Doctoral theses at NTNU, 2020:359

Morten Rønnevig Martinsen

Development of an On-Line Monitoring Platform and Procedure for Rapid Environmental and Process Monitoring of Heavy Oil Extraction Operations and Industrial Activity

Doctoral thesis

NTNU
Norwegian University of Science and Technology
Thesis for the Degree of
Philosophiae Doctor
Faculty of Natural Sciences
Department of Chemistry

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ISBN 978-82-326-5064-4 (printed ver.)
ISBN 978-82-326-5065-1 (electronic ver.)
ISSN 1503-8181 (printed ver.)
ISSN 2703-8084 (online ver.)

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Printed by NTNU Grafisk senter

Acknowledgments

The work presented in this doctoral thesis has been carried out at the Department of Chemistry at the Norwegian University of Science and Technology (NTNU) between 2009 and 2018. Financial support from the Nature and Science Faculty (NV).

First and foremost, I would like to thank my supervisor Professor Øyvind Mikkelsen and co-supervisor Rudolf Schmid. Thank you for believing in me through all these years. It has been a long struggle with ups and downs and you have, throughout all these years, pushed me to complete. Thank you both for being positive, expanding my horizon of knowledge, for always having time for a chat. Thank you both for giving me the opportunity to partake in this very interesting and challenging project.

I have had some great years at the Department of Chemistry at NTNU, and I would like to thank all my former colleagues and fellow PhD-students. There are many people who deserve to be mentioned here; Svein Jacob, Thor and Karina are some of them. Thank you for great lunches, coffee breaks and talks over a pint.

During the work with my degree I have also had the pleasure of working at Applied Environment Research Laboratory (AERL) at Vancouver Island University, Nanaimo. There I've had the pleasure of working with Professor Erik Krogh and Professor Chris Gill and their group. Thank you, Kyle Duncan, Megan Willis and Ryan Bell for your insight and your willingness to share knowledge with me. A special thanks to Nick Davey. The number of hours we have spent together in a car during field work or crunching data before a conference are far too many to count. Your friendship will always be cherished.

Thanks to my current employer, Sweco Norge AS, and Yvonne Johansen, for giving me time to complete my thesis.

A very special thank goes to my wife and better half, Lise. Your support to help me complete my doctoral thesis means the world to me and I will always be thankful for it. It's been a trial time with both of us having jobs, kids and everything that comes with being a family of five. This would not have happened if it hadn't been for you!

List of papers included in this thesis

Paper I

Nicholas G. Davey, Cole T.E. Fitzpatrick, Jacob M. Etzkorn, Morten Martinsen, Robert S. Crampton, Gretchen D. Onstad, Timothy V. Larson, Michael G. Yost, Erik T. Krogh, Michael Gilroy, Kathy H. Himes, Erik T. Saganić, Christopher D. Simpson & Christopher G. Gill. Measurement of spatial and temporal variation in volatile hazardous air pollutants in Tacoma, Washington, using a mobile membrane introduction mass spectrometry (MIMS) system, *Journal of Environmental Science and Health, Part A, 2014, 49, 1199-1208*

Paper II

Ryan J. Bell, Nicholas G. Davey, Morten Martinsen, Christian Collin-Hansen, Erik T. Krogh, Christopher G. Gill. A field-portable membrane introduction mass spectrometer for real-time quantitation and spatial mapping of atmospheric and aqueous contaminants. *Journal of The American Society for Mass Spectrometry, 2015, 26, 212-223*

Paper III

Ryan J. Bell, Nicholas G. Davey, Morten Martinsen, R. Timothy Short, Chris G. Gill, Erik T. Krogh. The Effect of the Earth's and Stray Magnetic Fields on Mobile Mass Spectrometer Systems, *Journal of The American Society for Mass Spectrometry, 2014, 26, 201-211*

Paper IV

Morten R. Martinsen*, Nicholas G. Davey, Ryan J. Bell, Erik T. Krogh, Chris G. Gill, Oyvind Mikkelsen, Rudolf Schmid. A field portable membrane introduction mass spectrometer with in-line standard infusion and sample heat exchanger for real-time monitoring of volatile organic compounds in aqueous samples. *Environmental Chemistry and Ecotoxicology, 2020, 2, 168-174*

Paper V (draft)

Morten Martinsen. *Proton Transfer Chemical Ionization – A short review, draft.*

Summary

Developing monitoring systems for micro-pollutants and toxic substances to be able to protect particularly valuable and vulnerable areas against negative environmental pressures and impacts, and be in the forefront concerning environmental issues, several basic research aspects within environmental monitoring needs to be addressed. Of specific important and urgent need is to develop new and reliable analytical methods with sensitivity in the range capable of measuring real concentrations in filed. New and reliable methods, of sensitivities that allow measuring realistic concentrations in the field, are important to be able to address several basic aspects in environmental research and monitoring.

With an increasing demand for on-site online and real-time monitoring in the areas of environmental surveys, membrane introduction mass spectrometry (MIMS) has seen increased use. For flexible and thorough analysis of VOCs/SVOCs, e.g. in the environment, the analytical system should preferably be brought to the location of interest and allow continuous monitoring, locally or remote/on-line. This would allow to immediately respond to undesirable levels of analyte and provide instant feedback regarding analyte levels of any measures taken at the site. An optimized heat exchanger – MIMS interface is presented in combination with a continuous flow internal standard addition for quantification. Both continuous infusion of toluene-d8 and standard addition into the sample line while analyzing samples ensures the ability for online calibration together with correcting for any drift in signal, and without any need for more comprehensive calibration steps pre or post analysis.

The advent of portable chemical sensing technology enables a new framework for environmental monitoring, where it is possible to take high precision, high accuracy chemical measurements to the field. The collection of continuous real-time datasets affords additional challenges and opportunities for data storage, presentation, and interpretation. In-field data collection is eased through the use of cellular networks and cloud-based storage. These systems allow any user with an internet connection to inspect the data at any time, while simultaneously creating an integrated data backup system. Data presentation and interpretation is eased through the use of free Geographic

Information System (GIS) applications, such as Google Earth™. A portable battery operated highly sensitive membrane introduction mass spectrometer system was assembled and demonstrated for on-line measurements in air and water samples. The system was tested close to an oil sand facility in Northern Alberta during 2010-2012. The novel portable system was capable of resolving and quantifying VOC and SVOCs with high spatial and temporal resolution, in the field, in real-time.

The popularity of field portable mass spectrometry is growing as many of the technical hurdles of bringing laboratory equipment into the field are overcome. The effect of external magnetic fields though, such as the Earth's magnetic field, on portable mass spectrometer signal intensity has not yet been addressed by the mass spectrometry community. When precise, low-energy electron beams are employed, care must be taken to reduce the influence of uncontrolled magnetic fields. For example, photoelectron spectrometer components are intentionally lined with or constructed from magnetically permeable materials to limit the influence of magnetic fields. Field portable instrumentation also experiences varied magnetic fields as a result of changing its orientation with respect to the Earth's magnetic field. The resulting transient deflection of electron trajectory may generate a significant source of instrumental variability. Characterization of the influence of magnetic bearing on the relative instrument response of several field portable mass spectrometers, simulations of the electron beam transmission efficiencies for several instrumental conditions and demonstration of simple instrumental modifications that provide magnetic shielding for better signal stability and sensitivity gains have been shown.

An interesting recent alternative technique to electron ionization (EI) is Chemical ionization (CI). CI, and specifically proton transfer, differs from EI because bimolecular processes are used to generate analyte ions. The process of these bimolecular reactions requires sufficiently many ion-molecule collisions during the dwell time in the ion source. Multiple methods for environmental applications have been reviewed.

The work presented in this thesis demonstrates the capability of Membrane Introduction Mass Spectrometry as a method for on-line and real-time measurement of VOC's and SVOC's in atmospheric and aqueous matrices. Several improvements and method developments have been studied and tested to improve analyte response, quantification, data sampling and handling, georeferencing and the elimination of external influence of the earth’s magnetic field on electron ionization.

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Introduction

Several basic research aspects within environmental monitoring need to be addressed and monitoring systems for micro-pollutants and toxic substances need to be developed to be able to protect particularly valuable and vulnerable areas against negative environmental pressures and impacts and to be in the forefront concerning environmental issues. Of specific important and urgent need is to develop new and reliable analytical methods with sensitivity in the range capable of measuring real concentrations in field. This thesis aims at contributing to develop analytical techniques for field use to monitor volatile and semi-volatile organic compounds in air and/or water. The focus in this work is both instrumental and method development for monitoring micro-pollutants and toxic substances in the field both in aqueous and atmospheric matrices. Utilizing modified miniature GC-MS instrumentation coupled with membrane introduction mass spectrometry (MIMS) requires extensive work in the laboratory prior to real-time and on-line field measurement. This thesis and the work presented demonstrates real-time, on-line field measurements of both aqueous and atmospheric matrices, calibrations done both pre-, during-, and post field deployment, solving complex interferences regarding the earth's magnetic field and the development of a heat-exchanger for preheating aqueous samples together with an in-line continuous infusion of an internal stand. Furthermore, a review on alternative methods, in particular proton transfer mass spectrometry (PTR-MS) is presented, as traditional electron ionization (EI) has issues with isobaric interferences. New and reliable methods, of sensitivities that allow measuring realistic concentrations in the field, are important to be able to address several basic aspects in environmental research and monitoring. Developing monitoring systems for micro-pollutants and toxic substances can also help secure that hydrocarbon production is done in an environmentally sustainable manner (1), for which properly designed monitoring programmes are essential for.

Theory

Membrane Introduction Mass Spectrometry (MIMS)

Membrane introduction mass spectrometry (MIMS) is a powerful technique with demonstrated capabilities as an on-line monitor for volatile and semi-volatile organic compounds (VOC/SVOCs) in complex environmental samples. A number of recent review articles describe the theory and practice of the technique, including a number of environmental and process control applications (2-4). MIMS uses a semi-permeable membrane to introduce mixtures of hydrophobic organic analytes from samples of air, water, slurries, etc. into a mass spectrometer, where their signals can be resolved based on their mass to charge ratio, or by using advanced techniques such as tandem mass spectrometry (MS/MS). The advantage of using this approach over conventional analytical techniques is that the sample can be directly measured in a continuous fashion via flowing the sample over a membrane inlet. This eliminates sample preparation and chromatographic separation, giving an effective analytical duty cycle that is limited only by the analyte transport rate through the membrane (typically seconds to minutes).

Conventional MIMS uses a hydrophobic membrane material, such as polydimethylsiloxane (PDMS, Silicone™) in, e.g., a capillary hollow fibre geometry. The bulk sample is rejected, while the hydrophobic organic analytes partition into the membrane and diffuse across to an acceptor fluid phase, e.g. helium gas (pervaporation), or a liquid in the case of condensed phase MIMS, (CP-MIMS). The diffusion across the membrane is governed by Fick's law of diffusion. There are mainly two equations that describes the permeation process, assuming that the constants for solvation and diffusion are independent of partial pressure. These equations are:

$$I_m(x,t) = -AD[\partial C_m(x,t)/\partial x] \qquad (1)$$

$$\partial C_m(x,t)/\partial t = D[\partial^2 C_m(x,t)/\partial x^2] \qquad (2)$$

where I_m(x,t) is the analyte flow inside the membrane (mol/s), A is the membrane surface area (cm^2), D is the diffusion constant of the analyte inside the membrane (cm^2/s), C_m(x,t) is the concentration inside the membrane (mol/cm^2), x is the depth in the membrane (cm), and t is time (s). Equation 1 describes the rate of molecular flow inside the membrane and equation 2 describes the rate at which concentrations change with time. At steady-state the concentration gradient in the membrane is constant and the flow rate can be calculated using Henry's law ($S=C_m/P_s$)

$$I_{ss} = ADS(P_s/l) \qquad (3)$$

where I_{ss} is the steady-state flow through the membrane (mol/s), S is the solubility constant (mol/torr cm^3), P_s is the vapor pressure of the analyte on the sample side of the membrane (torr), and l is the membrane thickness (cm). As seen in equation 3 the steady-state flow depends on the product of diffusion constants and the solubility, whereas the rate at which measured analyte concentrations change depends only on the diffusion constants (5).

The fluid is introduced to the ion source of the mass spectrometer, allowing for continuous quantification. MIMS has been shown to have detection limits in the µg/L range for VOCs in air and water (6-10). By heating the membrane, thus increasing and accelerating pervaporation, semi-volatile organic compounds can also be detected (11).

MIMS is well suited for rapid and simultaneous measurement of volatile chemicals. It can be used as an on-line (continuous) analytical technique with sensitivity in the low ppb range for volatile compounds. Because MIMS introduces analytes to the ionization source of the mass spectrometer as a mixture, the use of tandem mass spectrometry (MS/MS) confers a significantly higher specificity for mixture resolution and analyte quantitation than single step mass spectrometry can provide (12).

Although MIMS has been known for almost four decades, (13) in the mid-1990s there was a resurgence in the use of MIMS for 'real--time' trace analytical measurements in both air (14) and water samples (15). There are several reviews on MIMS technique reported, including trends (1), environmental applications (16) and, recently, its use for environmental and in-situ measurements (2). Several groups have been applying MIMS as an on-line monitor for environmental contaminants. As examples, Feilberg and co-workers (17) used MIMS as an on-line monitor to study the removal of malodorous compounds in air by livestock air filtration systems, and Norgard et. al. (18) used a compact MIMS system to study the release of VOCs during the application of nanofilm spray products. Thompson et. al. used MIMS as a method for monitoring the release of biogenic VOCs from wounded plants (19) and Etzkorn et. al. have shown its potential use as an in-situ, mobile measurement strategy for investigating anthropogenic VOCs in both terrestrial and marine environments (12). Other examples of applications are in biochemistry (20) or in medicine (21).

The Applied Environmental Research Laboratories group at Vancouver Island University has developed MIMS systems for a variety of divergent applications ranging from monitoring aqueous contaminant destruction (22) to on-line atmospheric contaminant detection (6) as well as the development of MIMS systems with enzyme modified membranes (23), a thermally assisted MIMS systems for SVOCs (13), membrane based online monitoring devices with compound detectors (14), furthermore utilizing ion-molecule reactions for on-line speciation and quantitation of VOC (24) and MIMS instruments as mobile laboratories for air quality study in field (15).

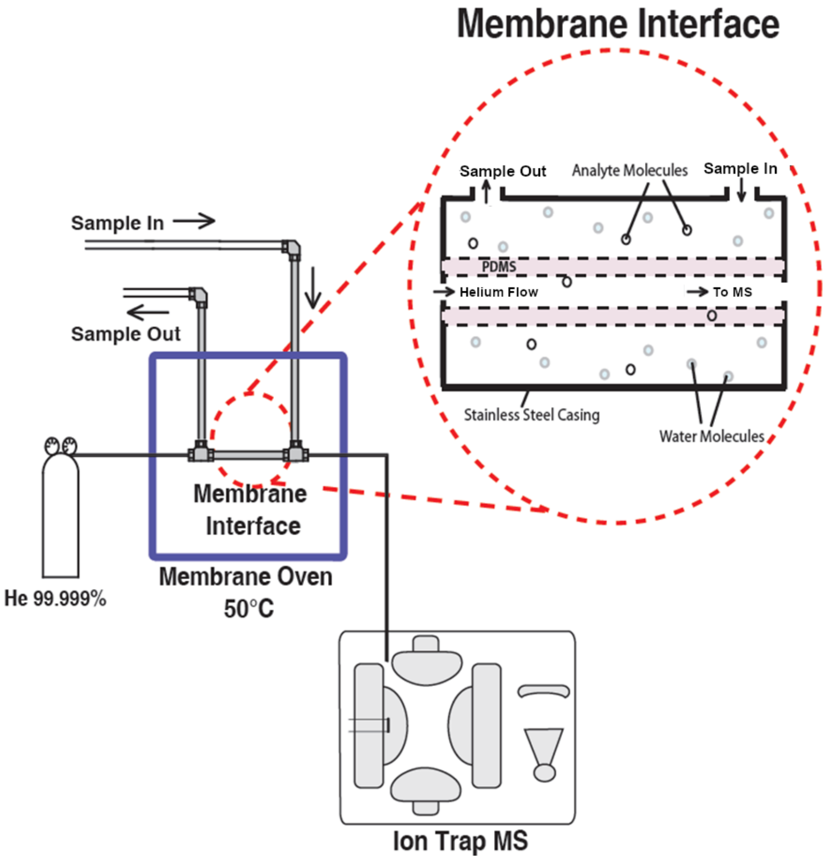

Figure 1. Simple schematic of the setup of a hollow fibre MIMS-interface coupled with an Ion Trap Mass Spectrometer.

Measurement of spatial and temporal variation in volatile hazardous air pollutants

Environmental organic toxicants in air encompass a diversity of chemicals, including both particulate and vapor phase components. Traffic exhaust and woodsmoke are two important sources of air toxics. Both of these sources emit complex chemical mixtures including particulate and vapor phase air toxics. A wealth of literature demonstrates associations between air pollution and adverse health outcomes (25-27). A number of recent studies have suggested that fine scale spatial variation in pollutant concentrations may be an important determinant of exposure to air pollution and adverse health outcomes. Significant associations have been reported between roadway proximity and various health outcomes (28-30). Fine scale spatial variability tends to be greater for specific air toxics, than it is for particulate matter (PM) in general (31, 32). Therefore, it is important to develop and evaluate in-situ monitoring tools and strategies that are able to measure multiple air pollutants simultaneously, with high spatial resolution. In the attached paper 2 (33) spatial and temporal variation in volatile hazardous air pollutants were measured. By use of an in-house assembled MIMS system (based on a standard bench-top GC/MS system), it was found that levels of VOCs and SVOCs were higher in winter compared to summer and were spatially uniform across the study area. Concentrations of vapor phase pollutants, notably benzene and toluene, had relatively uniform spatial distributions at night, but exhibited substantial spatial variation during the day-daytime, as levels were up to 3-fold at traffic-impacted locations than at a reference site. Although no direct side-by-side comparison was made between the MIMS system and traditional fixed site monitors, the MIMS system typically reported higher concentrations of specific VOCs, particularly benzene, ethylbenzene and naphthalene, compared to annual average concentrations obtained from SUMA canisters and gas chromatographic analysis at the fixed sites.

A Field-Portable Membrane Introduction Mass Spectrometer for Real-time Quantitation and Spatial Mapping of Atmospheric and Aqueous Contaminants

Several processes, both natural and anthropogenic, are associated with the release of volatile and semi-volatile organic compounds, and their concentrations in air can vary dramatically in time and space under the influence of environmental conditions (34). When considering hydrocarbon extraction and processing, emissions may be atmospheric (35) or aqueous (36), can be from point or diffuse sources (37), and are potentially harmful to nearby residents, biota and workers (38). Additionally, contaminant concentrations in the environment can be very dynamic as plumes migrate especially under the influence of mixing events driven by meteorological and hydrological processes (39, 40). Manual grab sample collection is often the primary sampling method used for current environmental monitoring programs. However, the time and expense required by such strategy often results in monitoring programs with relatively low data density that are limited in scope, and that can fail to provide information for making timely corrective decisions. Furthermore, improper documentation of baseline concentrations to compare industrially affected areas can lead to controversial situations that are difficult to assess (41, 42). As a result, grab sample collection programs are often very limited and frequently serve only to meet current regulatory compliance requirements. The advent of portable chemical sensing technology enables a new framework for environmental monitoring, where it is possible to take high precision, high accuracy chemical measurements to the field (12, 21, 33, 43-49). Membrane introduction mass spectrometry (MIMS), can provide continuous monitoring time series data that resolve multiple analyte concentrations simultaneously (2, 12, 33, 50-54). When operated on a mobile platform, these instruments can track transient concentration excursions in both spatial and temporal domains that may be missed by grab sampling strategies (50). Continuous datasets allow the analyst to better understand the spatial boundaries of contaminant plumes as well as temporal changes due to dilution, mixing and/or processing. For example, directly comparing plume intensities and background intensities in a single dataset can reduce the possibility of obtaining both false negative and/or positive measurements made in dynamic environments. Furthermore, with this information collected in real-time, sampling decisions and corrective actions can be made in a timely manner, helping to mitigate liability for both resource management and environmental stakeholders.

In general, MIMS systems allow continuous sampling of VOC/SVOC analytes as they diffuse through a semi-selective membrane, whereupon simultaneous quantification of multiple co-permeating molecules occurs by mass spectrometry (1, 2, 16). MIMS systems employing hydrophobic PDMS membranes yield sensitive and selective determinations of VOC/SVOCs in both aqueous and gaseous samples, by pre-concentrating hydrophobic compounds, enhancing their permeation, while impeding the diffusion of ionic and hydrophilic compounds. Because the membrane allows analytes to pass simultaneously as a mixture, it is important for quantitative analyses that the mass spectrometer can resolve each analyte without interference. Analyte interferences can be reduced using tandem mass spectrometric (MS/MS) techniques. In addition, corrections for known interferences can be applied by using simultaneous measurements for these interfering compounds and, sometimes, through inspection of analyte response times (55).

The collection of continuous real-time datasets affords additional challenges and opportunities for data storage, presentation, and interpretation. In-field data collection is eased through the use of cellular networks and cloud-based data storage. These systems allow any user with an internet connection to inspect the data at any time, while simultaneously creating an integrated data backup system. Data presentation and interpretation is facilitated through the use of free Geographic Information System (GIS) applications, such as Google Earth™. By using mass spectrometric data that is both time and location stamped, it is possible to provide real-time chemical concentrations that are geospatially mapped. In addition to providing environmental protection, through rapid screening and continuous monitoring applications, this approach can be used to inform intelligent adaptive sampling strategies, delineate plumes or contaminated sites, identify point sources, quantify fugitive emissions, monitor process efficiencies and provide discrete molecular information about complex mixtures (e.g. chemical fingerprinting).

A portable battery-operated highly sensitive membrane introduction mass spectrometry system was assembled and demonstrated for on-line measurements of air and water samples. The system was tested close to an oil sand extraction facility in Northern Alberta during 2010-2012. The novel portable system was capable of resolving and quantifying VOC and SVOCs with high spatial and temporal resolution, in the field, in real-time. An electron impact ionization cylindrical ion trap mass spectrometer modified with a capillary hollow fibre polydimethylsiloxane membrane interface was used for continuous air or water sampling. Tandem mass spectrometry by both selected ion monitoring scans performed in series allowed for the quantitation of target analytes, and full scan mode was used to survey for unexpected analytes. Pre-deployment and in-field external calibrations were performed with a continuously infused internal standard to enable real-time quantitation and monitor instrument performance. During field experiments, the system was operated in a moving vehicle with internet-linked data processing and storage. Software development was included to integrate MIMS and relevant meta-data for visualization and geospatial presentation in Google Earth™.

Field apparatus and magnetic fields

The popularity of field portable mass spectrometry is growing as many of the technical hurdles of bringing laboratory equipment into the field are overcome (33, 49, 56). On-site analysis requires that instrumentation can be transported conveniently, powered remotely, be free of self-contamination, and can be serviced in adverse conditions. Additionally, the instrumentation should be capable of data collection while moving, and overcome any additional hurdles resulting from changing environmental and sample conditions. For example, non-steady state or transient conditions are likely to be more prevalent and may require correction (4, 38). Additionally, varied sample conditions, such as temperature, pressure, and humidity, may alter the relative instrumental response (4, 38, 57-59), and changing environmental conditions may adversely affect the instrument itself (60). Apart from a report by Short, et al. (2000) (60), the effect of magnetic fields, such as the Earth’s magnetosphere, on portable mass spectrometer signal intensity has not yet been addressed by the mass spectrometry community.

Electron beams that have a short pathlength or have sufficiently high energies are not significantly affected by weak magnetic fields. Additionally, weak magnetic fields are likely to have a negligible impact on the deflections of ion beams due to their significantly greater relative momentum. However, when precise, low-energy electron beams are employed, care must be taken to reduce the influence of uncontrolled magnetic fields. For example, photoelectron spectrometer components are intentionally lined with, or constructed from, magnetically permeable materials to limit the influence of magnetic fields (61). Nickel-iron alloys such as mu-metal and other magnetically permeable materials have a magnetic permeability many times that of free space and tend to absorb passing magnetic fields by providing a preferred location for field transmittance. Thus, when instrumentation is encased in mu-metal, effects of external magnetic fields are greatly reduced inside the instrument, avoiding unintended electron beam deflections. Although impractical in the context of portable mass spectrometry instrumentation, Helmholtz cages have also been employed to compensate for the effects of the Earth’s magnetic field in testing facilities (62) and in high resolution cathode ray tubes (63).

Field portable instrumentation also experiences varied magnetic fields as a result of changing its orientation with respect to the Earth’s magnetic field. The resulting transient deflection of electron trajectory may generate a significant source of instrumental variability. In addition, the magnetic fields created by various mass spectrometer components (e.g. vacuum pumps, inductive coils, or filament current) may also affect electron beam deflection. The summation of multiple magnetic field vectors will have an additive effect that is directionally dependent.

These effects are difficult to observe when instrumentation is operated in GC mode due to the highly variable nature of the instrumental signal. Further, the effects are compensated for if instrument orientation is not changed between calibration and sample analysis, as recommended by instrument manufacturers. However, when operating in a continuous mode, signal variability becomes easily observed when underway.

Method development for aqueous measurements with Membrane Introduction Mass Spectrometer

The release of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) to the environment can be traced back to both natural and anthropogenic sources (2, 6, 33, 50). Monitoring the release of these compounds to the environment by monitoring programs is normally done using nationally or internationally standardized method, such as ISO or EPA methods. For aqueous solutions analyses using purge and trap gas chromatography mass spectrometry are the preferred methods of analysis for VOCs and SVOCs, e.g. EPA method 18 and EPA-NERL 542.2 (64, 65) These are well-proven and reliable methods for environmental monitoring programs, but require time-consuming sample preparations and chromatographic separation, reducing its capability to resolve detailed compound concentration variations in a highly dynamic environment.

With an increasing demand for on-site online and real-time monitoring in the areas of environmental surveys, membrane introduction mass spectrometry (MIMS) has seen increased use (1, 2, 66). Typically, MIMS uses a semi-permeable polymer membrane, such as polydimethylsiloxane (PDMS), with hydrophobic properties. The hydrophobic properties will prevent diffusion of particulates, water and highly polar and ionic compounds, while enhancing diffusion of compounds with a hydrophobic nature, yielding a MIMS system that is selective and sensitive for volatile and semi-volatile organic compounds (VOC/SVOC). This type of membrane will, thus, allow enrichment of these analytes from both liquid and gaseous samples. After diffusion through the membrane, they are then directly transferred, often using helium gas as the carrier acceptor phase, to a mass spectrometer for subsequent ionization, resolution and quantitative measurement (66).

For flexible and thorough analysis of VOCs/SVOCs, e.g. in the environment, the analytical system should preferably be brought to the location of interest and allow continuous monitoring, locally or remote/on-line. This would allow to immediately respond to undesirable levels of analyte and provide instantaneous feed-back regarding analyte levels of any measures taken at the site.

There are many challenges to be faced when developing mobile on-line analytical instruments capable of providing real-time data. For MIMS systems, one of these challenges is connected to the diffusion conditions when an analyte species permeates through the membrane interface. In general, the permeation through a membrane is dependent upon Fick’s law of diffusion, where permeation rates are governed by membrane properties affecting partition coefficient for the analyte species between membrane and sample, (the analytes' diffusion coefficients,) the thickness of the membrane and the concentration of the analyte species. Previous research has shown a temperature dependence of analyte response, which for field use might cause challenges not seen in laboratory under controlled temperature conditions. According to Arrhenius equation the permeability is dependent on the initial permeability at some initial temperature and the activation energy for diffusion. It is, therefore, of importance to regulate sample temperature to avoid sensitivity variations, and to maximize analyte response (67, 68). Further, analyzing complex matrices in an on-line manner can experience drift in the detector signal. It is therefore important to be able to calibrate, not only by standard additions to discrete samples, but continuously in an online manner while analyzing samples using field apparatus.

This work presents the development and characterization of a counter-current-flow heat exchanger suited for mobile deployment to overcome the challenges with membrane introduction at different sample temperatures and to limit power consumption for such field apparatus. An optimized heat exchanger – MIMS interface is presented in combination with a continuous flow internal standard addition for quantification. Both continuous infusion of toluene-d8 as the internal standard, and adding it directly into the sample line while analyzing samples, ensures the ability for online calibration together with correcting for any drift in signal. This happens without any need for more comprehensive calibration steps pre or post analysis. In this work calibration curves with different sample temperature are presented. Furthermore, experiments with additions of plumes containing different samples from the SAGD oil refinery process are presented.

Proton Transfer Chemical Ionization (PTR-CI), an alternative to electron ionization mass spectrometry

An interesting alternative technique to electron ionization (EI) is Chemical ionization (CI). CI, including proton transfer, differs from EI because bimolecular processes are used to generate analyte ions. The process of these bimolecular reactions requires sufficiently many ion-molecule collisions during the dwell time in the ion source (69). Proton transfer follows a general pathway to form ions from a neutral analyte M in CI: (69)

$M + [BH]^+ \rightarrow [M{+}H]^+ + B$

Sources of protons include water vapor, ambient air and internal CI gas.

Proton Transfer (Reaction) Mass Spectrometry (PTR-MS) instruments usually comprise an ion source to produce primary reagent ions (H_3O^+), a flow drift tube and a mass spectrometer to detect and quantify analyte(-derived) ions (70), see Figure 2 for a schematic example.

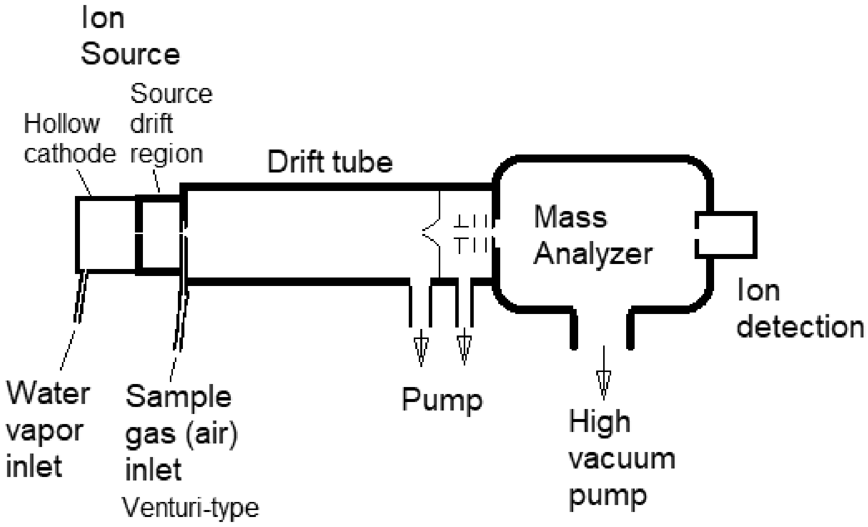

Figure 2. Schematic representation of a PTR-MS instrument (71).

There are several examples of CI-MS systems coupled with single quadruple mass analyzers. A compact atmospheric pressure chemical ionization mass spectrometer

(APCI-MS) was utilized for on-line monitoring of dimethyl sulfide (DMS) in seawater. DMS was measured in air equilibrated with flowing seawater across a porous Teflon membrane in a hollow-fiber membrane interface design. The gas stream was diluted in clean air containing an isotopically labelled internal standard and DMS was ionized at atmospheric pressure by proton transfer from water vapor. The equilibration was done by flowing the seawater containing DMS on the outside of a single tube flow-through membrane and dry clean air on the inside (72). The formation of water ions and ion clusters are done at 400ºC by passing the air with the analyte over a ^{63}Ni foil, ^{63}Ni being a low energy β-emitting (65,88 keV) radioactive isotope (72, 73). The pressure is about atmospheric (~760 Torr) from the equilibrator, reaches 1 torr in the collision region before it ends at 10^{-5} torr in the analyzer region. For quantification, deuterated DMS (CH_3SCD_3) is infused into the flow from the equilibrator to the MS. Detection limits for the system are estimated to be 220 pptv for field conditions and 148 ppt in the laboratory. The difference is explained by elevated signal-to-noise ratio in the field due to motion, thermal effect or electrical noise (72). A similar system has also been used for real-time measurements of HCN in air (74). Many volatile organic compounds are photo oxidized to oxygenated volatile organic compounds (OVOC) and contribute to both the gas phase and secondary organic aerosols (SOA). PTR-MS has shown to be a useful tool for determining many of these compounds in ambient air, e.g. acetaldehyde, acetone, propenal, methyl vinyl ketone, benzaldehyde, propene, toluene and 1,3,5-trimethylbenzene , both in particulate and ambient OVOC (75). The PTR-MS system has also been used for on-line measurements of gas phase hydrocarbon concentration in diesel engine exhaust as a function of engine load (76), to monitor selected hydrocarbon emissions like methanol, acetaldehyde, acetone, methyl *tertiary*-butyl ether (MTBE), benzene and toluene from vehicle exhaust emission (77), to measure oxygenated volatile organic compounds from crops after wounding and drying, e.g. alcohols, esters, aldehydes and ketones (78).

Environmental application of proton transfer chemical ionization coupled with triple quadruple mass spectrometers seems to be of lesser abundance than with other mass analyzers. The existing literature involving this coupling seems to orientate towards comparisons between selections of ionizing reagents, studies of kinetics, molecular structures and fragmentation pathways (79-86). Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) was used to find responses to selected polycyclic aromatic compounds (PACs) as a function of both solvents and source gases. These studies were done on light gas oil samples collected from Syncrude Canada Ltd. (87). Cisper et al. demonstrated in 1997 the use of membrane introduction mass spectrometry for determination of aqueous SVOCs, utilizing electron ionization and proton transfer chemical ionization in ion trap system. The authors stated that determination of 2-chlorophenol achieved higher response for proton-transfer chemical ionization than for/with electron ionization (8).

Allen et al. goes in further depth on the topic of analysis of benzene (VOC), naphthalene (SVOC) and ferrocene (organometallic compound) in aqueous solutions using membrane inlet mass spectrometry, with proton-transfer chemical ionization as ionization process. It was reported an increase in signal intensity yield from 2 to 800 times compared to electron ionization. The same compounds were also analyzed in air utilizing oxygen, O_2, for charge transfer CI (88).

Baudic et al. (89) have utilized a PTR-MS to measure a wide range of VOCs in Paris megacity. The measurements where done from January to February 2010 to show the seasonal variability of atmospheric VOCs and their various associated emission sources. In the article written by Parzeller et al. discusses the advantages of proton-transfer ion trap mass spectrometry (PTR-ITMS) over linear quadruple mass spectrometers. The main advantages of PTR-ITMS are the ability of specific identification i.e. overcoming problems with mass overlaps (isobaric compounds and isomers) and faster response times (90).

An on-line breath gas analyses by proton transfer time of flight mass spectrometer (PTR-TOF) has been developed for sensitive detection of VOCs. Time of flight instruments allows for the measurement of a complete mass spectrum within a fraction of a second, and the high mass resolving power enables the separation of isobaric molecules and the recognition of their elemental composition (91). A chemical ionization reaction time-of-flight mass spectrometer (CIR-TOF-MS) with H_3O^+ as primary chemical ionization source was used in the determination of concentrations of

OVOCs down to 10 ppbv. Measurements were done in real-time (92). Blake et al (93) describes a proton-transfer reaction time of flight mass spectrometer for the determination of VOCs with advantage in terms of mass resolution, mass range and ability to better resolve complex mixtures. Tanamito et al. developed a proton transfer reaction-time-of-flight mass spectrometer (PTR-TOFMS) for real-time measurements of VOCs as well. The detection limits for acetaldehyde, acetone, isoprene, benzene, toluene and p-xylene were determined to be at the sub-ppbv levels (94).

Environmental monitoring with PTR-CI single quadruple mass analyzers is limited to parent ion detection, $[M-H]^+$. Therefore, isobaric interferences and mass overlapping is a recurring problem and requires extra measures to be taken to overcome. Time of Flight (TOF), and triple quadruple mass analyzers constitute a category offering mostly bench top instrumentation. Triple quadruple mass analyzers serve more as an instrument for studying fragmentation pathways and more intricate experiments. TOF and ICR (or Orbitraps) offer great resolution compared to other analyzers mentioned in here, but on the other side these instruments are expensive compared to for instance ion traps and are therefore often out-competed by them. In terms of field-mobility,weight, volume and complexibility of magnetic sector instrumentation and Ion Cyclotron Resonance Mass Spectrometers (FT-ICR-MS) are far too big and complex . The ion trap mass analyzer has the capability to ionize, trap and isolate parent ions, fragment these ions, and trap isolate and detect the new fragments “at the spot”, also called tandem-in-time. Ion traps also offer the possibility for smaller instrumentation enabling field portability as described in some of the articles.

Developments in methods of sample introduction and ionization have opened the ability to analyse a wider range of compounds with PTR instrumentation. Zhang et al. (95) have shown how dipolar proton transfer ionization offers the availability to analyse both VOCs and inorganic substances, e.g. CO_2 and NH_3. Sulzer et al. (96) describes a method combining proton transfer with charge exchange analysing both trace VOCs (benzene, toluene etc.) and CO, CO_2, CH_4 and SO_2. Membrane introduction or spray inlet are examples of sample introduction methods that allows analysing VOCs in aqueous matrices (97, 98).

PTR-MS has found application not only in environmental analysis of the atmosphere and water bodies, but also in food science, medicine (breath analyzers), biology and biotechnology, a.o. New capabilities are also created by combining the PTR-MS data with other data into powerful information (topological, chronological, meteorological etc.).

Authors Contribution

The candidate's contribution to the work presented in paper I, "Measurement of spatial and temporal variation in volatile hazardous air pollutants in Tacoma, Washington, using a mobile membrane introduction mass spectrometry (MIMS) system", comprises crucial contribution to pre-deployment calibration, data collection and field experimentation. as well as post-deployment data workup and presentation. The candidate has also contributed significantly with commenting and editing on the paper draft.

In the work described in paper II, "A field-portable membrane introduction mass spectrometer for real-time quantitation and spatial mapping of atmospheric and aqueous contaminants.", the candidate has contributed significantly to the instrumental development, method development, pre-deployment calibration, field deployment data collection and edits and comments to the paper draft.

In the attached paper III "The Effect of the Earth's and Stray Magnetic Fields on Mobile Mass Spectrometer Systems" published in Journal of the American Society for Mass Spectrometry (2014) the candidate's contribution has been taking part in laboratory and field experimentation. The variation in signal intensity was first discovered during a field-deployment in 2010, where the candidate was partaking in collecting field data. It was not until the first author of the paper, Ryan Bell, connected the recurring issue of signal intensity variations with a similar issue he had had with a solenoid pump that the contribution of a magnetic field could be the problem.

Conclusions

Several processes, both natural and anthropogenic, are associated with the release of volatile and semi-volatile organic compounds, and their concentrations in air can vary dramatically in time and space under the influence of environmental conditions. In such cases traditional sampling methodology including manual spot sampling followed by shipping the samples to a laboratory for later analyses is not necessarily the optimal way to achieve representative results. There are few possibilities for on-line field monitoring of low concentrations of volatile and semi-volatile organic compounds (VOC/SVOCs) in air and natural water. However, membrane introduction mass spectrometry (MIMS) is a powerful technique with demonstrated capabilities as an on-line monitor for VOC/SVOCs in complex environmental samples. MIMS uses a semi-permeable membrane to introduce analyte mixtures from samples (air, water, slurries etc.) to a mass spectrometer, where they can be resolved based upon their mass to charge ratio, or by using advanced techniques such as tandem mass spectrometry (MS/MS). The advantage of using this approach over conventional analytical techniques is that the sample can be directly measured in a continuous fashion via flowing the sample over a membrane inlet. This eliminates sample preparation and chromatographic separation, giving an effective analytical duty cycle that is limited only by the analyte transport rate through the membrane (typically seconds to minutes). The current MIMS methodology for monitoring organic contaminants is, however, still sub-optimal for field apparatus, and challenges relate to complexity in introducing analytes in the MIMS system, detector drift, analyte carry-over, matrix effects and calibration routines among others. The aim of this thesis has been to contribute to develop an on-line monitoring platform and procedure for rapid environmental and process monitoring of heavy oil extraction and industrial activity. To solve challenges related to the complex diffusion conditions for analytes in the MIMS system in field apparatus and difficulties with calibrations, a counter-current-flow heat exchanger in combination with a continuous flow internal standard addition system has been developed and tested in field apparatus. The studies showed that the developed system was well suited for rapid on-line (continuous) and simultaneous measurement of volatile chemicals in the low ppb range. The papers constituting this thesis present the development of methods for on-line monitoring of VOCs and SVOCs in both atmospheric and aqueous matrices. Two papers demonstrate the use of the system in relevant field applications. Additionally, one paper presents an interesting study of the effect of earth’s magnetic field on mass spectrometers and how this effect was overcome during field deployment. As an alternative to MIMS EI one of the attached papers is a review of another method of ionization, in particular PTR-MS, to overcome isobaric interferences occurring with EI.

Future Aspects

Through the work with this thesis MIMS has proven a reliable, versatile, and rugged instrumentation for environmental monitoring of pollutants in both air and aqueous matrices. Efforts have been made to overcome difficulties with controlling sample temperature variabilities in aqueous sampling, quantification, and the effects of earth's magnetic field.

Further development within the field of methods of ionization, chemical fingerprinting and data collection and presentation can be made.

Collecting data in the field and displaying calibrated results connected to GPS signal to give special and temporal resolved data are mostly done post-deployment. For future development, the utilization of cloud-based storage for on-line and real-time data collection could be coupled with a spatial data integration platform, e.g. Feature Manipulation Engine (FME), one could be able to portray calibrated data real-time on a map.

Understanding the source and composition of a plume or a spill of oil can be crucial in terms of locating the source and controlling it. Different types of oil products will produce different types of mass spectra. Utilizing statistical methods one can separate and identify different types of hydrocarbon products (e.g. diesel, gasoline, oil sands, different types of North Sea oil). Clustering different hydrocarbon products by utilizing multivariate analysis one might be able to use these data to pinpoint or locate the source of a plume or an oil spill real time with MIMS.

Chemical ionization is a powerful and versatile method of ionization. Efforts have been made to employ ion-molecule reactions to overcome isobaric interferences. Further studies into reagent molecules and manipulation of reaction times can be done.

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Paper I

Paper II

J. Am. Soc. Mass Spectrom. (2015) 26:212–223
DOI: 10.1007/s13361-014-1028-3

FOCUS: HARSH ENVIRONMENT AND FIELD-PORTABLE MASS SPECTROMETRY:
RESEARCH ARTICLE

A Field-Portable Membrane Introduction Mass Spectrometer for Real-time Quantitation and Spatial Mapping of Atmospheric and Aqueous Contaminants

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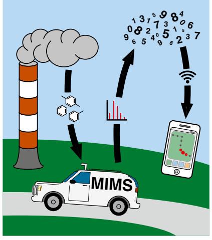

Abstract. Environmental concentrations of volatile and semivolatile organic compounds (VOC/SVOCs) can vary dramatically in time and space under the influence of environmental conditions. In an industrial setting, multiple point and diffuse sources can contribute to fugitive emissions. Assessments and monitoring programs using periodic grab sampling provide limited information, often with delay times of days or weeks. We report the development and use of a novel, portable membrane introduction mass spectrometry (MIMS) system capable of resolving and quantifying VOC and SVOCs with high spatial and temporal resolution, in the field, in real-time. An electron impact ionization cylindrical ion trap mass spectrometer modified with a capillary hollow fiber polydimethylsiloxane membrane interface was used for continuous air and water sampling. Tandem mass spectrometry and selected ion monitoring scans performed in series allowed for the quantitation of target analytes, and full scan mode was used to survey for unexpected analytes. Predeployment and in-field external calibrations were combined with a continuously infused internal standard to enable real-time quantitation and monitor instrument performance. The system was operated in a moving vehicle with internet-linked data processing and storage. Software development to integrate MIMS and relevant metadata for visualization and geospatial presentation in Google Earth is presented. Continuous quantitation enables the capture of transient events that may be missed or under-represented by traditional grab sampling strategies. Real-time geospatial maps of chemical concentration enable adaptive sampling and in-field decision support. Sample datasets presented in this work were collected in Northern Alberta in 2010–2012.

Key words: VOC/SVOC, Membrane introduction mass spectrometry (MIMS), Emissions, Alberta oil sands, Mobile mass spectrometry, Real time quantitative mapping

Received: 15 August 2014/Revised: 9 October 2014/Accepted: 11 October 2014/Published Online: 5 December 2014

Introduction

Many processes, both natural and anthropogenic, are associated with the release of volatile and semivolatile organic compounds (VOC/SVOCs) to the environment [1]. When considering hydrocarbon extraction and processing, these emissions may be atmospheric [2] or aqueous [3], can be from point or diffuse sources [4], and are potentially harmful to nearby residents, biota, and workers [5]. Additionally, contaminant concentrations in the environment can be very dynamic as plumes migrate, especially under the influence of mixing events driven by meteorological and hydrological processes [6, 7]. Grab sample collection (e.g., bottles, canisters, and sorbent traps) are often the primary sampling method used for current environmental monitoring programs and, although quantitative in nature, measured concentrations reflect a single point in space and time (or integrated over a specific time window), predominantly in an ‘off-line’ manner. The time

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and expense required by these strategies often results in monitoring programs with relatively low data density that are limited in scope, and that can fail to provide information for making timely corrective decisions. Furthermore, improper documentation of baseline concentrations to compare industrially affected areas can lead to controversial situations that are difficult to assess [8, 9]. As a result, grab sample collection programs are often very limited and frequently serve only to meet current regulatory compliance requirements.

The advent of portable chemical sensing technology has enabled a new framework for environmental monitoring, where it is possible to take high precision, high accuracy chemical measurements to the field [10–18]. Many of these analytical techniques, such as membrane introduction mass spectrometry (MIMS), can provide continuous monitoring time series data that resolve multiple analyte concentrations simultaneously [16, 17, 19–24]. When operated on a mobile platform, these instruments can track transient concentration excursions in both spatial and temporal domains that may be missed by grab sampling strategies [24]. Continuous datasets allow the analyst to better understand the spatial boundaries of contaminant plumes as well as temporal changes due to dilution, mixing, and/or processing. For example, directly comparing plume intensities and background intensities in a single dataset can reduce the possibility of obtaining both false negative and/or positive measurements made in dynamic environments. Furthermore, with this information collected in real-time, sampling decisions and corrective actions can be made in a timely manner, helping to mitigate liability for both resource management and environmental stakeholders.

Our research has involved the development of a portable MIMS system for the continuous analysis of VOCs and SVOCs in both atmospheric and aqueous samples that greatly improves upon our early work in this area [16, 17, 20]. In general, MIMS systems allow continuous sampling of VOC/SVOC analytes as they diffuse through a semiselective membrane, whereupon simultaneous quantification of multiple co-permeating molecules occurs by mass spectrometry [20, 25, 26]. The use of hydrophobic membranes, such as polydimethylsiloxane (PDMS), impedes the diffusion of ionic and hydrophilic compounds, while pre-concentrating hydrophobic compounds, enhancing their permeation. Thus, MIMS systems employing PDMS membranes yield sensitive and selective determinations of VOC/SVOCs in both aqueous and gaseous samples. Because the membrane allows analytes to pass simultaneously as a mixture, it is important for quantitative analyses that the mass spectrometer can resolve each analyte without interference. Analyte interferences can be reduced through the use of tandem mass spectrometric (MS/MS) techniques. In addition, corrections for known interferences can be applied by using simultaneous measurements for these interfering compounds and through inspection of analyte response times [27].

The collection of continuous real-time datasets affords additional challenges and opportunities for data storage, presentation, and interpretation. In-field data collection is eased through the use of cellular networks and cloud-based storage. These systems allow any user with an internet connection to inspect the data at any time, while simultaneously creating an integrated data backup system. Data presentation and interpretation is eased through the use of free Geographic Information System (GIS) applications, such as Google Earth. Using mass spectrometric data that is both time- and location-stamped, we are able to provide real-time chemical concentrations that are geospatially mapped. In addition to providing environmental protection through rapid screening and continuous monitoring applications, this approach can be used to inform intelligent adaptive sampling strategies, delineate plumes or contaminated sites, identify point sources, quantify fugitive emissions, monitor process efficiencies, and provide discrete molecular information about complex mixtures (e.g., chemical fingerprinting).

In summary, we present the development and application of a field portable, battery operated MIMS system based upon a quadrupole ion trap that utilizes MS/MS for direct, on-line, low level (e.g., $\mathrm{ppb_V}$/ppb) analyte measurements in air and water samples. This flexible measurement system is compact and can be operated in an automobile for mobile measurements. Since volatile and semivolatile analytes pervaporate through the membrane interface from a sample as a mixture, the full resolution of isobaric isomers may not be possible, and other techniques involving chromatographic separations may be more appropriate. Additionally, higher sensitivity for analytes in gaseous samples can be achieved via methods such as proton transfer reaction mass spectrometry (PRTMS) [18, 28] and selected ion flow tube mass spectrometry (SIFT-MS) [29, 30]. Despite these potential drawbacks, we have successfully employed mobile MIMS to provide continuous geospatially resolved quantitative information for target analytes in both air and water, using in-house developed data management software to process and visualize the data in real-time using cellular network communications.

Methods and Materials

Overview

A commercially available, portable cylindrical ion trap mass spectrometer system (Model Griffin 400; FLIR, West Lafayette, IN, USA), was modified in-house for in-field measurements by the addition of a MIMS sampling interface and internal standard (IS) infusion system, similar to that described previously [16]. In addition to the MIMS sampling system (which is described in detail below), the system also included several peripheral monitoring devices. A global positioning system (GPS, QStarz, Model BT-Q1000XT; Taipei, Taiwan) was used for geo-location and accurate time-stamping of all collected data. A cellular network card installed in the data system computer (Model M6600; Dell, Round Rock, TX, USA) was used to provide cloud data storage (Dropbox, San Francisco, CA, USA) and continuous data backup in the field. A portable weather meter (Kestrel, Model 4500; Birmingham, MI, USA) was used periodically to determine meteorological data, including wind speed, wind direction, humidity, temperature, and barometric pressure. Although not utilized for the presented study, a video camera (Model HERO2; GoPro Inc., San Mateo, CA, USA) was incorporated to allow the potential creation of a video log of the surrounding environment during data collection events, to allow retrospective assessment of the data collection environment.

Membrane Introduction Mass Spectrometer

The cylindrical ion trap utilizing electron impact ionization (EI) was selected for use as the mass analyzer because of its compact, ruggedized, and field-portable design, and its ability to perform MS/MS for increased selectivity. Furthermore, the system is capable of multiple types of mass scan techniques in an interlaced series, allowing cycled quantitative analyte scans to be performed in sequence with general survey (full) scans. The entire mass spectrometer was encased in approximately 1.6 m^2 of 0.1 mm thick nickel alloy foil, or mu-metal ($\mu \approx 50{,}000$) (product number 8912 K32; McMaster Carr, Elmherst, IL, USA) to reduce the effects of the earth's magnetic field upon instrumental sensitivity. For additional information regarding the influence of magnetic fields upon portable EI mass spectrometers, the reader is directed to an article specifically addressing the topic, also in this issue of JASMS. The instrument was equipped with a temperature-controlled MIMS interface that replaced the supplied gas chromatograph system. For this work, the MIMS interface was constructed using a PDMS hollow fiber membrane (0.94 mm o.d., 0.51 mm i.d., 10 cm length, Silastic brand; Dow Corning, Midland, MI, USA) and a flow-over sample cell design. A similar experimental arrangement has been described previously [16], though a major difference in design is the use of an in-house constructed aluminum block heater to maintain a constant membrane temperature. The lumen (permeate side) of the membrane was swept with a helium carrier gas (~1 mL/min), provided by a miniature 16 L helium cylinder (Model 49617HE; Leland Ltd., South Plainfield, NJ, USA). In addition to acting as the membrane acceptor phase for analyte transport to the mass spectrometer, helium was also used as a buffer gas by the mass spectrometer. A schematic of the entire apparatus is given in Figure 1. For choosing desired sample flows, two three-way valves (Figure 1, valves A1, A2) were located on either side of the membrane inlet to facilitate convenient switching between aqueous or atmospheric samples (vide infra).

Gaseous Sampling

Sample was drawn into the MIMS system via two solvent-cleaned microporous stainless steel inlet filters in series (15 and 5 μm) (Model SS-6 F; Swagelok, Solon, OH, USA), and ¼in. o.d. Teflon transfer lines (Cole Parmer). The air-sampling inlet was mounted on the roof rack of a sport utility vehicle, approximately 30 cm above the roofline. Upstream from the MIMS inlet system, gaseous samples flowed through a temperature-regulated chamber housing a toluene-d_8 permeation tube to allow the continuous on-line infusion of IS (Figure 1). Since the permeation of analytes through the membrane is temperature-dependent, for the experiments described below the MIMS interface, permeation chamber, transfer lines, and inlet filters were independently temperature-regulated to 50°C. To utilize the system for SVOC analyses (data not shown), the inlet filter and transfer lines could be maintained at temperatures up to 200°C. The sample flow rate was set to the desired value using a rotameter equipped with a precision, 10-turn needle valve (Model FM4312(4); Advanced Specialty Gas Equipment, Middlesex, NJ, USA) and maintained by a mechanical diaphragm pump (Model B-Series Dia-Vac; Air Dimensions, Deerfield Beach, FL, USA) located after the membrane. A pressure gauge (Model PX209-30V15G5V; Omega, Laval, Canada) located on the sample flow line immediately following the membrane interface was used to monitor pressure changes (e.g., resulting from a clogged inlet filter). A second pressure gauge (Model PX209-030G5V; Omega), located between the diaphragm pump and rotameter, was used to monitor possible changes in sample flow rate. A pressure decrease here would suggest a leak in the sampling system, most notably a failure in the sampling pump diaphragm. Pumps and pressure transducers were controlled and monitored using a custom microcontroller (Arduino UNO, Torino, Italy) and in-house developed software (Labview 2011; National Instruments, Austin, TX, USA). While underway, the system was powered by a bank of four 6 V lead acid batteries (2011) (Model T-145 Plus; Trojan Battery Company, Santa Fe Springs, CA, USA) or smaller footprint Li-polymer batteries (2012) (Model 4784 AA; Portable Power Corp, Richmond, CA, USA), using the mass spectrometer's on-board 24 V voltage regulator to ensure a steady voltage supply to critical components.

Prior to field deployment, the system was calibrated for a variety of target analytes (Table 1). Tandem mass spectrometry scans (MS/MS) were optimized for suitable target analytes, and selected ion monitoring (SIM) scans where used in cases where analytes did not fragment well in the cylindrical ion trap (e.g., reduced sulfur compounds), or for those that were highly fragmented under EI conditions (e.g., pinene). A full scan was also performed to survey for any unexpected analytes (see Table 1). Performing each measurement in an interlaced series resulted in a total scan cycle time of 13.5 s (averaging 10 replicate scans per measurement). Continuous flow gas standards were produced using certified permeation tubes (Kin-Tek, La Marque, TX, USA) housed in a Dynacalibrator gas dilution apparatus (Model 340; VICI Metronics Inc., Poulsbo, WA, USA), with hydrocarbon scrubbed air used for the dilution gas. At an air sampling flow rate of 1850 mL/min, the in-line toluene-d_8 permeation tube produced a constant IS concentration of 75 $\mathrm{ppb_v}$ throughout calibration. Response factors for each analyte (relative to the IS) were obtained by flowing individual gas standards prepared using the Dynacalibrator through the in-line permeation chamber (Table 1). Detection limits reported for each analyte were based upon three times signal to noise ratio.

The satisfactory performance of the in-line permeation tube chamber and sample heat exchanger was confirmed by

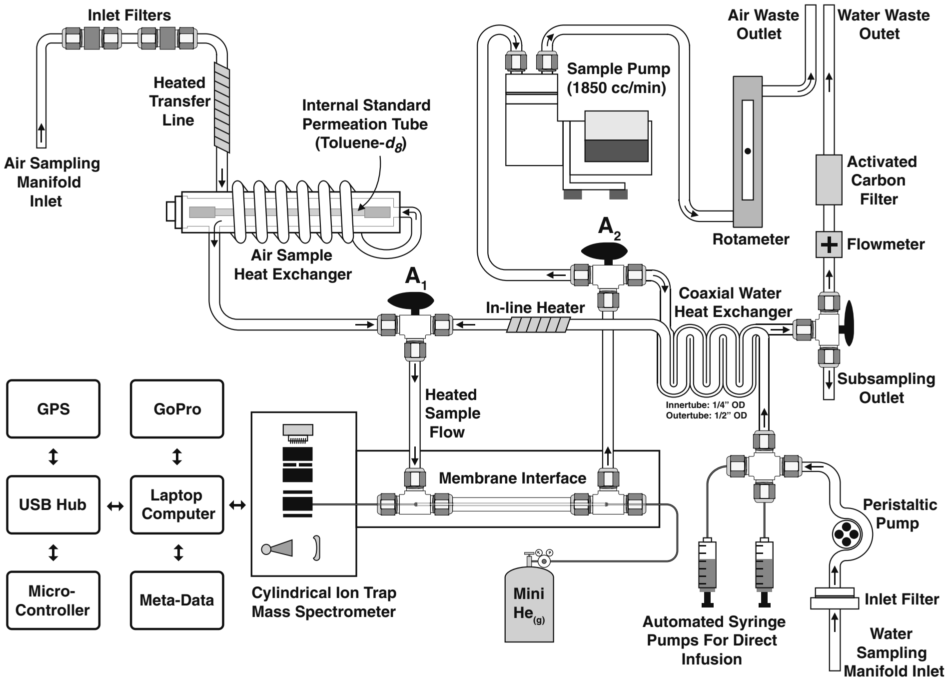

Figure 1. Schematic of the field portable MIMS system. Two flow selection valves (A1 and A2) are used to quickly switch between either the air or aqueous sample introduction manifolds

comparing calibration standards made using the in-line permeation chamber to those made externally using the Dynacalibrator. Figure 2 illustrates the results for gas phase ethylbenzene. Each point on the calibration curve was measured as the mean of 90 scans and fit with a weighted least-squares solution, using the inverse of the variance as the weighting factor. Importantly, the slopes of each calibration curve are in excellent agreement (within 0.4%). This indicates that the in-line permeation chamber and sample heat exchanger perform as anticipated, and field calibrations utilizing the in-line chamber for on-line IS addition can be trusted and directly compared with laboratory-based calibrations performed using the Dynacalibrator. A small offset (~380 counts) was observed (Figure 2) as a result of minor instrumental background shifts occurring overnight between the calibration runs, suggesting the necessity of daily background signal checks.

Interference correction factors were also calculated and employed for selected, known isobaric interferents. For example, ethylbenzene EI fragment ions trapped by the MS/MS scan for toluene result in isobaric interference. The fragmentation of ethylbenzene ($M^{\cdot+}$, *m/z* 106) under EI conditions yields the stable aromatic tropylium ion ($C_7H_7^+$, *m/z* 91), which is also used for toluene quantitation via MS/MS (*m/z* 91 → 65). This positive isobaric interference of ethylbenzene upon toluene was numerically corrected by using the ratio of isobaric interference between the ethylbenzene (*m/z* 106 → 91) and the toluene MS/MS scans (*m/z* 91 → 65) obtained during the analysis of a gaseous ethylbenzene standard. In this manner, signal contributions from the EI fragment ions of known interferents were numerically corrected. Although a similar, unaccounted for interference from xylene may result in a positive bias for toluene, the low xylene concentrations typically observed (data not shown) will lead to small biases. Future work will focus on resolving additional interference factors using more advanced spectral analysis or soft ionization techniques (e.g., CI) [31].

Experimentally, we have observed that with this system, reproducible measurements are possible for air sampling flow rates of >1000 mL/min (data not shown). In the field, the air sampling flow rate was maintained at 1850 mL/min (well above this threshold), yielding a constant 75 ppb_v toluene-d_8 IS concentration in the sample flow. This resulted in a sufficient IS signal from which analyte concentrations could be calculated using the experimentally determined response factors (Table 1). A sensitivity coefficient was also calculated, giving the user an indication of the overall instrument performance level. For example, if the IS response during an analysis is observed to be 80% of its response measured during predeployment calibration, a correction factor of 0.8 could be applied to the external calibration coefficients. Drift in the instrumental sensitivity was monitored continuously, allowing for corrective actions (e.g., replace the EI filament, optimize the detector voltage, etc.) when necessary. Thus, continuously infused IS allowed for both real-time calibration and instrument performance monitoring. Variations in operational parameters

Table 1. Summary of Mass Spectrometer Scan Methods and Analytical Performance Characteristics for Target Analytes

Analyte	Vapor pressure at 25°C (Pa)	Mass spectrometer scan method (m/z)	Response times t_{10-90}		Detection limits[d]		Response factors	
			Air at 50°C (min)	Water at 35°C (min)	Air at 50°C (ppb$_v$)	Water at 35°C (ppb)	Air at 50°C	Water at 35°C
Survey Scan		Full Scan 40-150	n/a	n/a	n/a	n/a	n/a	n/a
Toluene-d_8 (Internal Standard)		98 → 69,70	0.5	2	0.5	0.5	-	-
Toluene	3,715[a]	91 → 64,65	0.5	2	0.5	0.5	1.5	2.7
Benzene	12,590[a]	SIM 77, 78	0.5	2	2	1	0.3	0.17
Ethylbenzene/Xylenes	1,230/630[a]	106 → 91,92	0.5	2	0.75	1	1.0	0.04
Chloroform	25,120[a]	SIM 83,85	0.5	2	2	1	2.8	n/a
Chlorobenzene	1,580[a]	112 → 76,77,78	1	2	10	5	0.08	0.06
Naphthalene	200[a]	128 → 102	2	10	10	5	3.9	0.29
2-Methoxyphenol	20.9[a]	124 → 108,109	2	10	20	50	n/a	n/a
Pinene	582[b]	SIM 121	2	10	20	50	n/a	n/a
Dimethyl Sulfide	64,460[b]	SIM 62	1	5	20	50	0.03	n/a
Methyl Mercaptan	196,200[b]	SIM 47,48	1	5	20	50	n/a	0.04

[a] Reference [37].
[b] Reference [38].
[c] Selected reaction monitoring (SRM) transitions denoted with →; selected ion monitoring (SIM) and full scan data acquired as noted.
[d] Detection limits based upon signal/noise =3.

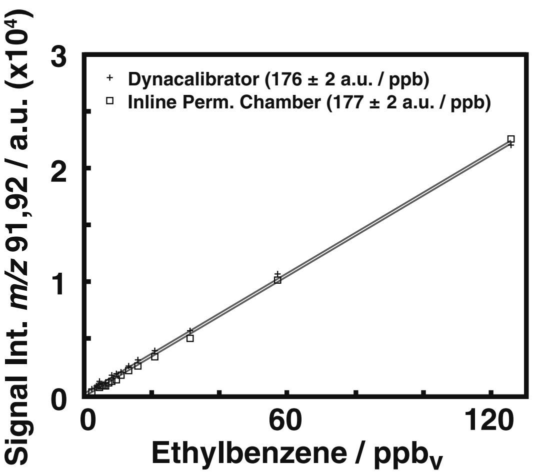

Figure 2. Direct comparison of the instrumental response for gas phase ethylbenzene concentrations with the permeation tube standard located in the Dynacalibrator versus the inline permeation chamber. Instrumental signal intensities are given in arbitrary units (a.u.)

are also detected by observation of the correction coefficient. For example, if the sample temperature, pressure, or flow rate changes, the concentration of the IS will also change, signaling potential problems to the operator during in-field measurements. For this study, we limited our measurements to relatively flat terrain, minimizing pressure variations arising from altitude changes. Sampling parameters were closely monitored and stored as interlaced meta-data to enable post-deployment data interrogation.

Prior to daily deployments during field monitoring campaigns, instrumental background values were reestablished after a 1 h warm up, using a small cylinder of zero air (Model AI 0.0UM; Praxair, Mississauga, ON, Canada). Periodic calibration checks were performed using toluene and benzene permeation tubes added to the in-line permeation chamber and varying sample gas flow rate from the zero air cylinder.

Aqueous Sampling

MIMS analysis of aqueous samples was carried out with the same instrumentation by changing the position of valves A1 and A2 (Figure 1). Aqueous sampling was performed at a sample flow rate of 150 mL/min using a battery-operated peristaltic pump (Model Masterflex E/S; Cole Parmer, Montreal, Canada) and monitored with a flow meter (Model FLR1000-8; Omega, Laval, Canada). Experimentally, we have observed with this system that reproducible measurements are possible for aqueous sample flow rates of >100 mL/min (data not shown). Incoming aqueous samples were maintained at 35°C using a flexible heating tape (thermocouple regulated) wrapped around the sample inlet tubing upstream of the MIMS interface. To reduce the power consumption required for sample heating before measurement, an in-house constructed coaxial tubing heat exchanger (~70% efficient) was used to recycle thermal energy from the exiting sample flow (Figure 1). Continuously infused IS was added to the aqueous sample stream, (e.g., toluene-d_8) using a software-controlled syringe pump (Model C24000; Tricontinent, Grass Valley, CA, USA). Additionally, a second syringe pump was incorporated to allow on-line analyte infusions for lab experiments, in-field calibration checks, and standard addition calibrations. The exiting sample flow was passed through an in-house constructed activated carbon filter trap (1000 g of activated carbon suspended between glass wool plugs in a 3-in. diameter plastic casing) before discharge from the system.

Prior to field deployments, the MIMS system was calibrated for a variety of aqueous analytes using closed 1-L glass recirculation flasks equipped with a Teflon lined septa in a manner similar to that described previously [32, 33]. Deionized water (maintained at 35°C by a constant temperature water bath) was recirculated through the MIMS interface at 150 mL/min, and stepwise injections of combined analyte stock solutions in methanol were used to generate low ppb (μg/L) aqueous concentrations (e.g., 3 to 30 ppb) for calibration. To avoid isobaric interferences during aqueous calibrations, two analyte suites were employed: Suite 1: benzene, toluene, chloroform, methyl iodide, dimethyl sulfide; Suite 2: ethylbenzene, chlorobenzene, naphthalene, guaiacol, iso-octane, 1-chloronaphthalene. Toluene-d_8 was included in both suites and used as an IS for the determination of response factors. Using these data, instrumental background, analyte sensitivity, detection limits, and response factors were determined for each target analyte (Table 1).

For in-field quantitation, incoming aqueous samples were continuously infused with toluene-d_8 at low ppb levels via a syringe pump, allowing on-line analyte quantitation by response factors as well as affording the continuous monitoring of overall instrument performance. For example, an infusion flow rate of 0.20 mL/min of 14 ppm toluene-d_8 (in methanol) into 150 mL/min on-line sample flow rate produced an on-line toluene-d_8 concentration of 19 ppb. The second syringe pump injection port was used to infuse analyte standards in the field for periodic target analyte calibration checks. Some of the aqueous samples were also calibrated by using standard additions methodology, whereupon a calibration solution containing toluene-d_8 and the desired target analytes was infused into the sample stream immediately following a sample measurement. Field samples included 4-L grab samples collected in amber glass bottles (Scientific Specialties Inc., Hanover, MD, USA) and also the continuous sampling of water directly drawn from rivers and streams over multi-hour sampling periods with the peristaltic pump. Extended periods of stationary aqueous monitoring in the field (>12 h) were enabled by switching to supplementary power, provided by a small gasoline-powered generator (EU2000i; Honda, Tokyo, Japan) located at least 100 m downwind from the sampling location. This prevented the complete depletion of the battery systems, and ensured uninterrupted data collection.

Software Development

Mass spectrometric scan methods were developed and executed using the mass spectrometer's operating software (Griffin System Software, GSS, v3.9; FLIR Systems, West Lafayette, IN, USA). Calibration software to quantitate the raw data and automate the handling of the associated meta-data was written in-house using Labview. Calibration results were stored in a custom file format that was subsequently employed by additional Labview-based software designed for real-time data collection and analysis. Briefly, the real-time software extracted quantitative ion signals from the raw GSS data files and applied the calibration data file, producing real-time quantitative results. These results were then plotted as multiple time series and as color proportional tracks on a map. Maps were downloaded as needed using Google Maps API. All data were automatically stored on Dropbox servers via the cellular data connection. After all mobile data were collected, data workup and re-analysis were performed using in-house developed MATLAB code (Mathworks, Natick, MA, USA). Meta-data and final result files were stored as time series for inspection and quality control. Final results were saved as .kmz files for presentation in Google Earth. These self-contained data files enable inspection of data both geospatially and temporally, are easily networked, and contain hierarchal data structures to enable the presentation and sharing of the large complex datasets in a clear and concise way.

Field Work Methods

The field monitoring examples presented were obtained in Northern Alberta in early July, 2012. Air sampling data sets were obtained in and around a Steam Assisted Gravity Drainage (SAGD) pilot facility (Statoil Canada Ltd.) located roughly 200 km south of Fort McMurray, and on public roads north of Fort McMurray along Highway 63. The MIMS system was operated in a sport utility vehicle (GMC Yukon). Stationary air sampling data sets were collected with the vehicle engine off and correlated with meteorological data determined at the sampling site. Aqueous sampling included the analysis of grab samples of on-site processed and ground water as well as measurements made by continuously sampling from nearby natural surface waters.

An example air monitoring dataset, presented here (vide infra), was generated during travel north of Fort McMurray on Highway 63 through areas adjacent to active oil sand recovery operations. Frequent stops (with the vehicle engine off) were performed to allow the collection of meteorological data and to obtain periods of stationary MIMS data. The example dataset was collected on July 7, 2012. The day was warm (27°C) and dry (30% relative humidity), with gentle wind speeds ranging between 4 and 7 m/s.

Aqueous samples of both on-site process water and off-site natural (stream, river, and ground) water were also collected during this field trip. An example dataset shown here was collected July 3, 2012 from an active steam generation system used by a Statoil Canada Ltd. oil recovery operation (vide infra). The SAGD site has been operational since 2010, and the small settling pond is used for holding recovery water prior to reuse in the steam injection process.

Results and Discussion

Field Work – Air Monitoring

Data collected with the mass spectrometer operating continuously in a moving vehicle is presented as a time series in Figure 3, and the progression of data workup is presented in each subpanel. The raw data for toluene measurement is shown in Subpanel a and indicates several toluene detections throughout the day. Generally, the data consists of long periods where toluene was not detected, punctuated periodically by transient excursions to higher signal levels. For example, at 16:02, a very strong signal was observed (14,240 counts) when the vehicle passed over a stretch of road that had been very recently paved with fresh asphalt. At 16:24, a sustained signal was detected while the vehicle was stationed downwind of a tailings settling pond used by an active heavy oil extraction operation. Several other minor concentration excursions above detection limit levels may have been the result of passing vehicle exhaust emissions or air masses influenced by other settling ponds. Detections of vehicle exhaust were rather infrequent because of the elevated sampling intake, the very large dilution that rapidly occurs in the turbulence behind a moving vehicle (roughly estimated to be 25,000:1 at highway velocity), and the effective catalytic conversion of hydrocarbon emissions that occurs for hot, underway vehicles [34].

As noted above, ethylbenzene readily fragments under EI to yield *m/z* 91, and this can lead to a positive bias in the toluene concentration as determined by *m/z* 91 → 65. To compensate for this, we independently measure ethylbenzene by measuring *m/z* 106 → 91 and applying an interference factor calculated during predeployment calibration. The interference contribution data were smoothed (five-point boxcar) prior to being subtracted from to the analyte signal. Smoothing prevents the inclusion of additional instrumental noise into the signal data and allows signal corrections to be made on a time scale comparable with the MIMS response time for ethylbenzene (Table 1). The contribution of ethylbenzene to the *m/z* 91 → 65 signal is typically small (e.g., during the detection of emissions from fresh asphalt, 1.2%,

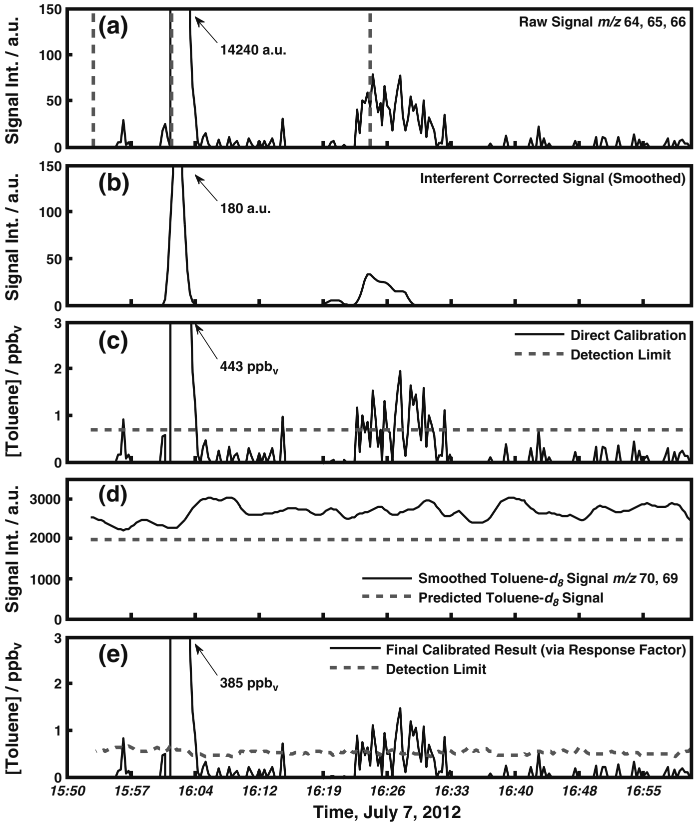

Figure 3. Time series representation of the instrumental data used for real-time toluene quantitation collected north of Fort McMurray, Alberta, Canada. The x-axis represents the time of day when the data was collected. Subpanels show data progression through the data workup process and the final data time series result is given in subpanel **e**

16:02), but can in some instances be significant (e.g., during detection of settling pond off gassing, 40%, 16:24). The variability, of course, is strongly dependent on the particular sample composition. We cannot rule out positive interference in the toluene quantitation arising from other alkylbenzenes and hydrocarbons likely present near fresh asphalt paving [35]. Therefore, we caution the reader not to over-interpret the displayed toluene concentrations, even after correction for specific interferences such as those arising from ethylbenzene. Although EI is relatively simple to implement, it is a 'hard' ionization strategy, resulting in the extensive fragmentation of many analytes, especially alkyl hydrocarbons. Further improvements in the use of interference factors as well as on-line standard addition strategies and softer ionization sources are currently being investigated to address the challenges of resolving isobaric interferents.

The ethylbenzene corrected toluene signal is converted to concentration in Subpanel c (Figure 3) using direct calibration factors from gaseous calibration standards prepared predeployment. Displaying this data along with the calculated detection limits is an additional quality control check and allows the user to quickly assess any signal deviations in the final data time series (Subpanel e).

Subpanel d (Figure 3) shows the instrumental signal for the continuously infused IS, toluene-d_8 (m/z 98 → 70), and is compared with the expected response to the IS given the sample flow rate and laboratory predeployment calibration (predicted toluene-d_8 signal). The IS concentration was calculated from the analyte constant, K_0 (cc/mg), derived from molecular weight and the ideal gas constant, permeation tube emission rate, (E , ng/min), and sampling gas flow rate (F, mL/min at STP) (Eq. 1). Expected IS response is calculated as the product of IS concentration$[IS]$ and instrumental sensitivity to the IS (m_{IS}). The ratio of actual response to expected response provides a sensitivity coefficient that is a real-time measure of the instrument performance (Eq. 2). For example, rapid changes in the sensitivity coefficient may be indicative of transient events that can impact instrument sensitivity (e.g., due to a matrix interference or space-charge effects resulting from a highly contaminated sample or from membrane rupture/fouling). Long-term changes are useful in reporting drift in the instrumental state (e.g., filament or electron multiplier wear). As can be seen in Subpanel d (Figure 3), the instrument was slightly more sensitive to toluene-d_8 on this deployment than during predeployment lab-based calibrations. The IS data was also boxcar smoothed with a moving average (n =5) to reduce the addition of unnecessary electrical noise to the analyte signals, while allowing sensitivity corrections to be made on a time scale that is comparable to the MIMS signal response times (Table 1).

$$[IS] = \frac{K_0 {*} E}{F} \tag{1}$$

$$Sens\ \ Coeff = \frac{Counts_{IS}}{m_{IS}\ {*}[IS]} \tag{2}$$

Subpanel e (Figure 3) shows the toluene concentration time series calibrated from an instrumental response factor (e.g., toluene/toluene-d_8) determined during lab calibration, the raw analyte counts and the smoothed IS counts along with the sensitivity adjusted detection limit (DL_{Adj}, Eq. 3). As the instrumental sensitivity declines during multi-day deployments, the adjusted detection limit will increase. This can happen, for example, when the EI filament is nearing failure. When the detection limit crosses a predetermined threshold, the user can be warned by the software interface and corrective actions (e.g., replace the filament) can be taken. It is important for the instrument field operator to have real-time knowledge of the detection limit for immediate assessment of anomalous signals and to ensure the detection limits are adequate for the collection of meaningful data.

$$DL_{Adj} = DL {*} Sens\ \ Coeff \tag{3}$$

As a final data assessment, Subpanel a (Figure 3) indicates two distinct detections. These detections are marked with vertical dashed bars (16:02 and 16:24) and for these intervals, the 30 s of full scan data following the vertical bar were averaged and presented as insets in Figure 4. The spectra were normalized using the IS signal (measured at m/z 98), then corrected by subtracting the spectrum for the IS. The IS spectrum was determined immediately prior to collection of this time series, and this time stamp is also marked with a vertical bar in Subpanel a (Figure 3, 15:54 h). The spectra indicate a complex suite of analytes permeating the membrane. The spectra insets in Figure 4 are distinctly different and suggest that MIMS full scan m/z data can be used in multivariate statistical approaches, such as Principal Component Analysis (PCA) for source apportionment and tracking. They also emphasize the importance of employing selective techniques such as MS/MS for quantitation.

The response factor calibrated toluene mass spectrometric data (m/z 91 → 65) collected north of Fort McMurray, Canada (Figure 3, Panel e) was time-matched to GPS data and meteorological data, and is presented in Figure 4. White dots represent data collected that were below the detection limit. Wind vectors are represented by the red arrows and can be queried (with a computer mouse click) in Google Earth to inspect the data file source, wind direction, wind speed, temperature, humidity, barometric pressure, time, latitude, and longitude. The 16:02 detection discussed above is noticeable as a large dot just north of Fort McMurray, and the 16:24 detection is labeled at "Settling pond 16:24." The data track presented in Figure 4 is a small subset of a much larger dataset navigable by Google Earth.

Multiple analyte concentrations are embedded in the Google Earth *.kml data file(s) and can be depicted as individual tracks for inspection in real-time or post-deployment. Figure 5 shows a 5 h continuous time series collected while driving and parked in a discrete pattern (termed a 'Rosette') at strategic locations in and around a SAGD demonstration facility, similar to the methodology employed in other work by our group [17]. Subpanel a illustrates the data obtained for benzene, toluene, and ethylbenzene (+xylene). The shaded regions represent data

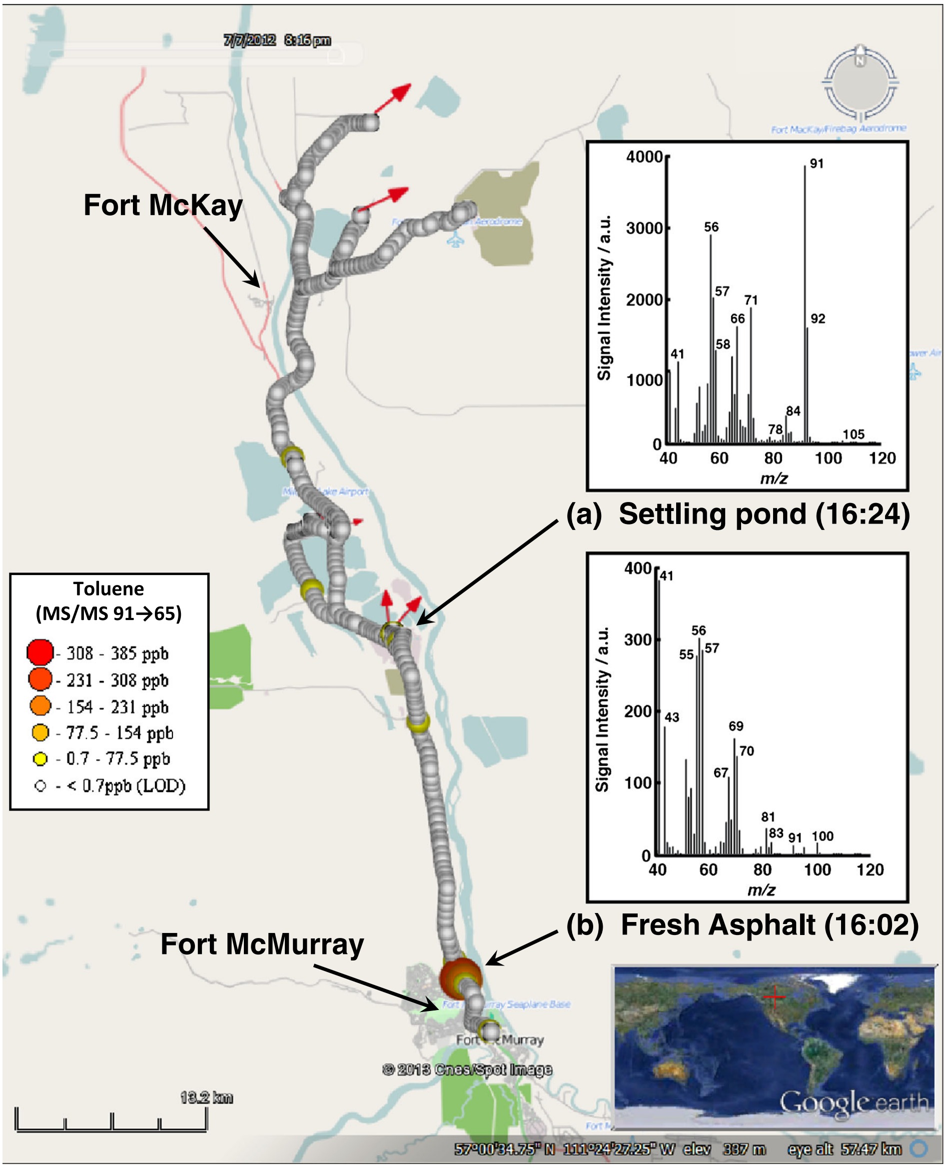

Figure 4. Google Earth snapshot of atmospheric toluene data collected north of Fort McMurray, Alberta, Canada. Data are multidimensional and time-stamped, allowing for a fully navigable data environment and video creation. The insets illustrate full scan mass spectra of selected survey data obtained during detection events. Inset (**a**) shows the mass spectrum of the air space downwind of a waste-water settling pond (16:24) and (**b**) shows the mass spectrum for atmospheric monitoring while travelling on a freshly paved asphalt roadway (16:02). Both spectra were normalized to the toluene-d_8 IS, with background and IS spectra subtracted

collected while the vehicle was stationary (with the vehicle engine off), whereas the unshaded data was collected while moving. Most of the time VOC concentrations are well below our observed detection limits (dashed horizontal line). The signal appearing around 12:00 h was observed while the vehicle was parked just downwind of a relatively small, lined settling pond used to hold process reuse water. Subpanel b displays a whisker plot of the stationary data only and illustrates the distribution of chemical concentrations as 25–75 percentiles as well as outliers. Subpanel c illustrates a Google Earth screenshot depicting the toluene concentration track. The navigation panel on the left sidebar of the screen

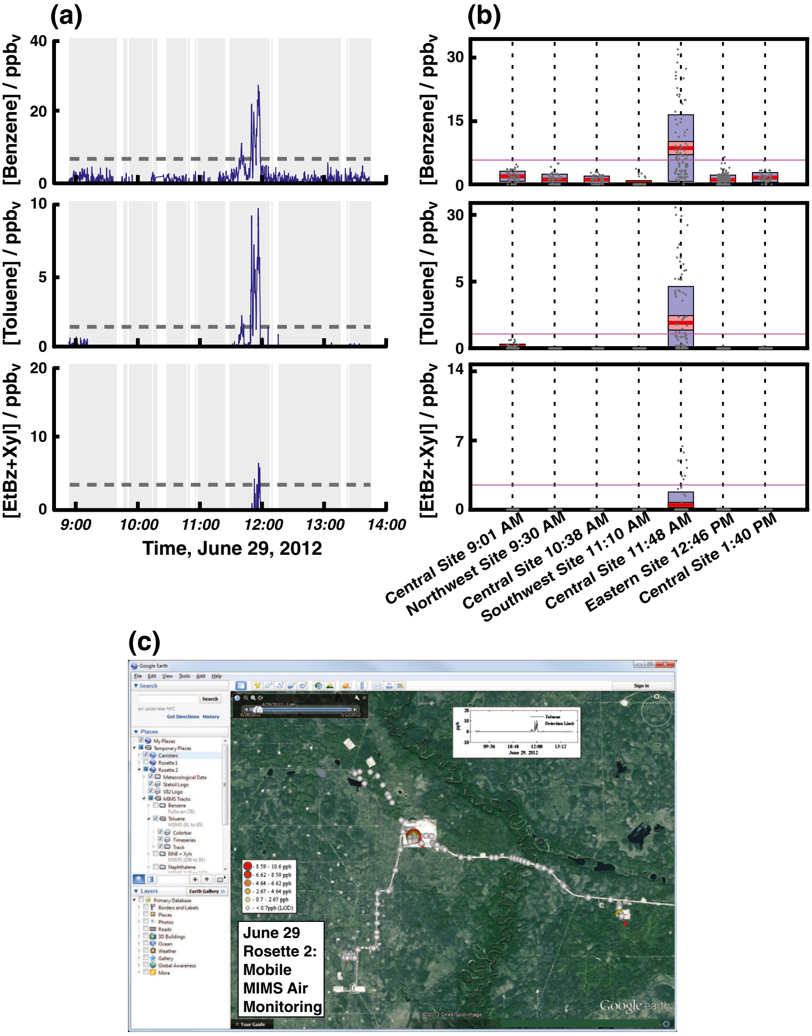

Figure 5. (**a**) Five-hour time series for atmospheric benzene, toluene, and ethylbenzene + xylenes (EtBz + Xyl) showing data collected in moving vehicle (white background) and while stationary (gray background). The horizontal dotted line represents the calculated detection limits. (**b**) Whisker box plots for stationary deployments only showing mean concentrations, 25–75 percentiles and data outliers. (**c**) Google Earth screenshot of the atmospheric toluene data collected on-site. Geospatial time series data for all analytes can be inspected in a single *.kmz file along with the relevant meta-data

allows the user to select the analyte to display. The data can be viewed in a 'video' mode, playing back the data evolution over time. Screen overlays that include legend, data time series, and institutional logos can also be generated when desired. Importantly, each data point can be queried for its source file, scan information, raw counts, concentration, detection limit, time, latitude, and longitude. In summary, Google Earth has proven to be an extremely useful tool for data visualization and analysis due to its data structure and wide availability.

Field Work – Aqueous Monitoring

Water samples can be readily analyzed using the same membrane interface and ion trap mass spectrometer system by diverting the aqueous sample stream into the MIMS interface using the aqueous sampling manifold (Figure 1, valves A1 and A2). Continuously infused IS delivered via a syringe pump can be utilized for real-time calibrations using predetermined response factors as above. The other syringe pump (Figure 1) can be loaded with analyte standards and employed for periodic in-field calibrations by standard addition methods. The in-line sample heater and heat exchanger system can be used to preheat samples and improve response times, if necessary. Figure 6 illustrates data for the analysis of a VOC contaminated boiler feed water sample, diluted 24:1 to avoid space charge effects in the ion trap from excessively high analyte concentrations. The sample inlet line was switched from deionized water to diluted boiler feed water at 21:24. Data analysis indicated the diluted sample had a concentration of 29 ppb. At 21:39 (dashed bar A), the continuous infusion of a standard solution containing both benzene (19 ppb) and toluene-d_8 (19 ppb) was initiated. The software system allows for sample analysis by IS and/or standard addition methods, depending on the injected solution. The benzene signal was calibrated using the standard addition data, whereas the toluene-d_8 is shown as a demonstration of the use of an IS. Once again, the use of an IS relays important information to the field operator about instrument performance by comparing on-site signal intensities to those observed predeployment. The sudden jump in signal at 21:50 is a result of an entrained air bubble that occurred when switching the sample stream to a washout blank (DI water). The abrupt change observed for the IS signal would be a suitable trigger to suggest that this is compromised data, allowing it to be censored (if desired) from any further data analyses.

Since the instrument can be employed to report continuous, calibrated VOC concentrations in aqueous samples in real-time, it is a powerful in-field monitoring tool for dynamic chemical systems. Industrial sites such as SAGD operations have numerous operational systems to process and reuse water supplies. On-line process monitoring can provide important information to industrial operators. Furthermore, sensitive and selective on-site monitoring of contaminants in surrounding surface and ground waters aids in better environmental stewardship and protection initiatives.

Implications and Future Work

The combination of instrumentation, data analysis, and visualization software presented here provides a novel approach that provides quantitative, information-rich data sets that enable real-time, on-site decision making. This is especially useful for timely process control decisions, emergency response scenarios, adaptive sampling during field measurement campaigns, and long-term environmental monitoring studies. The presented system is amenable to several improvements including the inclusion of a thermally assisted membrane [33] to improve detection limits for SVOC analytes and the implementation of various chemical ionization methods to improve instrument selectivity [28, 30, 36]. Future software development will focus on cataloguing data for improved online database access, additional data input features (e.g., real-time dilution calculations), and improved data (and meta-data) presentation for real-time quality control analysis. Additional peripheral equipment development will include continuous wind vector determinations and simultaneous video monitoring capabilities. The presentation of more extensive datasets including validation studies for hydrocarbons in both air and water will follow in subsequent publications.

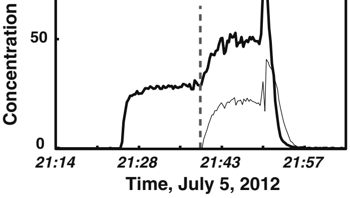

Figure 6. In-field analysis of a heavy oil process water sample. At 21:39 (dashed bar A), an infusion containing both benzene (19 ppb) and toluene-d_8 IS (19 ppb) commenced. Pre-analysis dilution was 24-fold

Conclusions

A novel field portable membrane introduction mass spectrometry (MIMS) system is presented that utilizes in-house developed real-time data analysis and visualization software for geospatial mapping of VOC/SVOCs in the environment. The system has been used for monitoring hydrocarbon contaminants in air and water samples during in-field sampling campaigns in and around oil and gas extraction facilities in Northern Alberta, including the direct, in-field measurement of process waters. Real-time detection limits are in the low ppb range. The presented system allows operators to develop intelligent, adaptive sampling strategies based on data being produced in real-time, and provides data to enable remotely located decision makers to implement corrective actions when needed. Continuous mass spectral time series datasets are obtained, processed, and visualized using in-house developed software. Data are temporally resolved and, therefore, capable of capturing transient concentration excursions. In the case of air monitoring, data capture over a wide spatial area by using the system in a moving vehicle is also possible. Although the presented system is currently limited to electron impact ionization (EI), we are exploring the use of softer chemical ionization strategies to alleviate isobaric interferences that arise from the EI fragmentation of matrix species.

Acknowledgments

The authors gratefully acknowledge Alexander Thompson, Oyvind Mikkelsen, Rudolf Schmid, and the students and staff of the Applied Environmental Research Laboratory (AERL) for their assistance with this project. Special thanks are given to Gregory Vandergrift (AERL) for his assistance with preparing the technical illustrations. The authors thank Vancouver Island University and the University of Victoria for their ongoing support of their research and graduate students. This work was supported in part by funding from Statoil ASA (Grant No 4502457485).

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Paper III

J. Am. Soc. Mass Spectrom. (2015) 26:201–211
DOI: 10.1007/s13361-014-1027-4

FOCUS: HARSH ENVIRONMENT AND FIELD-PORTABLE MASS SPECTROMETRY:
RESEARCH ARTICLE

The Effect of the Earth's and Stray Magnetic Fields on Mobile Mass Spectrometer Systems

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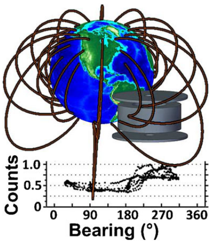

Abstract. Development of small, field-portable mass spectrometers has enabled a rapid growth of in-field measurements on mobile platforms. In such in-field measurements, unexpected signal variability has been observed by the authors in portable ion traps with internal electron ionization. The orientation of magnetic fields (such as the Earth's) relative to the ionization electron beam trajectory can significantly alter the electron flux into a quadrupole ion trap, resulting in significant changes in the instrumental sensitivity. Instrument simulations and experiments were performed relative to the earth's magnetic field to assess the importance of (1) nonpoint-source electron sources, (2) vertical versus horizontal electron beam orientation, and (3) secondary magnetic fields created by the instrument itself. Electron lens focus effects were explored by additional simulations, and were paralleled by experiments performed with a mass spectrometer mounted on a rotating platform. Additionally, magnetically permeable metals were used to shield (1) the entire instrument from the Earth's magnetic field, and (2) the electron beam from both the Earth's and instrument's magnetic fields. Both simulation and experimental results suggest the predominant influence on directionally dependent signal variability is the result of the summation of two magnetic vectors. As such, the most effective method for reducing this effect is the shielding of the electron beam from both magnetic vectors, thus improving electron beam alignment and removing any directional dependency. The improved ionizing electron beam alignment also allows for significant improvements in overall instrument sensitivity.

Key words: Mobile mass spectrometry, Membrane introduction mass spectrometry (MIMS), Online in situ analysis, Field portable, Earth's magnetic field, SIMION, Simulation, Mu-metal, Metglas, Electron beam trajectory deflection, Electron ionization

Received: 8 August 2014/Revised: 10 October 2014/Accepted: 11 October 2014/Published Online: 20 December 2014

Introduction

The popularity of field portable mass spectrometry is growing as many of the technical hurdles of bringing laboratory equipment into the field are overcome [1–3]. On-site analysis requires that instrumentation can be transported conveniently, powered remotely, be free of self-contamination, and can be serviced in adverse conditions. Additionally, the instrumentation should be capable of data collection while moving, and overcome any additional hurdles resulting from changing environmental and sample conditions. For example, non-steady state or transient conditions are likely to be more prevalent and may require correction [4, 5]. Additionally, varied sample conditions, such as temperature, pressure, and humidity, may alter the relative instrumental response [3, 6–8], and changing environmental conditions may adversely affect the instrument itself [9]. To our knowledge, apart from a report by Short et al.

Electronic supplementary material The online version of this article (doi:10.1007/s13361-014-1027-4) contains supplementary material, which is available to authorized users.

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(2000) [9], the effect of magnetic fields, such as the Earth's, on portable mass spectrometer signal intensity has not yet been addressed by the mass spectrometry community.

Electron beams that have a short path length or have sufficiently high energies are not meaningfully affected by weak magnetic fields. Additionally, weak magnetic fields are likely to have a negligible impact on the deflections of ion beams because of their significantly greater relative momentum. However, when precise, low-energy electron beams are employed, care must be taken to reduce the influence of uncontrolled magnetic fields. For example, photoelectron spectrometer components are intentionally lined with or constructed from magnetically permeable materials to limit the influence of magnetic fields [10]. Nickel-iron alloys such as mu-metal and other magnetically permeable materials have a magnetic permeability many times that of free space, and tend to absorb passing magnetic fields by providing a preferred location for field transmittance. Thus, when instrumentation is encased in mu-metal, magnetic fields inside the instrument are greatly reduced, avoiding unintended electron beam deflections. Although impractical in the context of portable mass spectrometry instrumentation, Helmholtz cages have also been employed to compensate for the effects of the Earth's magnetic field in testing facilities [11] and in high resolution cathode ray tubes [12].

In mass spectrometry, relatively low energy electron beams (e.g., 70 eV) are used in electron ionization (EI) sources. Though generally the ion source is located as close as possible to the mass analyzer, maintaining a flexible design sometimes necessitates transmission distances of several centimeters before electrons enter a small ion source electron aperture (e.g., < 3 mm diameter). In these cases, ionization efficiency (and therefore the instrument's relative sensitivity) will be dependent on the electron beam flux stability. Normally, in a stationary mass spectrometer, local magnetic fields are constant, and electron beam deflections go unobserved, or are compensated for by instrumental tuning optimizations. Occasionally, these fields are not constant; for example, we have observed that locating a solenoid pump or solenoid valve near the mass spectrometer's vacuum housing may result in a detectable effect on the signal intensity. For example, when sampling underwater vents in Yellowstone Lake in September 2003 with a portable underwater membrane introduction mass spectrometry system, an observable beat in the measured signals resulted from the operation of the solenoid sampling pump (Supplementary Figure S1). Post-deployment, it was discovered that the beat intensity was proportional to the proximity of the solenoid pump to the instrument's vacuum chamber. Encasing the pump in magnetically permeable metal resolved the issue (data not shown).

Field portable instrumentation also experiences varied magnetic fields as a result of changing its orientation with respect to the Earth's magnetic field. The resulting transient deflection of electron trajectory may generate a significant source of instrumental variability. In addition, the magnetic fields created by various mass spectrometer systems (e.g., vacuum pumps, inductors, or filament current) may also affect electron beam deflection. The summation of multiple magnetic field vectors will have an additive effect that is directionally dependent.

These effects are difficult to observe when instrumentation is operated in a GC mode because of the highly variable nature of the instrumental signal during a GC scan. Further, the effects are compensated for if instrument orientation is not changed between calibration and sample analysis, as recommended by instrument manufacturers. However, when operating in a continuous measurement mode, signal variability becomes easily observed when underway. In our case, the effect was highly intensified during operation with a sub-optimum electron lens voltage.

In this study, we characterize the influence of magnetic bearing on the relative instrument response of several field portable mass spectrometers, simulate the electron beam transmission efficiencies for several instrumental conditions, and demonstrate simple instrumental modifications that provide magnetic shielding, resulting in better signal stability and sensitivity gains.

Experimental

As noted above, we have experimentally observed a directional dependence of the relative instrument response for a variety of field portable mass spectrometers. To better understand this phenomenon, simulations were performed using SIMION (v8.1, Scientific Instrument Services Inc., Ringoes, NJ, USA) software that incorporated the influence of the Earth's magnetic field on an electron impact ion source as an instrument is rotated through 360°. Results from the rotation of a vertical electron beam were compared with that for a horizontal electron beam. Additional simulations explored the result of asymmetries generated from the use of a linear filament geometry as an electron source in an otherwise cylindrical system, and also the additive effect of local instrumental magnetic fields with the Earth's magnetic field. Simulation results were directly compared with experimental data collected in the laboratory.

To reduce the influence of magnetic fields on the relative instrumental response, three methods were explored experimentally and compared with simulations. First, the ion source's electron beam focus was altered, allowing the comparison of unfocused and well-focused electron beams. Next, the entire instrument was protected from the Earth's magnetic field by a mu-metal casing, reducing the presence of directionally dependent magnetic fields. Last, Metglas (an amorphous metallic ribbon material with very high magnetic permeability) was used to line the inside the instrument's vacuum chamber surrounding the electron beam to reduce the influence of both the Earth's and the much of the instrument's magnetic field.

Mobile Mass Spectrometer Relative Response Versus Orientation

To demonstrate the effects of the orientation of the Earth's magnetic field on the relative instrumental response of different mobile mass spectrometers, experimental field data obtained from four different instruments were compared by analyzing a steady-state internal standard signal while the mass spectrometer's magnetic orientation (azimuth) was changed. All mass spectrometers utilized membrane sampling inlets employing polydimethylsiloxane capillary membranes maintained at constant temperatures. Membrane introduction mass spectrometry (MIMS) provides a direct analysis approach for the continuous quantitative online monitoring of specific analytes and internal standards. For additional background on MIMS, which is often employed in mobile mass spectrometry systems because of its simplicity, several reviews of the technique have been published [13–15].

The first instrument used was a field operable MIMS system made from a bench top, hyperbolic electrode quadrupole ion trap (QIT) (Model Saturn 2000; Agilent Technologies, Santa Clara, CA, USA), employing internal ionization. In this instrument, the electrons ejected from a hot filament are accelerated to 70 eV and transmitted ~1.7 cm before a focusing gate electrode guides the electrons through a 1 mm aperture in one of the ion trap's endcaps. The quantity of ions formed (and thus the relative signal intensity) is proportional to the number of electrons that pass through the 1 mm aperture. In addition, this instrument has the electron beam on a horizontal axis, parallel to the Earth's surface. To compare instrument response to magnetic orientation, a continuously infused 1 ppb aqueous dimethylsulfide solution was analyzed using full scan mass spectra (*m/z* 62) while operated onboard a moving marine research vessel (R/V Suncoaster, St Petersburg, FL, 1999) that was intentionally rotated 360°. Field orientation was determined by measuring the magnetic field perpendicular to the electron beam using a three-axis magnetometer (Model 2300; Honeywell, Morristown, NJ, USA) [9].

Data were also collected from a field portable cylindrical electrode quadrupole ion trap (CIT) (Model Griffin 400; FLIR Systems, West Lafayette, IN, USA), equipped with a custom-built membrane interface. This instrument uses a 75 eV electron beam for ionization within the ion storage volume of the trap. The electron path length from the filament to the end cap aperture is approximately 4.6 cm and a simple, three electrode cylindrical Einzel lens is used to focus the electron beam through a 2.5 mm aperture in one of the trap endcap plates. In this system, the electron beam axis is perpendicular to the Earth's surface (i.e., a vertical electron beam). Toluene-d_8 (used as an internal standard) was supplied to the membrane interface in air samples using a permeation tube (Kin-Tek, La Marque, TX, USA) housed in a thermally regulated permeation chamber in line with the membrane interface. The full scan instrument response with respect to orientation was obtained by operating the mass spectrometer inside a moving vehicle while analyzing exterior air continuously infused with 75 ppbv toluene-d_8 (*m/z* 98). Orientation was derived from GPS data while the vehicle was traveling in a 'figure eight' pattern.

The third instrument included in the study was a compact linear quadrupole mass spectrometer (Model Transpector CPM; Inficon, Syracuse, NY, USA) implemented as the mass analyzer in an underwater membrane introduction mass spectrometry system [16]. This mass spectrometer uses a closed electron ionization source, whereby 70 eV electrons produced by the filament travel about 2 mm before passing through a 5 mm × 2 mm slot. The data used here, collected from field studies made in Lake Maggoire, St Petersburg, FL, were also used in work published by Wenner et al. (2004) [17]. In this work, orientation was also derived from GPS data while the vehicle was travelling in a 'lawn mower' pattern. Electron beam direction (vertical vs. horizontal) was not determined.

The final instrument examined in this study was also a hyperbolic electrode quadrupole ion trap that utilizes an external electron ionization source (Model GCQ; Finnigan MAT, San Jose, CA, USA). This system employs an ion source in which 70 eV electrons from the filament are collimated into a spiraling beam by two permanent magnets (~300–400 G). The focused electrons are passed through two apertures (each about 2.6 mm diameter) over 4.8 mm distance prior to entering the ion source, travelling on a vertical axis (i.e., perpendicular to the Earth's surface). Ions generated in the source are subsequently injected into the ion trap by a compact ion lens system. Full scan data (*m/z* 98) from a toluene-d_8 internal standard infused into ambient air at 341 ppbv were obtained in the same manner as described for the CIT (*vide supra*). The data used here, collected while conducting field measurements in Tacoma, WA, was analyzed as part of a study published by Davey et al. (2014) [1]. Orientation was derived from GPS data.

Electron Beam Deflection Simulations

Ten simulations conducted using SIMION software are presented to understand the contributing factors and possible solutions to unintended electron beam deflections by magnetic fields in a mass spectrometer ion source. The electron beam was simulated as it traveled from the electrons' origin, through the focusing lens, and either passing through the end plate aperture or impacting the endplate. For these simulation studies, the ion source geometry and voltages of the CIT (*vide supra*) were used. The 2D-cylindrical model used to simulate the CIT ion source and transmission efficiency is shown in Figure 1. Constant values for the simulations included the electron deflector plate (–10 V), the ion trap endplates (0 V), and ring electrode (75 V), the initial electron kinetic energy (0.2 eV), mean electron source location (x = 0 mm, y = 0 mm), and filled electron axial cone angle (80°). The initial electron kinetic energy was calculated assuming a 2050°C filament [18], using a Maxwellian distribution [19, 20]. Simulations were performed using 10,000 electrons at each of eight rotational steps (45°) relative to the Earth's magnetic field, with an additional ninth condition of no magnetic field from the Earth. Set-points that

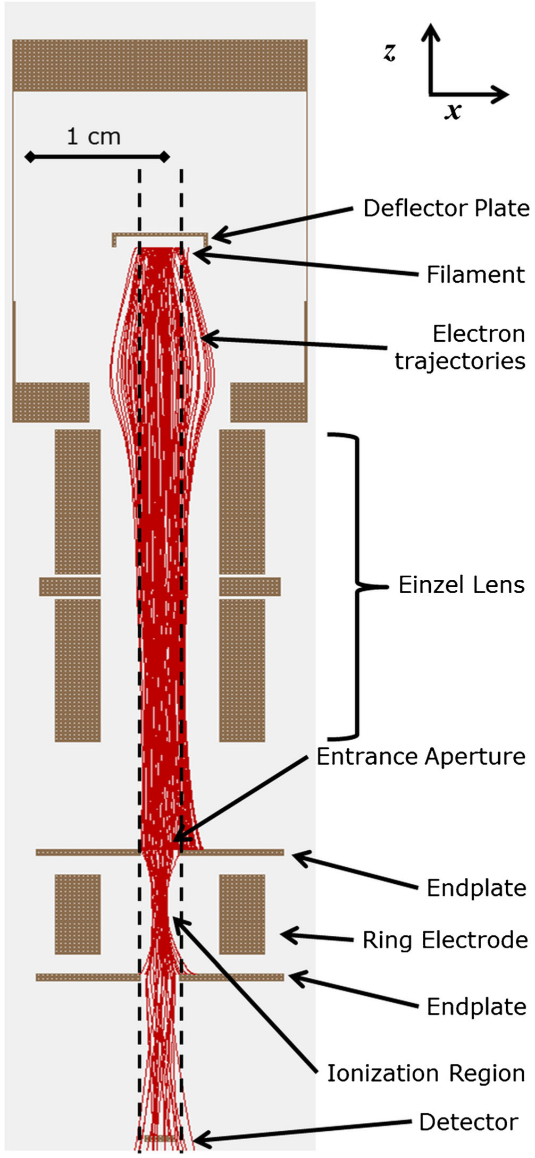

Figure 1. SIMION model approximating the CIT ion source shown in a vertical orientation relative to the Earth's surface (xy plane). The electron trajectories shown in this example are influenced the Earth's magnetic field, the sum of which is out of the page (y) and, as a result, electron deflection is rightward (x). The dashed reference lines demarcate the entrance aperture's x position and are intended to help visualize electron deflection

were varied between simulations are summarized in Table 1. Intensities for the Earth's magnetic field in Nanaimo, Canada (B_x = 0.18 G, B_y = 0.054 G, and B_z = 0.51 G) were obtained using the IGRF function from the Matlab (Mathworks, Natick, MA, USA) file exchange, and confirmed using the an Android smartphone (Model Incredible; HTC Corporation, Taoyuan City, Taiwan). The smartphone contained a vector magnetometer that was monitored and logged using the AndroSensor (ver. 1.9.4.4a) application.

Simulations 1 through 3 were conducted to test whether the cause of observed signal variations in field measurements could be due to the relative orientation of the Earth's magnetic field. The electron beam in these simulations was oriented perpendicular to the Earth's magnetic field (i.e., a vertical electron beam), as is the case for the normal operation of the CIT system. Simulation 1 (intended to be the idealized case) was conducted with all electrons originating from a point source. Simulation 2 was identical, except that the origin of the electrons approximated the linear filament found in the CIT system. Here, the electrons were sourced from a Gaussian distribution (SD = 0.3 mm) along a line in the y direction. Simulation 3 was performed using the same conditions as Simulation 2, with the exception of an additional secondary magnetic field. This secondary field was not rotated with the Earth's magnetic field, thus simulating the measured magnetic field originating within the instrument itself. The intensity of this vector ($Bx = -0.047$ G, $By = 0.21$ G, and $Bz = -0.63$ G) was determined using a magnetometer adjacent to the instrument's vacuum housing, and subtracting the Earth's magnetic contributions. Because the magnetic field in the instrument housing varies strongly within a few centimeters, this determination is likely one of the largest sources of error for these simulations. Simulations 4 through 6 were parallel experiments to Simulations 1 through 3 except that the magnetic vectors were altered to reproduce the Earth's field rotating about the instrument's yz plane, simulating a horizontal electron beam. The horizontal beam has a distinctly different symmetry with respect to the Earth's magnetic field than the vertical electron beam. Although the CIT was not designed to be operated in this orientation, a horizontal electron beam was employed in the hyperbolic electrode quadrupole ion trap (i.e., Saturn 2000, *vide supra*).

Electron Beam Defocusing Studies

Together, Simulations 3, 7, and 8 were designed to determine the importance of electron trajectory deflection when the electron beam is refocused by altering the Einzel lens voltage while in the vertical electron beam configuration. Simulation 3 was used as a reference, employing the manufacturer recommended set-point of 25 V for the Einzel lens, whereas Simulation 7 and 8 used a lens voltage of 75 V and 200 V, respectively.

For direct comparisons with the simulations, analogous experiments were conducted on the CIT system. Toluene was used as a constantly infused analyte (via 70 ppb_v air samples continuously infused to the membrane interface), and the instrument was located on a free moving turntable where 0° is magnetic north in Nanaimo, Canada. In this case, the instrument analyzed the toluene using an MS/MS scan (m/z 91 → 65, 10 μA electron current, 150 ms ionization time, 1.5 V dissociation voltage, and 20 ms dissociation time).

Table 1. Parameters Varied Between Simulations of the CIT Ion Source. Electron Beam Orientation is with Respect to the Earth's Surface (i.e., the *xy* plane). Lens and Ion Trap Design are Depicted in Figure 1 and Described in Text

Sim. #	Description	Electron beam orientation	Lens (V)	SF of electron source on y (mm)	Earth's field (G)			Instrument referenced field (G)		
					Bx	*By*	*Bz*	*Bx*	*By*	*Bz*
1	Earth's field only	vertical	25	0	0.18	0.054	0.51	0	0	0
2	Earth's field + filament	vertical	25	0.3	0.18	0.054	0.51	0	0	0
3	Earth's field + filament + instrument's field	vertical	25	0.3	0.18	0.054	0.51	0.21	–0.047	–0.63
4	Earth's field only	horizontal	25	0	0.18	0.054	0.51	0	0	0
5	Earth's field + filament	horizontal	25	0.3	0.18	0.054	0.51	0	0	0
6	Earth's field + filament + instrument's field	horizontal	25	0.3	0.18	0.054	0.51	0.21	–0.047	–0.63
7	Earth's field + filament + instrument's field + altered focus	vertical	75	0.3	0.18	0.054	0.51	0.21	–0.047	–0.63
8	Earth's field + filament + instrument's field + very altered focus	vertical	200	0.3	0.18	0.054	0.51	0.21	–0.047	–0.63
9	Earth's field + filament + instrument's field + mu-metal around instrument	vertical	25	0.3	0.060	0.018	0.17	0.21	–0.047	–0.63
10	Earth's field + filament + instrument's field + Metglas in vacuum chamber	vertical	25	0.3	0	0	0.51	0	0	–0.63

Magnetic Field Shielding Effects

Simulations 3, 9, 10, and their associated parallel experiments (again, using the CIT) were performed to determine the effectiveness of using magnetically permeable materials to reduce the intensity of the Earth's magnetic field experienced by the mass spectrometer. Simulation 3 was used as a reference point, and Simulation 9 was designed to match the conditions that were determined after paneling the entire instrument with mu-metal. In this case, the instrument's outside casing was covered with about 1.6 m^2 of 0.1 mm thick nickel alloy foil, or mu-metal ($\mu \approx 50,000$) (Product Number 8912 K32; McMaster Carr, Elmhurst, IL, USA), held in place with adhesive tape. Magnetic fields inside the instrument after the mu-metal was installed were determined by locating the magnetometer next to the vacuum housing and rotating the operational instrument through 360°. The magnitude of instrument's and Earth's magnetic field vectors were resolved using custom Matlab code. It was determined that the mu-metal resulted in a 66% reduction in the intensity of the Earth's *x*, *y*, and *z* magnetic field vectors. The instrument's internal magnetic fields changed slightly, but this was highly dependent on the exact location of the magnetometer. Because of this, it was decided to retain the original numbers for the instrument's magnetic field for consistency with each simulation.

Simulation 10 was designed to match the conditions that were determined after the interior of the vacuum chamber was lined with a 10 layer thick cylinder of 0.015 mm thick Metglas ($\mu \approx 290,000$, Metglas 2075 M; Metglas, Conway, SC, USA) mounted on the interior wall of the CIT instrument's vacuum chamber. Several small holes were cut in the Metglas cylinder to allow the necessary electrical feed-through connections required for normal operation. The magnetic fields in the vacuum housing were characterized by locating the magnetometer within the vacuum chamber and rotating the (nonoperational) instrument through 360°. It was determined that the *xy* components of both the Earth and instrument magnetic fields were negligible. Because the top and bottom of the chamber were not protected by Metglas, there was a significant *z* field. Over the course of the study, it was also determined that the difference between the instrument's internal magnetic field was small when operating or not, suggesting the instrument's fields are primarily sourced from the permanent magnets in the turbomolecular vacuum pump (Model TC100; Pfeiffer Vacuum, Asslar, Germany). Neither the mu-metal foil nor the Metglas were annealed for this work, which would further increase their relative magnetic permeability.

Figures were generated using Matlab, and the data plotted with respect to the field orientation was best fit with a line determined by a nonlinear fit to $y = a + b{*}sin(c + x) + d{*}sin(2{*}(e + x)$. Error bars shown in simulated data represent the SD of electron transmission through the aperture for the 10,000 simulated electrons binned into groups of 10. Error bars shown in experimental data represent the SD of the 24 steady state signal measurements.

Results

Mobile Mass Spectrometer Sensitivity Versus Directional Bearing

For the purpose of demonstrating the in-field response of a mobile mass spectrometer to relative to the Earth's magnetic orientation, internal standard signal intensities for the four mobile mass spectrometer systems examined are plotted in Figure 2. Data shown in Figure 2a and b were produced by quadrupole ion traps using internal ionization directly within the ion storage volume, requiring the injection of electrons through an endcap aperture. In both cases, there was an observed dependence on directional bearing in which the signal intensity displays one maxima per 360° rotation. Shown in Figure 2c are data obtained for a quadrupole ion trap with an external ion source that generates ions using electrons focused

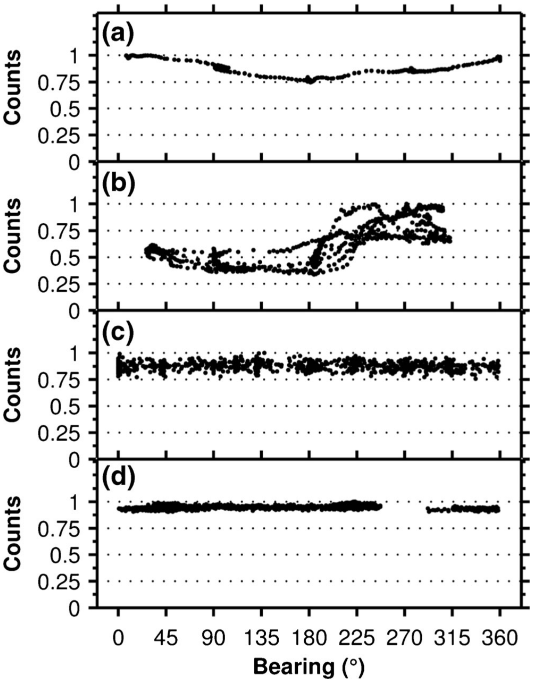

Figure 2. Moving mass spectrometers' response to an internal standard plotted versus directional bearing. **(a)** An ion trap with internal ionization (e.g., electrons are injected into the ion trap where ionization occurs) and an electron beam horzontal to the Earth's *xy* plane. **(b)** Another ion trap with internal ionization but vertical electron beam. **(c)** An ion trap with external ionization (e.g., ionization occurs outside the trap and ions are subsequently injected into the trap). **(d)** A closed source quadrupole mass spectrometer. Models and ion source designs are further described in the Experimental section. It is notable that only instruments with internal ionization exhibit a directional dependency

by a strong magnetic field. Ions produced in this system were subsequently injected into the ion trap. The data illustrate the external ion source exhibited no signal dependence with respect to magnetic orientation, suggesting the strong magnets focusing the electrons into the ion source effectively overcome any influence from stray magnetic fields. Similarly, the data collected using the single quadrupole mass spectrometer, shown in Figure 2d, indicated no signal dependence with respect to the directional bearing. This mass spectrometer has a very short electron trajectory and a relatively large electron aperture slot in the ion source; as such, it is unlikely that electron beam deflections were significant under such conditions.

On the whole, the field data indicate mass spectrometers with relatively long electron trajectories and small entrance apertures (e.g., internal ionization ion trap type systems) are strongly affected by directionality, whereas short path lengths, large apertures, and strong collimating magnetic fields are likely to negate any directional bearing dependency. Regardless of horizontal or vertical ionizing electron beam axes relative to the earth's magnetic field, one maximum per rotation was observed in the directional dependence of the relative instrumental sensitivity of the mobile mass spectrometer systems exhibiting this effect.

Ion Source Simulations

Simulation 1 has an ion source that is cylindrically symmetric and has the electron beam traveling in the vertical direction. As a result, the transmission of electrons through the endplate aperture in Simulation 1, which rotates the Earth's magnetic field about the vertical axis, showed no reproducible directional dependence (Figure 3a). The mean transmission was 8.7%, which is almost half the 14.7% that is simulated to occur without the Earth's field present. The inclusion of the Earth's field, while reducing electron transmission by deflecting the center of the electron beam away from the aperture, had no directional dependency attributable to the cylindrical symmetry and vertical orientation.

Simulation 2 adds an asymmetry to the system by including the length of the filament when simulating the origin of each electron. Set-points were such that over 99.7% of electrons were sourced from the middle 1 mm section of filament wire. Figure 3a illustrates that there was little effect from this asymmetry. When the length of the filament was exaggerated (e.g., electrons sourced from a 5 mm long filament, data not shown) two maxima per rotation were observed. This would be the expected result from a system with bilateral symmetry. The inclusion of the asymmetry did not have a significant effect on the directional dependency, and the resulting two maxima were not observed in any of the experimental field data.

Simulation 3 is the closest representation of the operating conditions of the CIT instrument. In addition to including the accurate representation of the filament and the Earth's magnetic field, it includes a static secondary field that is referenced to the instrument itself. A strong directional dependency with one maximum per rotation is illustrated in Figure 3a. In this simulation, the Earth's magnetic field is of similar magnitude to the static field. Therefore, when the two fields interfere destructively (e.g., at 135°–180°), the electrons were not significantly deflected and experienced a higher transmission efficiency through the aperture. However, when the two fields interfere constructively (e.g., at 315°–360°), the electrons were strongly deflected, and fewer electrons were transmitted. Figure 4a depicts, in greyscale, the relative likelihood of an electron's position as it reaches the ion trap's endplate. The effect of the summation of the two magnetic field vectors becomes clear, demonstrating why the constructive and destructive interference of the two magnetic fields has the strongest influence on directional dependence. It is also worth noting that under 'standard conditions' (i.e., Simulation 3), while the electron beam was unfocused, there was still a greater electron density in the center of the beam. Whether or not the central area of the

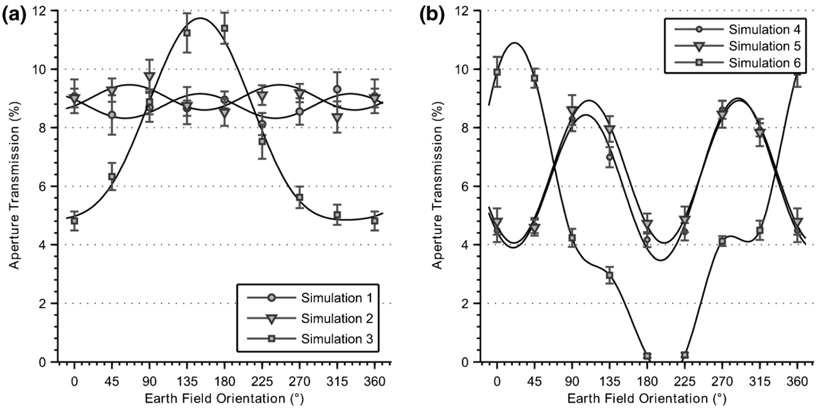

Figure 3. Simulation of electron transmission of a vertical **(a)** and a horizontal **(b)** electron beam through endplate aperture versus the Earth's field orientation. Simulation 1 and 4, Earth's field + point source filament; Simulation 2 and 5, Earth's field + transverse filament wire; and Simulation 3 and 6, Earth's field + transverse filament wire + instrument's field

electron beam passes the aperture had a significant effect on the number of electrons ultimately entering the ion trap and subsequently ionizing neutral molecules.

In the case of the vertical electron beam, Simulation 3 (Figure 3a) accurately predicted the one maximum per rotation signal observed in the field measurements for the mobile mass spectrometers. Given the additional asymmetry that results from a horizontal electron beam, one might expect two maxima in such a system. However, Figure 2a depicts a mass spectrometer in the field with a horizontal electron beam—also with one maximum per rotation. Simulation 4 (horizontal electron beam, point source electron source, Figure 3b) shows that the effect of the Earth's field alone does, in fact, create a two maxima directional dependency. The inclusion of the filament wire in the electron source has a rather small effect (Figure 3b, Simulation 5). However, Simulation 6, which included the additional instrument referenced magnetic field, shows a dramatic one maximum directional dependency (Figure 3b). The constructive/destructive interference of the two fields clearly had a very strong effect on the system and explains why the QIT, with a horizontal electron beam, displays a dominant one maximum direction dependency on the field. It is noteworthy that the dimensions of the QIT are different from the CIT and the magnitude of signal variation was not expected to be in agreement between Simulation 6 (Figure 3b) and Figure 2a.

Reducing the Relative Response Variability

Having established a plausible mechanism for the variation in signal intensity with respect to the instrument's magnetic

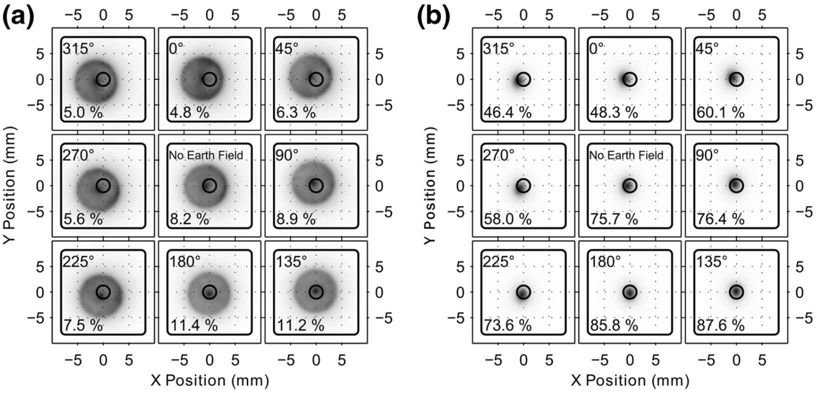

Figure 4. Density maps indicating the xy location of electrons as they reach the ion trap endplate for Simulations 3 [25 V lens, **(a)**] and 8 [200 V lens, **(b)**] under different magnetic bearing conditions. Each subplot is calculated from 10,000 electrons, the dark grey represents high probability of an electron at that position, and light grey represents low probability. The outside rectangle represents the outside edge of the endplate and the central circle represents the endplate aperture. Magnetic bearing and percent of electrons passing the aperture are indicated

orientation, Simulation 3 was used as a starting point for subsequent simulations and experiments. These studies were aimed at determining an effective way to reduce the observed sensitivity dependency related to directional bearing. Simulations 3 and 7–10 were matched with a parallel experiment performed in the lab with a CIT instrument mounted on a turntable. Simulations 7 and 8 simulate the results when the electrons are not focused according to manufactures specifications by the Einzel lens prior to the aperture. Figure 4b shows the improved aperture transmission relative to Figure 4a resulting from altering the lens voltage from 25 V (Simulation 3) to 200 V (Simulation 8). Experimental data are in relatively good agreement with Simulations 3, 7, and 8 (Figure 5). These data suggest that a defocused electron beam (Simulation 3) does not necessarily reduce the directional dependency, but does reduce instrumental sensitivity. Not shown are simulations with an increased secondary field. In these simulations, a well-focused beam can result in an extreme directional dependency as the entire beam may be transmitted or rejected by the aperture depending on the state of interference with the Earth's magnetic field.

Simulation 9 compared electron aperture clearance with Simulation 3 after a reduction in the Earth's magnetic field by adding mu-metal on the outside of the instrument, and Simulation 10 compared transmittance after a reduction in both the Earth's and instrument's fields by adding Metglas on the inside of the vacuum chamber. These simulations were directly compared with instrumental data collected under the same magnetic conditions (Figure 6). Simulation 3 indicates a 58.7% variation in signal intensity as a result of the additive effect of the Earth's and the instrument's fields. Simulation 9 indicates that this is reduced to a 21.7% signal variability with the addition of mu-metal on the outside of the instrument (a reduction of 62.9% in the signal variability). This result is comparable to the experimental data, which demonstrated a 47.4% reduction in actual signal variance between the standard and mu-metal conditions. Simulation 10 indicates we can expect 4.9% signal variability (a reduction of 93.2% in the signal variability) as a result of the Metglas addition. This result is comparable to the actual data from the CIT that displayed a 92.3% reduction in signal variability between the standard and Metglas conditions. This reduction made the relative response variability due to the instrument's magnetic orientation virtually indistinguishable from other instrumental noise.

Discussion

Regardless of the specifics of the mass spectrometer instrument symmetry, the results of these studies suggest the best way to minimize directional response dependency is to shield low energy electron beams from both the Earth's and instrument's magnetic fields. In doing so, the electron beam can be properly aligned for optimum ionization, regardless of the orientation of the instrumentation during mobile measurements. Both simulation and experimental results indicate that in addition to significantly reducing the signal variability during deployment, the focusing lens may be tuned to ensure a higher electron throughput yielding significant improvements in sensitivity. Simulations indicate that a well-tuned lens can improve instrumental sensitivity nearly 10-fold. However, it should be noted that shielding of the electron beam from stray magnetic fields becomes imperative in this case, as it is possible that the tightly focused electron beam could miss the entrance aperture entirely. With increased sensitivity, the opportunity to reduce the required filament emission current arises; this may be desirable

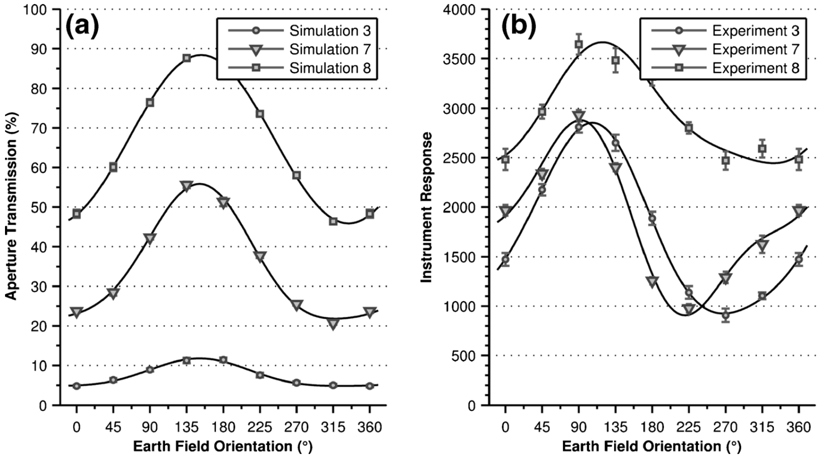

Figure 5. Electron transmission versus Earth's field orientation under varied lens set-points. **(a)** Illustration of the percentage of electrons transmitted with a lens set-point of 25 V (Simulation 3), 75 V (Simulation 7), and 200 V (Simulation 8); **(b)** plots the instrument response to an internal standard during a parallel experiment performed on a mass spectrometer under the same conditions as the simulation

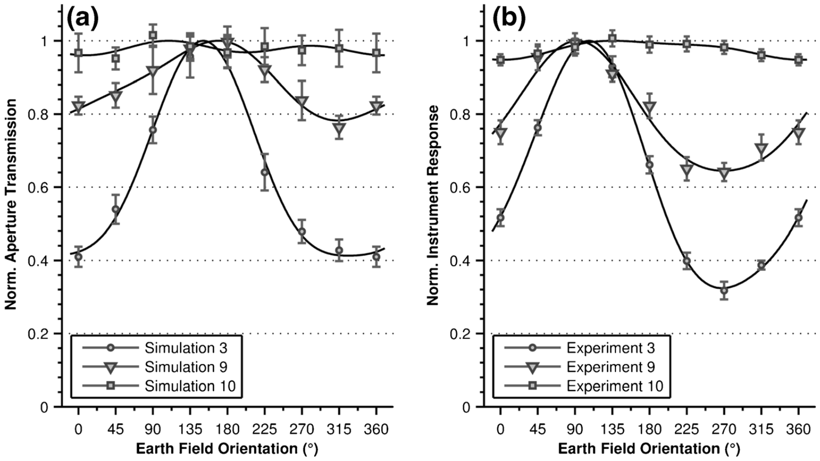

Figure 6. Electron transmission versus Earth's field orientation under varied magnetic field conditions. **(a)** The percentage of simulated electrons transmitted through the aperture with no protection from magnetic fields (Simulation 3), 66% reduction of the Earth's magnetic field by an exterior mu-metal casing (Simulation 9), and 95% reduction of both the Earth's field and instrument's field by interior Metglas (Simulation 10); **(b)** plots the relative instrumental response to an internal standard during a parallel experiment performed on a CIT mass spectrometer operated under the same conditions as the simulation

when the vacuum chamber is under relatively oxidative conditions, as is common in MIMS systems. This would yield longer filament lifetimes and lower the signals from background gases [7, 21].

Another factor that should be considered is the electron current control feedback mechanism. In order to produce a constant electron ionization current, ion sources are designed to maintain a constant flow of electrons by using a feedback control system. Typically, there are two methods to monitor and control filament emission current. One is achieved by monitoring the filament emission current using the filament power supply circuitry; this methodology provides no correction for the variations in transmission through the ion trap entrance aperture. Another method is to monitor the electron current on an aperture plate in the ion optical system (e.g., the ion trap entrance aperture); use of this method assumes that the current collected on this plate is a constant fraction of the transmitted electron current. This methodology provides feedback control for emission control circuitry but unfortunately may serve to exaggerate the directional dependence. In this case, fewer electrons may be entering the ionization region because of deflection by external magnetic fields. With more electrons striking the aperture plate, this would provide erroneous feedback that acts to decrease filament current, resulting in further reduction of the transmitted electron current. Another feedback option, however, could be to measure the electron current on the ion trap exit endplate. This feedback mechanism would compensate for variations in transmitted electron current by increasing filament current when transmission is decreased. Since only the transmitted electrons contribute to the feedback, this method would compensate for deflections resulting from the Earth's magnetic field. However, it may prove impractical because of the radio frequency trapping fields of the trap, which may direct a portion of transmitted electrons into the ring electrode instead.

Additionally, the use of automatic gain control may help compensate for the observed phenomena, although gain control was fixed during these studies. Since mass spectrometers can have several scan types and pre-scans, and the directional dependence of the full scan and an MS/MS scan varies slightly with the CIT (data not shown). Such variability is likely due to changes in ionization time estimated by instrumental gain control pre-scans. Investigation of this phenomenon was beyond the scope of the current study.

Solutions not explored in this work include the use of magnetically permeable paints or magnetically permeable components, especially those components closest to the electron beam (e.g., the lenses and vacuum housing). Additionally, simulations suggest that in some situations where precision is key, it may be prudent to use a pointed filament that would give a more cylindrically symmetric electron beam than that produced by a linear filament wire perpendicular to the electron beam. Locally shielding specific instrumental components that are contributing to the instrument's magnetic field may also be beneficial, especially if it is not practical to sufficiently shield the electron beam.

Some instrumental components can have very strong magnetic fields (e.g., from the filament current, turbo pump magnetic bearings, or induction coils). Further, if the component generates cyclical fields (e.g., a motor or pulsing solenoid), the field coming in and out of phase with specific mass scans may significantly affect instrument stability. Depending on aliasing and frequency reproducibly, this noise may show up as a beat (as demonstrated in Supplementary Figure S1) or as random noise. A noteworthy source of instrumental magnetic fields may be the electric current through the filament. A filament operating at 5 amps (a high but not unusual current for an ion source), would have a field equal to the Earth's at a distance of 2 cm. While this field intensity would decrease rapidly with distance (Ampere's Law), it will be very intense in close proximity to the filament. This will cause significant deflection near the filament and be very difficult to prevent; however, the subsequent focusing via the Einzel lens dampens the effect of deflections prior to and within the lens. Magnetic fields located between the lens and ion trap entrance endplate will have the most significant impact on electron beam deflections. This effect can be observed through careful examination of electron trajectories relative to the aperture reference lines shown in Figure 1, and suggests this effect could be minimized by placing the Einzel lens as close as possible to the ion trap endplate.

Last, as this study occurred in Nanaimo, Canada, all simulations were done assuming a field at that location (latitude, longitude, and near sea-level altitude). At higher latitudes, the Earth's magnetic z vector is rather strong and subsequently x and y vectors are rather weak. Since the z vector does not contribute to the deflection of electrons travelling in the vertical axis, the effects observed in this manuscript will be stronger at more equatorial latitudes.

Conclusions

To our knowledge, this is the first rigorous study of the influence of stray magnetic fields from the Earth and/or instrumental sources on the relative signal response and sensitivity of portable mass spectrometers. Signal variability is observed with instruments in which ionizing electrons have long path lengths and must pass through a small aperture, and are observed when the instrument is physically moved with respect to the Earth's magnetic field. It was found that the predominant source of signal variability is a result of the vector sum of the Earth's magnetic field and a secondary, instrument-referenced magnetic field. Removing either one will result in a significantly reduced directional dependence. Preferably, both fields can be shielded from the electron beam by the addition of magnetically permeable material to the vacuum chamber. In this case, directional dependence will become increasingly negligible as the deflection of the electron beam is eliminated. Subsequently, the optimum alignment of electron ionization beams may allow for improved electron beam focusing and significant gains in instrument sensitivity.

Acknowledgments

The authors gratefully acknowledge the assistance of the staff of the Center for Ocean Technology, College of Marine Science, and the C. D. Simpson Laboratories at the University of Washington for their assistance with the collection of various field data. The authors also thank the students and staff of the Applied Environmental Research Laboratories (AERL) for their assistance with this project, and the notably insightful input from Kyle Duncan. They also thank two anonymous reviewers for their thoughtful reviews and intellectual contributions to this manuscript. They are grateful to Vancouver Island University and the University of Victoria for their ongoing support of graduate students and the Natural Science and Engineering Research Council of Canada for support.

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Paper IV

Environmental Chemistry and Ecotoxicology 2 (2020) 168–174

Contents lists available at ScienceDirect

Environmental Chemistry and Ecotoxicology

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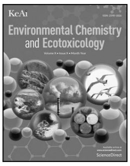

A field portable membrane introduction mass spectrometer with in-line standard infusion and sample heat exchanger for real-time monitoring of volatile organic compounds in aqueous samples

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ARTICLE INFO

Article history:
Received 3 July 2020
Received in revised form 14 September 2020
Accepted 16 September 2020
Available online 22 September 2020

Keywords:
VOC
Water contamination
Membrane introduction mass spectrometry (MIMS)
Mobile mass spectrometry
On-site contaminant analysis
Sample stream heat exchanger

ABSTRACT

Maintaining a steady sample temperature when analyzing real-time samples in the field is crucial for Membrane Introduction Mass Spectrometry (MIMS). Diffusion through the membrane interface is temperature dependent, and sample temperature might vary depending on the sample source. In order to reduce this source of inaccuracy, an in-field and online continuous monitoring system based on (MIMS) coupled with a heat exchanger and in-line standard addition was developed for monitoring volatile organic compounds (VOC) in actual field samples. Parametric studies of the heat exchanger have been conducted in the laboratory. In order to maintain control on instrumental signal drift during continuous, long-term analysis periods, the system used continuous infusion of internal standard (tuloene-d_8) into the sample stream and also provided the possibility to infuse, in the same way, an analyte for standard addition calibration. This set-up has been utilized in the field for analyzing both natural water sources and heavily polluted process water. The system was demonstrated to offer a rapid method for quantifying volatile hazardous pollutants in aqueous matrices with good time-resolution.

1. Introduction

The release of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) into the environment can be traced back to both natural and anthropogenic sources [1–4]. Monitoring the release of these compounds to the environment by monitoring programs is normally done using nationally or internationally standardized methods, such as ISO or EPA methods. For aqueous solution analyses, purge-and-trap gas chromatography/mass spectrometry is the preferred method of analysis for VOCs and SVOCs, e.g. EPA method 18 and EPA-NERL 542.2 [5,6] These are well-proven and reliable methods for environmental monitoring programs, but require time-consuming sample preparation and chromatographic separation, reducing their capabilities to resolve detailed compound variations in highly dynamic environments.

With an increasing demand for on-site online and real-time monitoring for environmental surveys, membrane introduction mass spectrometry (MIMS) has seen increased use [3,7–10]. Typically, MIMS uses a semi-permeable polymer membrane, such as polydimethylsiloxane (PDMS), with hydrophobic properties. The hydrophobic properties will prevent diffusion of particulates, water and highly polar and ionic compounds, while enhancing diffusion of compounds with a hydrophobic nature, yielding a MIMS system that is selective and sensitive for volatile and semi-volatile organic compounds (VOC/SVOC). This type of membrane will reject hydrophilic sample matrix and, thus, allow enrichment of these analytes from both liquid or gaseous samples. After diffusion through the membrane, analytes are directly transferred, often using helium gas as the carrier acceptor phase, to a mass spectrometer for subsequent ionization, resolution and quantitative measurement [10].

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http://dx.doi.org/10.1016/j.enceco.2020.09.003

For flexible and thorough analysis of VOCs/SVOCs, e.g. in the environment, the analytical system should preferably be brought to the location of interest and allow continuous monitoring, with system control and data analysis locally, or even remote/online. This would allow users to immediately respond to undesirable levels of analyte and it could provide, for any measures taken to adjust/correct analyte levels at the site, instant feedback regarding analyte levels.

There are many challenges faced when developing mobile on-line analytical instruments capable of providing real-time data. One of these challenges for MIMS systems is caused by variable diffusion conditions when an analyte species transfers through the membrane interface. In general, the permeation through a membrane is dependent on Fick's law of diffusion, where permeation rates are governed by, among other parameters, membrane properties affecting the partition coefficient for the analyte species between membrane and sample, the thickness of the membrane and the concentration of the analyte species. Previous research has shown a temperature dependency of analyte response, which, for field use, might cause challenges not observed in the laboratory under controlled conditions. The temperature dependence of the membrane permeability usually follows the Arrhenius equation well and, thus permeability depends on its values at some standard temperature and the activation energy for diffusion. It is, therefore, important to control sample temperature to avoid sensitivity variations, and to maximize analyte response [11,12]. The capability to resolve multiple "plumes" of pollutants in real-time online monitoring is governed by the rise and washout time of the compounds in the plume. Temperature will also influence the rise and washout time, and maintaining a steady sample temperature will therefore also be advantageous. Another challenge in analyzing complex matrices in an online manner can be drift in detector signals. Proper calibration routines are therefore crucial for online field apparatus.

This work presents the development and characterization of a countercurrent-flow heat exchanger suited for mobile deployment that corrects for variable sample temperatures, while also reducing power consumption in such field instruments. An optimized heat exchanger – MIMS interface is presented. It is used in combination with continuous-flow internal standard addition, which previously has demonstrated promising results for both aqueous and atmospheric sampling by MIMS [13–15]. Continuous infusion of toluene-d_8 standard into the sample line while analyzing samples could, potentially, allow for online internal standard calibration, correcting for any drift in signal. A second automated syringe pump allows in-line introduction of analyte for additional standard addition calibration, reducing, or even removing, the need for more comprehensive calibration steps pre or post analysis. This work presents the calibration curves for the hydrocarbon VOCs benzene and toluene and test experiments with plumes containing different samples from the Steam Assisted Gravity Drainage (SAGD) oil refinery process. It also reports the results of some in-field water measurements by this method, and compares them to results obtained by an established standard method.

2. Materials and methods

2.1. Reagents and standards

Target analytes (Table 1) and internal standard were ACS grade or better, and obtained from Sigma Aldrich Ltd. (Oakville, ON, Canada). HPLC grade methanol from Fisher Scientific (Ottawa, ON, Canada) was used for the preparation and dilution of single and combined standards. Sample water for the laboratory experiments was either deionized (DI) water (Model MQ Synthesis A10, Millipore Corp., Billerica, MA, USA) or surface water collected from a Koi pond (Nanaimo, BC, CA). Samples presented from the field experiments were collected at various sites of SAGD operation near Conklin, AB, Canada, and in and around Fort McMurray, AB, Canada.

Table 1
Flow mixing conditions for standard solutions in the calibration experiments, specifying syringe pump flows and calculated final concentrations in the interface for selected analytes and the internal standard, respectively.

Analyte	Aqueous flow (mL/min)	Standard addition flow (mL/min)	Dilution factor	Standard concentration (g/L)	Final concentration (μg/L)
Benzene	150	0.150	1000	0.0014	14
Toluene	150	0.150	1000	0.0014	14
Toluene-d_8 (IS)	150	0.08	1875	0.0012	6.4

2.2. Laboratory instrumentation

A schematic diagram of the instrumentation used for these studies is given in Fig. 1.

Aqueous samples were pushed through the sample train by a peristaltic pump (Masterflex L/S Economy with L/S 25 Viton pump tubing, Cole Parmer, Vernon Hills, IL) at 150 mL/min to ensure turbulent flow at the membrane interface. For infusion of standard solutions, two syringe pumps (C3000 Syringe Pump, TriContinent, Grass Valley, CA and R99-E, Razel Scientific Instruments, St. Albans, VT) were connected in line via a stainless-steel Swagelok 4-way cross-junction (Swagelok, Solon, OH, USA) upstream of the heat exchanger. The in-house built, 2.4 m long, coiled tube-in-tube heat exchanger consists of an outer tube of copper (OD 1.27 cm, ½ inch; ID 0,95 cm, 3/8 in.) and an inner tube of stainless steel (OD 0.635 cm, ¼ inch; ID 0.53 cm 0,209 in.). It was connected to the sample train through stainless-steel Swagelok Union T fittings. The inner tube of the heat exchanger extends through the Tee union to connect to the sample inlet whereas the outer tube connects to the sample waste outlet. A heating tape was wrapped around the thermally regulated heat exchanger, controlling sample temperature with a Ramp/Soak controller (1/32 DIN Ramp/Soak Controllers, Omega Engineering Inc., Stamford, CT). The reference temperature for the controller (and thereby the sample temperature T_3 in Fig. 1) was recorded at the T-junction with a thermocouple (Omega Engineering Inc., Stamford, CT) located after the heat exchanger in the sample flow. The sample (inner tube) and return (outer tube) flowed countercurrent to each other to maximize the heat transfer from the return flow from MIMS to the flow to the sample.

A quadrupole ion trap mass spectrometer (Polaris-Q™; Thermo Electron, San Jose, CA, USA), operated in tandem mass spectrometry mode was used to optimize the heat exchanger, the addition of internal standard in-line, and in-line calibration through standard addition. Benzene and toluene were selected as the analytes for the experiments, and as the internal standard toluene-d_8 was used. Vapor pressure data and specific mass spectrometry scan parameters for them are given in the Supplementary material (Table ST1).

A 10.0 cm long polydimethylsiloxane hollow fiber membrane (ID 0.51 mm, OD 0.94 mm, Dow Corning, Midland, MI) was housed in a 6.35 mm OD (1/4 in.)) stainless steel tube and affixed at both ends to stainless steel capillary tubing (ID 0.51 mm, OD 0.71 mm, Vita Needle, Needham, MA) mounted in 2 stainless steel 1/4 in. Swagelok Tee Unions (Solon, OH) by means of reducing Teflon ferrules. The membrane interface was housed in the GC oven at 35 °C with a He-gas flow of ~1 mL/min passed through the lumen of the hollow fiber membrane. A metal jet separator (P/N 113617, SGE, Inc., Austin, TX) was installed downstream of the membrane to achieve analyte enrichment by removing excess air and helium.

Physical characterization of the in-house built heat exchanger was conducted by calculating the consumption of effect (Watts) required to heat a sample to 35 °C with varying sample reservoir temperatures (5 to 35 °C with 5 degrees increments). The calculations were carried out with Eq. (1) [16].

$$Q = \rho \times C_\mathrm{p} \times \Delta T \times q \tag{1}$$

where Q is the effect in watt (J/s), ρ is the density of water (g/mL), C_p is the specific heat of water (J/g*K), ΔT is the temperature difference between

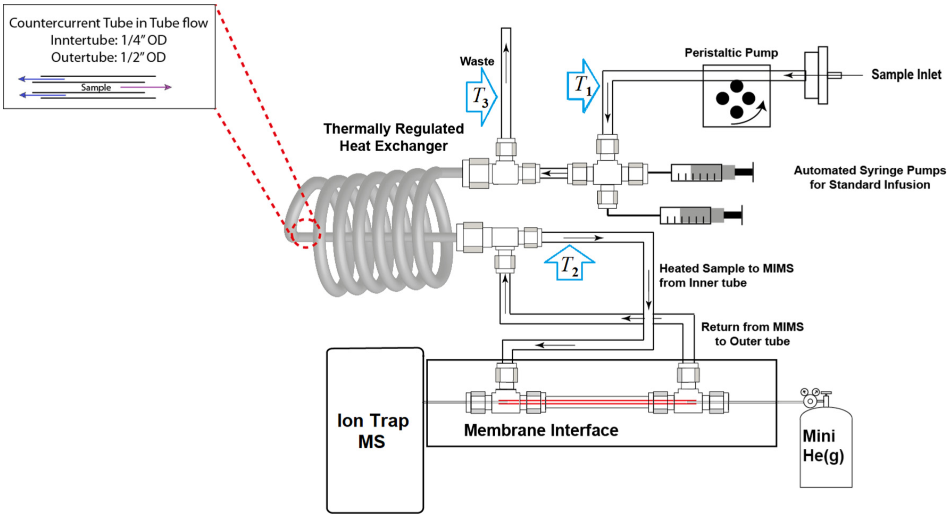

Fig. 1. Schematics of MIMS apparatus with a dual syringe pump setup for direct standard infusion. An in-house built heat exchanger was connected in-line to ensure stable sample temperatures in the membrane interface at low energy consumption. The three locations for temperature measurements for the test of the heat exchanger are indicated in the figure as T_1, T_2 and T_3. Specific adaptations for use in the laboratory and the field experiments, respectively, are shown in the Supplementary Material (in Figs. SF1 and SF2).

sample temperature and the heated sample temperature (K), and q is the volumetric flow rate (mL/s).

Power consumption needed to heat the sample from its original temperature to a final temperature for analysis was linked directly to recorded temperature of the sample. This was done in real time, by using the given temperature difference (ΔT). As seen in Fig. 1 Three different temperatures were recorded at specific locations in the sample stream. For the calculation of effect to heat the sample, ΔT comes from the subtraction of T_1 from T_2 ($\Delta T = T_2 - T_1$). The externally required effect corresponds to the subtraction of power required to heat and power given from the sample in the heat exchanger on the return, from T_2 to T_3.

Analyte calibrations were performed by using continuously infused internal standard calibration. The delivery of a combined standard and the internal standards was achieved with the two syringe pumps, infusing standards directly to the aqueous sample flow at the 4-way cross-junction (Fig. 1). A combined standard was prepared with toluene, benzene and naphthalene in methanol to a final concentration of 14 mg/L each (however, the naphthalene data were not used further). The toluene-d_8 used as internal standard (IS) and was prepared in methanol to a final concentration of 12 mg/L. With deionized water (DI) flowing at a set flow rate of 150 mL/min over the membrane, the internal standard was infused with one syringe pump at a constant flow rate of 0,080 mL/min while the combined standard was injected with the second syringe pump at varying flow rates, yielding specific dilutions and thereby a range of concentrations from 3 to 50 μg/L. See Table 1. For some examples of a setup of infusion flows, dilutions and concentrations. Relative Response factors, RRF, for the analytes (A) were calculated from Eq. (2) based on the standard and internal standard concentrations, [A] and [IS] respectively, and used for quantification in further experiments.

$$RRF = \frac{Signal_A/[A]}{Signal_{IS}/[IS]} \tag{2}$$

Plume experiments were simulated by injecting various solutions into a sample stream of DI water (150 mL/min) at various lengths of time with a syringe pump at a set flow rate (0.150 mL/min). Plumes of contaminants producing both steady- and non-steady state conditions were created. The artificial plume was made up of a standard containing benzene only in methanol at a concentration of 14 μg/L. For quantification of the contaminants, a constant flow of IS was infused at a set flow rate (0.08 mL/min) to the same sample stream. Test experiments for plume detection with more realistic matrices were also performed successfully where the DI water was replaced by surface water collected from a koi pond (results not reported). Furthermore, a process water sample from a (tar sand) oil extraction process was injected in plume experiments (with dilution in DI water) to better simulate contamination during field operation of the instrumentation.

2.3. Field instrumentation

The instrumental setup used during field deployment is shown in Fig. SF2. A modified GC/MS system with a cylindrical ion trap mass spectrometer (Griffin™ 400, FLIR© Systems, Inc., West Laffayette, IN, USA) operated in tandem mode was used to obtain the MIMS data. Additional details regarding the field portable ion trap system have been published elsewhere [1].

Calibrations done pre-deployment were acquired by using a dilute methanol standard of target analytes (Table 1) combined with toluene-d_8 as an internal standard injected at set volumes to a separate closed loop recirculation MIMS system (not represented in Figs. 1 and SF2) with a flow of 150 mL/min. Relative response factors were calculated at several different μg/L sample concentrations using MIMS steady state signals based on Eq. (2).

Water samples were collected from the source (e.g. lake, pond, creek or river) with a peristaltic pump, described earlier in this section. These samples were analyzed in real time and online at specific locations. The temperature of sample entering the MIMS interface was regulated (35 °C) by means of the heat exchanger. Sampling time varied between 1 h and 3 h. A standard comprised of target analytes (Table 1) was injected at the end of each run by means of an automated syringe pump (Figs. 1 and SF2) for an additional in-field calibration check. When continuous monitoring was not feasible, samples were analyzed as grab samples (e.g. ground water, process water and, in general, water from inaccessible locations), by collecting the water in 4 L brown glass bottles and analyzing them in the MIMS system within 3–4 h. Quality Control subsamples for conventional analysis of BTEX compounds using static headspace-GC/MS (EPA 5021 and EPA 8260) by an accredited laboratory (ALS Environmental, Edmonton, AB, Canada) were collected in-line while sampling (Fig. SF2, at the Outlet for subsampling). Subsamples were collected both while analyzing the sample and during standard injection for method validation.

3. Results and discussion

3.1. Heat exchanger

The minimization of power consumption is of key importance when operating an instrument in-field, especially when operating on (limited) battery power. A heat exchanger system should be able to reduce power consumption of the temperature control of the sample stream. Utilizing temperature regulation of the sample gives the advantage of having a thermally more stable feed of sample to the membrane interface, as membrane permeation is dependent on temperature, among other parameters [12]. This is especially important when operating in-field, where sample temperatures may vary widely. Depending on the nature of in-field samples, temperatures may be from 5 °C, e.g. in a low temperature ground water reservoir, to well above 20 °C or higher for surface water bodies.

The developed heat exchanger and syringe pump assembly were employed to optimize our in-field aqueous MIMS analysis system including the use of a continuously infused internal standard. The power consumption of the heat exchanger was characterized with respect to sample feed temperature and sample flow first, in a laboratory MIMS system. This was done to optimize (and maximize) the efficiency of the heat exchanger for low power consumption, to allow longest possible field operation. In general, the energy consumption of the heat exchanger for maintaining a temperature above sample temperature increases with decreasing sample feed temperature.

The in-house built heat exchanger was investigated with regard to power consumption and was found to have a heat transfer efficiency of about 70%. To further characterize the heat exchanger, experiments were conducted to calculate the different sources of power consumption and their respective magnitude. Shown in Fig. 2 are the results of the calculation of (A) power required to heat the sample to 35 °C from varying sample reservoir temperature with varying flow and (B) externally required power for the heat exchanger to maintain the sample temperature of 35 °C under same physical parameters as (A).

With increasing flow rate and decreasing sample reservoir temperature the power required to heat the sample increases. With a sample temperature of 5 °C the heat exchanger was incapable of maintaining a sample temperature of 35 °C with flow rates above 250 mL/min.

A flow rate of 150 mL/min was selected, as higher flow rates required disproportionately more power by the heater to keep a stable sample temperature at low sample temperatures. For a flow of 150 mL/min about 140 W is required from an external power source to heat a sample from 5 °C to 35 °C. The dead volume of the inner tube of the heat exchanger is about 50 mL creating a thermal equilibration time of 20 s.

3.2. Calibrations

Calibrations for MIMS analyses are normally done in a recirculating system with standard addition of selected standards, which makes the process of in-field calibrations cumbersome [17]. With the dual syringe pump and the heat exchanger assembly, calibration could be performed with a continuous infusion of an internal standard simultaneously with the infusion of selected standards under controlled temperature conditions. For portable deployment, this allows improved calibration routines of the instrumentation for rapid QA/QC.

In the present laboratory experiments the typical procedure of calibration was for two selected compounds, benzene and toluene, using an internal standard. The concentrations of benzene and toluene in the calibration sample stream were regulated by the syringe pump with the standard mixture solution, controlling the analyte flow into the DI water sample stream by its pumping speed. Standard solution was added repeatedly in intervals with blank periods in between during the calibration, usually in a sequence of increasing concentration levels. Meanwhile, the internal standard is permanently infused at a set flow rate over the course of standard injections, maintaining a constant concentration.

An example of MIMS data from such a calibration sequence can be seen in Fig. SF3 for calibration levels of 0, 3, 5, 15, and 50 μg/L of benzene and toluene, with lengths for standard and blank infusion intervals of approximately 10–20 min each. Under these conditions, it seems as if the traces at the lower concentrations reach, or get quite close to, steady-state levels (within 2–4 min), while the signal at highest concentration (for toluene in particular) seems to slowly increase in intensity until the end of the interval plume. This requires an unambiguous specification of where signal size should be measured within a plume for clearly non-steady state plumes. Calibration curves and their linear regression functions for a representative internal standard-based calibration experiment are shown in Fig. SF4. The calibration offered a good linearity over a range of concentrations (R^2 = 0.9991 and 0.9997, respectively, for benzene and toluene) in the concentration range investigated (3–50 μg/L) with no, or small, deviations from steady state plume signals. For in-field calibrations the heat exchanger - syringe pump assembly offers a very convenient and simple way of

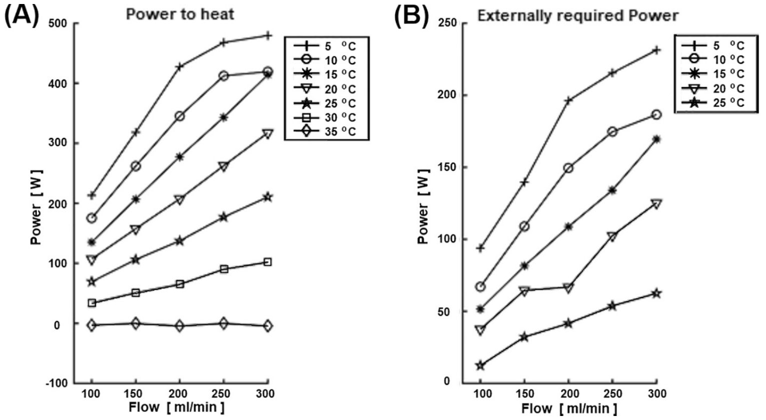

Fig. 2. Calculated power required to heat a sample from various reservoir temperatures (5–35 °C) at various flow rates assuming no heat exchange (A). The experimentally determined amounts of power needed externally for heating the heat exchanger to reach a sample temperature of 35 °C at specific flow rates with varying sample reservoir temperatures (5–25 °C) (B).

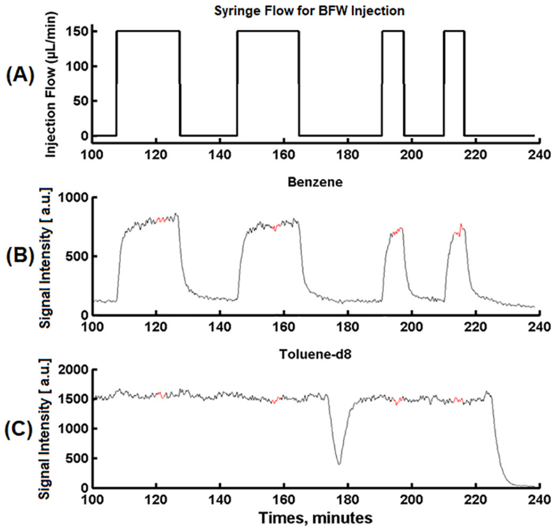

Fig. 3. (A) represents the flow rate of sample of heavy oil process water (boiler feed water, BFW) added by the automated syringe pump to the DI water sample stream. (B) Shows the variation in signal intensity for the benzene signal during the sequential injections of pulses of the process water sample. (C) shows the signal intensity of toluene-d_8 during the course of the experiment (with a signal dip during syringe refill at about 178 min, and at the end of internal calibration at 225 min).

calibration by the internal standard method, as well as the possibility to continuously infuse an internal standard while analyzing a sample of interest. As seen in Fig. 3.

In order to check the robustness of calibration, the variations in relative response factors, RRF, at various initial temperatures and flow velocities of the sample can be compared. Looking at the values for 10, 20 and 35 °C for temperature variation, and for 100, 150 and 200 mL/min for variation in flow velocities, the variations in RRF are moderate. Values are varying within about 15% between lowest and highest relative response, as is shown in Fig. SF5.

3.3. Resolution and quantification of sequential plumes

Resolving multiple plumes in an aqueous body, e.g. a running stream, can represent a problem as contaminants within a plume have different residence/pervaporation times within the membrane, depending on their chemical and physical properties. Having two plumes passing a sample inlet in a limited time window can, therefore, result in undesireable overlap of the tailing signal of the less volatile compounds from the first plume with the signals from the second one. For environmental monitoring, however, the ability to resolve sequential plumes of pollution within an often limited window of time is important. With aqueous MIMS analysis this is, among many factors, limited by the nature of the compounds of interest within a plume. The retention time within the membrane, i.e. the rate of pervaporation to the gas phase will depend primarily on the volatility of the compounds (transfer/evaporation into the acceptor gas phase) for a given membrane. For testing this context, attempts were made to simulate plumes in the laboratory, with a combined standard of benzene and toluene. In addition, for more realistic testing, a SAGD process water sample containing volatile aromatic hydrocarbons was injected, which created a plume simulating contamination from a heavy oil process facility. In these experiments plume time lengths of several minutes were tested, where signal responses for analytes were expected not to be at, but hopefully not too far from, steady state behavior. The scope of this experiment was to demonstrate plumes passing over a sample inlet during a limited time window where steady state therefore is not expected to be achieved.

Fig. 3 (A) shows artificial pulses (plumes) of the process water sample injected by one syringe pump into a DI water stream at two different lengths of exposure, while, for quantitative purposes, an internal standard was infused continuously alongside by the other pump. Fig. 3 (B) shows the SIM trace from plumes of the benzene in the sample from a this heavy oil processing facility. Firstly, two plumes were simulated with a 20 min injection time, then two shorter plumes with an 8 min injection time of the same sample. As shown in the figure, neither the 8 min nor the 20 min plume reaches steady state.

It is also evident, that at the same infused concentration, the shorter plumes only reach about 80–90% of the maximum height of the longer ones. Calibration accuracy will, therefore, (also) be dependent on how long the sample plume lengths are compared to the plume lenghts during calibration. In the simple (but probably unrealistic) case of clear-cut square pulse plumes, the width of the signals recorded could indicate the plume width to be used for post analysis calibration work. For such a case, hypothetically, one could also derive signal width- dependent correction factors for the quantitation of peaks calibrated at a different plume duration, if high accuracy is required and makes the considerable extra effort worthwhile.

The signal of the internal standard, continuously infused at a concentration of 8 μg/L, can be seen in Fig. 3(C).

Using the regression equation from the calibration (see Fig. SF4) the concentration of benzene was calculated to about 3 μg/L for each concentration. As the signal height is dependent on the plume length, the accuracy for these plumes in the experiment of Fig. 3 is coarsely estimated at +/− 10%, based on the observed peak height dependence on plume length (reduction of 10–15% for the shorter plume). This uncertainty might be more significant than the uncertainty by precision determined in the calibration curve, as long as plume lengths are variable (not identical to the calibration

Table 2
Comparison of concentration data for benzene of real samples obtained from MIMS data in the field, and data measured by a commercial laboratory (ALS, using standard sampling and analysis methods), respectively. For an overview of sampling locations please refer to Fig. SF8.

	Benzene			
Sample	MIMS - Sample (μg/L)	ALS - Sample (μg/L)	Qual. Contr.: MIMS - Sample with Comb. Standard (μg/L)	Qual. Contr.: ALS – Sample with Comb. Standard (μg/L)
A (McLean creek)	< 0.5	< 0.5	13.8	20.6
B (Paw pond)	< 0.5	< 0.5	14.6	10.6
C (Rommegrot creek)	< 0.5	< 0.5	13.9	14.6
D (Christina River)	< 0.5	< 0.5	14.4	0.7
E (Tailing pond 1)	0.7	< 0.5	15	20.2
F (Process water)	28.6	29.1	50.3	46.5
G (Tailing pond 2)	13.5	13.7	23.6	36.8
H (Clearwater River)	< 0.5	< 0.5	13.4	14.2
I (Athabasca River)	< 0.5	< 0.5	13.5	16.8
J (ALS DI experiment)[a]	< 0.5	< 0.5	13.7	18.3

[a] Experiment conducted with deionized water (DI), where DI with and without combined standard was analyzed with MIMS and ALS.

Table 3

Comparison of concentration data for toluene of real samples obtained from MIMS data in the field, and data measured by a commercial laboratory (ALS, using standard sampling and analysis methods), respectively. For an overview of sampling locations please refer to Fig. SF8.

Sample	Toluene			
	MIMS - Sample (μg/L)	ALS - Sample (μg/L)	Qual. Contr.: MIMS - Sample with Comb. Standard (μg/L)	Qual. Contr.: ALS – Sample with Comb. Standard (μg/L)
A (McLean creek)	<0.5	<0.5	20.3	19.2
B (Paw pond)	<0.5	<0.5	20.2	14.1
C (Rommegrot creek)	<0.5	<0.5	20.3	13.9
D (Christina River)	<0.5	<0.5	20.4	1.1
E (Tailing pond 1)	1.5	1.5	21.2	15.3
F (Process water)	18	17.3	31.2	35
G (Tailing pond 2)	10.1	9.1	26.7	25.6
H (Clearwater River)	<0.5	<0.5	20.8	13.4
I (Athabasca River)	<0.5	<0.5	22	17.4
J (ALS DI experiment)[a]	<0.5	<0.5	21.5	15.5

[a] Experiment conducted with deionized water (DI), where DI with and without combined standard was analyzed with MIMS and ALS.

pulses). It will lead to systematic underestimation of concentrations in short plumes - the shorter the plume, the more pronounced the error.

Limiting factors for time-resolving successive plumes are the rise and washout times of analytes in the membrane interface (illustrated for a 20 min rectangular concentration pulse (plume) of benzene in heavy oil process water in Fig. SF6). The $t_{10–90}$ rise times for each plume of benzene in a sequence of rectangular plumes in Fig. 3B were calculated to be, respectively, 3.3, 2.8, 2.4 and 2.3 min (Fig. SF7). These values are slightly higher than determined earlier [1]. The washout time ($t_{90–10}$) was estimated to be respectively 5, 5.5, 3.3 and 5.5 min for the same plumes.

As Figs. 3 and SF7 show for the 20 min plumes of benzee, the baseline is reached about 10 min after the end of the plume for this highly volatile analyte. Signals for less volatile analytes will return more slowly (compare benzene and toluene in Fig. SF3) and settling times might be significantly higher than these 10 min, maybe as high as 30 min. Considering the observed rise- and washout times, one can assume a resolving power of one plume, depending on the nature of the analytes, to be 30–50 min if full resolution of the plumes is desired. The estimations presented here are not based on a steady state signal, as plumes occurring during sampling in a creek or a stream (especially when close to the location of introduction into the water body) might be short and not reach a steady state when passing by the sample inlet. To attempt a quantitation by peak height, that does not massively deviate from a probable real value, we would estimate that signals with widths (at 10% of maximum height) of at least about 1.5 to 2 times the sum of rise and washout time ($t_{10–90} + t_{90–10}$) would be recommended. Alternatively, calibration with adapted realistic plume widths should be performed.

3.4. Quality control and data verification

During experiments carried out in the field, several grab samples ranging from process water to streams and rivers were collected. Sampling locations are given in Fig. SF8. Each sample was collected in duplex, where one part was injected with a combined standard of BTEX compounds (in this paper we focus on benzene and toluene, with a concentration of about 20 μg/L) and the other was not. Both these samples were then split into two parts where one set of subsamples without and one with combined standard added were analyzed with a field portable MIMS, and the other two subsamples were sent for laboratory analysis by an accredited commercial analysis laboratory (ALS Environmental). Results for benzene and toluene are presented in Table 2 and Table 3, respectively. As can be seen the results of the analyses with MIMS and those of conventional sampling and analysis (by ALS Environmental) are comparable, both for the real samples and the quality control samples. Actually, the results for the control samples show larger deviations between MIMS measurements and conventional analyses than the quantifiable results of the field samples (E - G). In the majority of cases, the conventional analyses measure lower concentrations, some of them up to 35% lower values (sample H). However, the statistical basis is too weak to draw any firm conclusions. In the quality control sample D (containing injected combined standard) the concentrations of both benzene and toluene show very low measured values in the analysis with conventional methods. This may be attributed to either a fault in the addition of the combined standard to water sample D, or to an error with the combined standard itself in this specific case, as all other samples have reasonable concentrations.

4. Conclusions

An in-field membrane introduction mass spectrometry (MIMS) system using a countercurrent-flow heat exchanger has been successfully tested in the field for online determinations of VOCs in the μg/L range. Optimized parameters with respect to stability and heating power savings were found. This, together with the continuous infusion of toluene-d_8 as an internal standard into the sample stream was used to both achieve stable online calibration and to compensate for signal drift. Quantitative results of in-field MIMS analyses for benzene and toluene of water samples, both from SAGD oil refinery process operation, and from various freshwater bodies in Alberta (Can), and corresponding control (grab) samples analyzed by a commercial laboratory are found to be in good agreement. The technique was successfully used for rapid and simultaneous measurement of volatile organic chemicals in a variety of freshwater samples.

Acknowledgements

The authors gratefully acknowledge the students and staff of the Applied Environmental Research Laboratory (AERL) for their assistance with this project. The authors thank Vancouver Island University and the Norwegian University of Science and Technology for their ongoing support. This work was supported in part by funding from Statoil ASA (Grand No 4502457485).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.enceco.2020.09.003.

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Paper V

Proton Transfer Mass Spectrometry – a short review *draft*

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Introduction

This short review is intended to give a selective overview of environmental applications where proton transfer reaction chemical ionization (PTR-CI) is used as ion source for different mass analyzers. Several reviews of similar topics (1-8) have been published, whereof those of Dong et al. and Badjagbo et al., both published in 2007, appeared to be of most relevance. The review by Dong et al. (2) seems to cover the topic of this review, but as the full text only was available in Chinese to the author, this was not possible to establish to full extent. Two larger reviews summarized the status in 2009 (9) and in 2017 (focused towards atmospheric sciences) (10), and a book was published on PTR-MS in 2014 (10). A review of Biasioli et al. also included other direct-injection MS techniques for Volatile Organic Compound (VOC) analysis (11). The span of articles used in this review covers mid-1990s and up recently.

The mass analyzers used in conjunction with PTR include: Single (Linear) Quadruple, Triple Quadruple, Ion Trap (IT), Time of Flight (TOF) and Ion Cyclotron Resonance (ICR). The aforementioned analyzers and their applications will be reviewed separately.

Chemical ionization (CI) and hence proton transfer differs from classical electron ionization mass spectrometry because bimolecular processes are used to generate analyte ions. The process of these bimolecular reactions requires sufficiently large number of ion-molecule collisions during the dwell time of the analyte in the ion source (12).

Proton transfer forms ions from a neutral analyte M in CI by the following reaction: (12)

$M + [BH]^+ \rightarrow [M+H]^+ + B$

Sources of protons include water vapor, ambient air and internal CI gas. In PTR-MS the most used proton source is the hydronium ion formed from water (12).

Other cations than H_3O^+ for charge transfer reaction MS may be obtained by selecting another source gas than water (e.g. O_2), or by selecting the more elaborate SIFT (Selected Ion Flow Tube) technique, providing selected ionization ions such as NO^+ or O^+, thus generating alternative selectivities and mass spectra.

PTR-MS instruments comprises an ion source (often a hollow cathode discharge ion source) to produce primary reagent ions (H_3O^+), a flow drift tube and a mass spectrometer to separate, detect and quantify ions (13), see figure 1 for a schematic view.

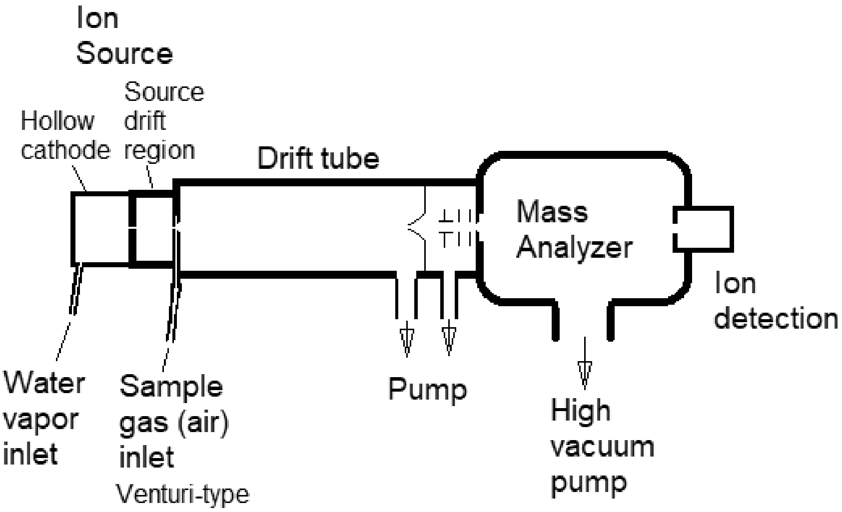

Figure 1: Schematic representation of a PTR-MS instrument(14)

Selected applications of different PTR-Mass Spectrometer types

Single Quadruple Mass Analyzer

In the pioneering paper of PTR MS (13) a quadrupole-based system was used to analyze both human breath, indoor air and air at a city road crossing, sampled off-line, at low ppb levels.

A further development of this PTR-MS instrument showed the ability to detect compounds down to the low pptv range for on-line monitoring of VOCs, making it possible to observe the time-dependence of measured concentrations of selected aromatic VOC analytes between day and night levels outdoor. These data allowed the calculation of detection limits of 2 to 5 pptv. It was also emphasized that this equipment now was of a size that made it transportable, and mobile (14).

A PTR-MS instrument was calibrated for benzene- and toluene measurements in ambient air and its dependence on humidity was investigated. The findings were verified in a field inter-comparison by comparing PTR-MS measurements of benzene and toluene with gas chromatographic analyses of gas samples. It was also observed that the humidity dependence was varying with the type of analyte (15).

A compact atmospheric pressure chemical ionization mass spectrometer (APCI-MS) has been utilized in the on-line monitoring of dimethyl sulfide (DMS) in seawater. DMS was measured in air equilibrated with flowing seawater across a porous Teflon membrane. The gas stream was diluted with air containing an isotopically-labelled internal standard and DMS was ionized at atmospheric pressure by proton transfer from water vapor (16). The hydronium ions and ion clusters are generated by passing the humid air with the analyte over a radioactive β-emitting ^{63}Ni foil, where the emitted electrons initiate the ionization process.

Drying and wounding of plant material during harvest of crops may causes VOC emission to the atmosphere. A proton-transfer chemical ionization mass spectrometer (PT-CIMS) has been used to measure these oxygenated volatile organic compounds e.g. alcohols, esters, aldehydes and ketones (17).

When studying VOC emissions from wounded leaves, isomeric compounds could be separated in a coupled gas chromatography-PTR-MS system for identification and quantification. However, gas chromatography run lengths of 30 minutes drastically reduced measurement frequency (18). This could be dramatically improved by coupling Fast GC to the PTR-MS system, reducing cycle time to 1.5 minutes for the analysis of monoterpenes in air (19).

As a part of the Nitro Europe field study, a PTR-MS method was developed for the time-resolved measurement of ammonia (NH_3) emitted from grassland (20). The PTR-MS method was modified by the use of O_2 instead of H_2O, to generate O_2^+ as the reactant ion (changing the mechanism from a PTR to a charge transfer reaction, CTR) (21).

Many volatile organic compounds are photo-oxidized to oxygenated volatile organic compounds (OVOCs) and contribute to both the gas phase and secondary organic aerosols (SOA). PTR-MS has shown to be a useful tool for determining many of these compounds in ambient air (22).

A PTR-MS was adapted by employing NO^+ as the ionization reagent instead of water vapor, by switching the reagent ion source gas to dry air. The advantage of dry air over water vapor is that it is a cleaner reagent gas. Its only minor impurity, NO_2^+, can be kept to below 2% of total ion intensity by controlling operational conditions of the hollow cathode ion source. This CTR technique allowed real-time on-line measurement of 1,3-butadiene in a suburban atmosphere at sub-ppb levels (23).

A PTR-MS instrument was modified for short time response (<2 s total cycle time), tolerance of shock and vibrations of a mobile laboratory and necessary sensitivity for rapidly changing hydrocarbon concentrations. By on-road measurements in the Mexico City metropolitan area selected organics emissions from vehicle traffic exhaust were monitored, including methanol, acetaldehyde, acetone, methyl tertiary butyl ether (MTBE), benzene and toluene (24).

By rapidly switching between H_3O^+, NO^+ and O_2^+ as reagent ions in a SIFT-MS system exhaust gas emission from a Caterpillar 3304 diesel engine could be analyzed both on-line and in real time (25).

PTR-MS was used for on-line measurements of VOC concentrations in diesel engine exhaust as a function of engine load. Calculated sensitivities for non-polar species were found in agreement with experimental results with gas standards. A slight humidity-dependent sensitivity was also observed. Complex mass spectra were observed resembling typical alkane fragmentation patterns for EIMS. In the exhaust small aldehydes (C1 and C2) dominated at all engine loads over small aromatics, the latter increasing at higher loads. Compositions determined by PTR-MS were in agreement with literature values determined by gas chromatography, and about 75% of the PTR signals could be assigned to organic ions. (26).

By utilizing a spray inlet coupled with a PTR-MS Zou et al. developed a method to analyze benzene in aqueous samples which had low detection limits, short response times and good reproducibility. Ionization of the water vapor was accomplished by a glow discharge ion source (27). The same author also has reported utilizing the same ionization technique for rapid and sensitive monitoring of multiple VOCs in aqueous samples, offering short response times, low LODs and very good repeatability. Target analytes in this study were acetonitrile, acetaldehyde, ethanol, acetone, ether and methylbenzene (28).

Triple Quadruple Mass Spectrometer

Environmental application of proton transfer chemical ionization coupled with triple quadruple mass spectrometers seems to be much less common than with other mass analyzers. The existing literature involving this coupling seems to orientate towards comparisons between selections of ionizing reagents, studies of kinetics, molecular structures and fragmentation pathways (29-36).

Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) was used to find responses to selected polycyclic aromatic compounds (PACs) as a function of both analyte solution solvents and ion source (nebulizer, sheath, bath) gases. These studies were done on light gas oil samples collected from Syncrude Canada Ltd. (37).

Ion Traps

Cisper et al. demonstrated in 1997 the use of membrane introduction mass spectrometry for determination of aqueous SVOCs utilizing electron ionization, charge exchange ionization and proton transfer chemical ionization. The authors stated that proton-transfer chemical ionization achieved higher response for the determination of 2-chlorophenol than electron ionization (38).

Allen et al. investigated further on the topic of analysis of benzene (VOC), naphthalene (SVOC) and ferrocene (organometallic compound) in aqueous solutions using membrane inlet mass spectrometry, with a proton-transfer chemical ionization ion source. The authors report an increase in signal intensity from 2 to 800 compared to electron ionization. The same compounds were also analyzed in air utilizing oxygen, O_2, for charge transfer CI (39).

In the article by Parzeller et al. the authors investigated the advantages of proton-transfer ion trap mass spectrometry (PTR-ITMS) over PTR linear quadruple mass spectrometers. The two main advantages of PTR-ITMS are the ability of specific identification i.e. overcoming problems with mass overlaps (isobaric compounds and isomers) by the possibility to use MS/MS, and a higher duty cycle (40); a disadvantage of PTR-ITMS was a lower sensitivity.

A method for quantitative determination of VOCs by a proton-transfer reaction-linear ion trap mass spectrometer (PTR-LIT) system was developed by Mielke et al. (41). This instrumentation enabled MS/MS measurements and, thus, allowed quantitation by mass spectral differentiation of isoprene, methyl vinyl ketone and methacrolein.

Ion Cyclotron Resonance Mass Spectrometry (ICR)

Ion cyclotron resonance mass spectrometry is not a widely used mass analyzer for environmental applications. As ICR has such a big advantage in mass resolution compared to other conventional mass analyzers (42-47), its field of use has mainly been focused in the field of larger molecules e.g. proteomics (proteins) and peptides (48-50). Its price and size make it a non-fieldable technique used for special tasks that require extreme high-resolution mass spectrometry.

Sarrabi et al. (51) developed a method for monitoring thermal oxidation of polypropylene with proton transfer Fourier transform ion cyclotron resonance mass spectrometry (PTR-FTICR). This method offered real time monitoring of the oxidative degradation of polypropylene, producing VOCs.

Time of Flight Mass Spectrometry (TOF)

PTR-TOF is the second most used combination of PTR source and mass analyzer, and the second type of system that is commercially available. Its advantage is the potentially extremely high scan speed of the TOF, and more important even, its high resolution capabilities which allow the separate identification and quantitation of compounds of identical nominal mass but different element composition – a possibility not available with low resolution mass analyzeres (52).

Blake et al (53) describe a proton-transfer reaction time of flight mass spectrometer for the determination of VOCs. The system uses radioactive α-particle emitting ^{241}Americum as the ionization source for the gases O_2, NO/N_2, NH_3 and H_2O. The authors explain, in detail, the advantage of TOF over QMS in terms of mass resolution, mass range and ability to better resolve complex mixtures.

Tanamito et al. developed a proton transfer reaction-time-of-flight mass spectrometer (PTR-TOFMS) for real-time measurements of volatile organic compounds (VOC). A custom-built discharge source enhanced the sensitivity over the commercially available radioactive sources. The detection limits for acetaldehyde, acetone, isoprene, benzene, toluene and *p*-xylene were determined to be at the sub-ppbv levels (54).

A chemical ionization reaction time-of-flight mass spectrometer (CIR-TOF-MS) with H_3O^+ as primary chemical ionization source was used in the determination of concentrations of OVOCs down to 10 ppbv. Measurements were done in real-time (55).

An on-line breath gas analysis by proton transfer time of flight mass spectrometer (PTR-TOF) has been developed for the sensitive detection of VOCs. Time of flight instruments allows for the measurement of a complete mass spectrum within a fraction of a second, and the high mass resolving power enables the separation of isobaric molecules and the recognition of their chemical structure (56).

By utilizing a membrane inlet interface to introduce sample into a PTR-MS, Beale et al. (57) developed a method for analyzing methanol, acetaldehyde and acetone in seawater. This method offered good selectivity, but compared to other methods, the membrane inlet showed limitations in terms of permeation rate of compounds through the membrane.

Baudic et al. (58) utilized a PTR-MS to measure a wide range of VOC in Paris megacity. The measurements where done from January to February 2010 to show the seasonal variability of atmospheric VOC and their various associated emission sources.

Recent developments within PTR-MS have shown the advantage of combining ionization techniques to acquire a broader selection of target analytes to be monitored.

Zhang et al. (59) utilized a dipolar proton transfer mass spectrometer (DP-PTR-MS) to be able to analyze VOC's and inorganic gases whose proton affinities are greater than that of H_2O, and thus not accessible by normal PTR. The hydroxide ion (OH^-) can be used to identify VOC's, cooperating with the reagent ion H_3O^+, and also for some inorganic gases like CO_2 (in negative ion mode). For the accurate detection of NH_3 , which suffers from interferences in PTRMS with water, the reagent ion $(CH_3)_2COH^+$ can be used. These three reagent ions can be switched depending on the compound to be analyzed for (59).

Sulzer et al. (60) describe a modification to the PTR-MS instrument that allows to switch from proton transfer ionization to charge transfer reaction (ionization) (CTR), by changing to reagent gas types that allow CTR. This offers the capability to analyze VOC through PTR with water, and CO, CO_2, CH_4, NO_X and SO_2 through CTR using krypton as the reagent gas, requiring a high-resolution TOF MS system for resolving interferences of some isobaric analytes and contaminants.

Conclusion

Proton transfer reaction mass spectrometry has proven to be a highly sensitive, fast and mobile technique for identification and quantification of volatile organic compounds in air, and with some restrictions, also in water. The addition of alternative ionization methods, reagent ions, increased sensitivities and mass spectral resolution power have strengthened the position of this technique in recent time, and made it the method of choice for the analysis of organic compounds in trace concentration in air, especially where mobile detection is required on ships, planes or in cars. The accessibility of high-resolution MS allows separate observation of isobaric compounds, and the possibility of using MS/MS has been shown to allow identification of isomers, in favorable cases - if they produce distinguishable dissociation patterns.

PTR-MS has found application not only in environmental analysis of atmosphere and water bodies, but also in food science, medicine (breath analyzers), biology and biotechnology, a.o. New capabilities are also created by combining the PTR-MS data with other data into powerful information (topological, chronological, meteorological etc.).

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ISBN 978-82-326-5064-4 (printed ver.)
ISBN 978-82-326-5065-1 (electronic ver.)
ISSN 1503-8181 (printed ver.)
ISSN 2703-8084 (online ver.)

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