated with MIMS technology, and is hard to avoid and minimize. For example, in figure 13, Oxygen and Ammonia are present but Oxygen has three stable isotopes ^{16}O, ^{17}O and ^{18}O. Therefore, the peak at mass 17 could be Ammonia which is also mass 17, or an isotope of Oxygen. However, ^{16}O is the most abundant isotope, so it's likely that the peak at 17 is Ammonia, but the MIMS instrument is not accurate enough to say this for sure. One way of improving the accuracy of this study would have been to replace the silicon semi-permeable membrane in-between each new test to reduce the risk of any contamination. A new membrane was attached at the beginning of this study and the sample interface of the instrument was flushed out between all tests to minimize contamination. Human error is also a factor that could lead to inaccurate results e.g. pipetting the designated volume of contaminant.

Concluding remarks

To conclude, our MIMS instrument demonstrated its suitability for *in-situ* environmental field based monitoring programs, for example assessing the quality of a river system over time. Its ability to monitor continuously unmanned means it saves time, and reduces the chance of any contaminates being missed in systems. It also illustrated it can selectively detect and monitor common VOC contaminates accurately in the lab, at concentrations as low as 50µl. The MIMS instrument therefore has a range of applications including: Assessment and monitoring programs of contaminates in many environmental water systems, fermentation research, drinks industry, human breath analysis, aquatic research and environmental pollution research. Unlike other analytical methods, MIMS technology is relatively simple to use, meaning expert knowledge is not needed, and it's cheaper to purchase and run. Its exchangeable interface means it can be changed between a MIMS instrument

and normal Quadrupole Mass Spectrometer. Further research could include trialling the MIMS instrument on a wider variety of chemical contaminates.

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