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Field-deployed underwater mass spectrometers for investigations of transient chemical systems

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Abstract

The mass spectrometer developments and underwater deployments described in this work are directed toward observations of important reactive and influential inorganic and organic chemicals. Mass spectrometer systems for measurement of dissolved gases and volatile hydrocarbons were created by coupling a membrane analyte-introduction system with linear quadrupole and ion trap mass analyzers. For molecular masses up to 100 amu, the in situ quadrupole system has detection limits on the order of 1–5 ppb. For masses up to approximately 300 amu, the underwater ion trap system detects many volatile hydrocarbons at concentrations below 1 ppb. Both instruments can function autonomously or via interactive communications from a remote control site. Continuous operations can be sustained for up to approximately 12 days. Deployments have initially involved shallow water proof-of-concept operations at depths less than 30 m. Future modifications are planned that will allow operational depths to 200 m.

Keywords: Mass spectrometry; Membrane introduction; Volatile organic compounds; Dissolved gases

1. Introduction

Development of interpretative and predictive models of the natural environment is a very challenging endeavor. Biological productivity and biogeochemical fluxes are strongly influenced by a diverse variety of key macronutrients, micronutrients, and toxicants [1]. Furthermore, different classes of chemicals can function both synergistically and antagonistically. Adequate bioavailability of essential nutrients such as phosphorous and nitrate can be offset, for example, by limitations in the availability of iron at trace concentrations [2–4], and excess concentrations of elements such as copper can limit the productivity of biological systems that are nutrient replete [5,6]. The intertwined relationships between biological productivity and the solution concentrations of a wide variety of key chemicals compels the development of increasingly comprehensive environmental monitoring capabilities.

In addition to problems surrounding the diversity of analytical measurements that are required to adequately characterize biogeochemical systems, the distributions of organisms in the environment are inherently patchy and time-dependent [7,8]. Ever increasing recognition that environmental systems are severely undersampled has motivated development of improved monitoring systems to enhance both the spatial and temporal coverage of environmental observations. Among the analytical methodologies best suited to address requirements for measurement diversity, mass spectrometry (MS) is a particularly noteworthy example. Mass spectrometry provides sensitive analytical access to an extraordinary range of organic and inorganic chemical species [9–11]. Whereas mass spectrometry offers, in general, the possibility of panoramic chemical analysis, in situ analysis adds capabilities for adaptive sampling, rapid chemical mapping, detailed measurements of temporal variations, and improved safety and endurance in hazardous environments. Toward the goal of adding new dimensions to environmental measurements, and in view of the inherent versatility and sensitivity of mass spectrometry, development of MS systems for in situ analysis of seawater, lakes and rivers has been undertaken. The membrane introduction mass spectrometry (MIMS) systems described in the

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present work were developed to facilitate environmental measurements of important natural and anthropogenic chemicals. MIMS systems are, for example, well suited to high-resolution observations of carbon fixation and remineralization (i.e., primary production and respiration) via contemporaneous measurements of dissolved O_2 and CO_2. MIMS also provides an excellent means of assessing the distribution and dispersion of volatile organic carbon species subsequent to inadvertent or surreptitious releases of hydrocarbons to the environment.

Submersible MS development faces substantial challenges and limitations [12,13]. In situ systems must function over a considerable range of external hydrostatic pressures while a system's ion optics is maintained at high vacuum. Temperature and salinity are important, but unconstrained, variables. In the absence of sample pretreatment, the concentrations of trace reactive analytes must be determined in a complex and variable chemical matrix. Power requirements can put substantial constraints on mission longevity. Finally, in order to fully realize the potential of real-time in situ measurements, development of remote operation strategies and intelligent feedback algorithms, a challenging process, is highly desirable.

Both linear quadrupole and ion trap mass analyzer systems have been developed for underwater analysis of gases and volatile organic species. The configurations and principles of operation of membrane introduction MS systems are described, and several representative field experiments that demonstrate the systems' capabilities are presented. Issues arising from efforts to create algorithms for real-time mapping of chemical plumes are discussed along with potential applications of underwater MS for observation of dynamic biogeochemical systems.

2. Experimental procedures

2.1. Instrumental configuration

In anticipation of requirements for frequent reconfiguration, especially with respect to the mass analyzer and sam-

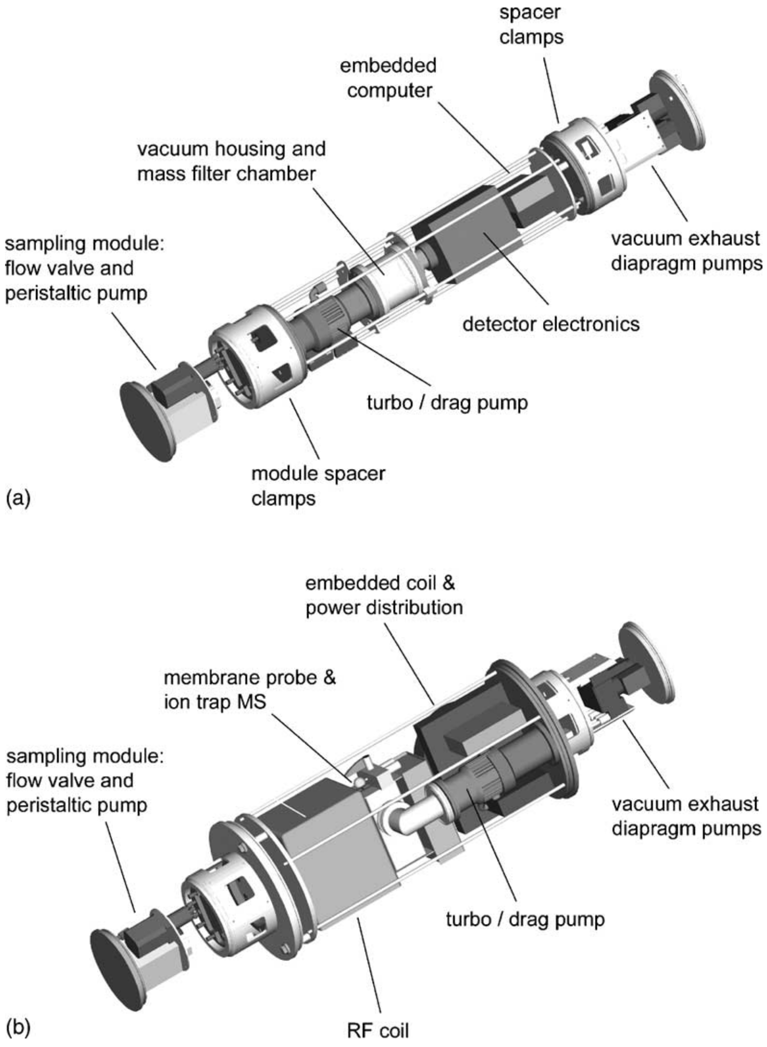

Fig. 1. (a) Underwater linear quadrupole mass spectrometer system. Mass 39 kg; length 1.40 m; diameter 0.19 m. (b) Underwater ion trap mass spectrometer system. Mass 68 kg; length 1.35 m; large diameter 0.31 m; small diameter 0.19 m.

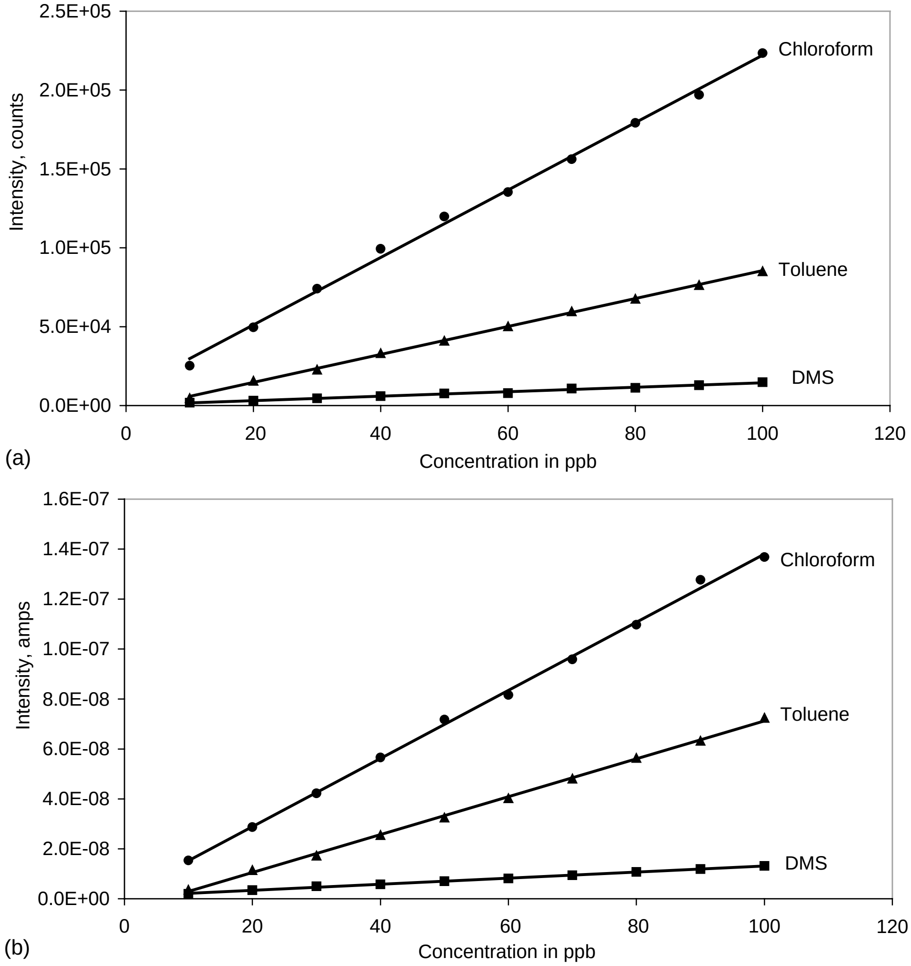

Fig. 2. (a) VOC calibration lines generated on the underwater ion trap MS (chloroform: $y = 2138x + 8382$, $R^2 = 0.9974$; toluene: $y = 886x - 3038$, $R^2 = 0.9993$; DMS: $y = 142x + 282$, $R^2 = 0.9899$. (b) VOC calibration lines generated on the underwater linear quadrupole MS (chloroform: $y = 7 \times 10^{-09}x + 2 \times 10^{-09}$, $R^2 = 0.9985$; toluene: $y = 8 \times -10^{-10}x - 5 \times 10^{-09}$, $R^2 = 0.9990$; DMS: $y = 1 \times 10^{-10}x + 7 \times 10^{-09}$, $R^2 = 0.9980$).

ple introduction systems, the general design of the mass spectrometers is modular. Three pressure vessels separately house the sample intake subsystem, the mass analyzer subsystem and the roughing pump subsystem (Fig. 1). The linear quadrupole system (Inficon Inc., Syracuse, NY, USA) and ion trap system (Saturn 2000, Varian Analytical, Walnut Creek, CA) currently have identical intake and roughing pump subsystems. Introduction of analytes into the MS systems is accomplished via membrane diffusion. Membrane introduction is simple and robust, and polydimethysiloxane (PDMS) membranes provide very low detection limits for dissolved gasses and volatile organics [14,15]. A detailed description of system design and component sources is found in Short et al. [16,17].

2.2. *Laboratory evaluations*

Standard calibration curves were generated in the laboratory to assess the instrumental response to dissolved volatile organic and inorganic substances (Figs. 2 and 3). Fig. 2 shows the response of the underwater linear quadrupole system (Fig. 2b) and the underwater ion trap system (Fig. 2a) to volatile organic compounds (VOCs). Target VOCs were diluted in seawater to concentrations ranging from 10 to 100 ppb, and introduced into the mass analyzer through a membrane interface. A typical CO_2 standard calibration curve for the linear quadrupole system is shown in Fig. 3. CO_2 standard solutions were prepared by diluting a 0.05 mM $NaHCO_3$ stock solution with milliQ ultrapure water. The resulting solutions, which ranged in concentration from 0.05 to 0.5 mM, were acidified with 1 M HCl immediately prior to introduction into the quadrupole MS.

Ion intensities were recorded as a function of time for each analysis. Plotted intensities (Figs. 2 and 3) represent the integrated peak areas in these time series analyses. All calibration curves show linear responses over an order of magnitude and low detection limits. For VOCs the sensitivity of the ion trap system is typically an order of magnitude greater than that of the linear quadrupole system.

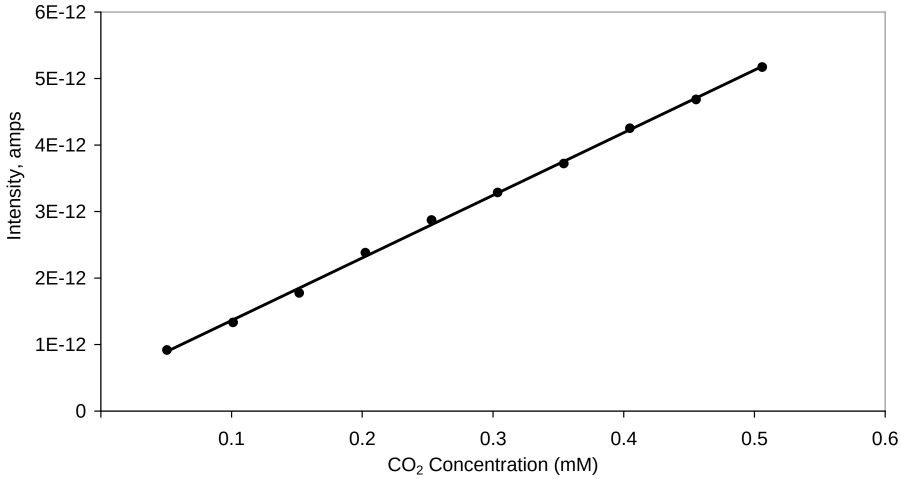

Fig. 3. CO_2 calibration lines generated on the linear quadrupole MS ($y = 9\times10^{-12}x + 4\times10^{-13}$, $R^2 = 0.9990$).

3. Field measurements

The performance characteristics of the underwater MS systems have been evaluated in a variety of field deployments. These evaluations have included in situ monitoring of municipal effluents, hydrothermal vents and urban embayments. While all of these locales present severe conditions for a mass spectrometer, arguably the most rigorous test was encountered during deployments within a wastewater treatment plant (St. Petersburg, FL, USA).

3.1. Monitoring urban wastewater

The linear quadrupole MS was deployed in sewage influent from the first treatment stage after coarse filtration of reclaimed water and raw sewage. The MS was immersed in the treatment tank and data acquisition was continuous. At 12 min intervals the quadrupole MS sampling system autonomously injected 1 mL samples of wastewater into a continuously flowing stream of charcoal-filtered wastewater in contact with the membrane interface. The overall flow rate was maintained between 0.5–1 mL min^{-1}, and the stream of flowing water was heated to 60 °C. The quadrupole mass filter was programmed to monitor ion intensities of 12 selected *m*/*z* values. The dwell time at each *m*/*z* was 512 ms, and cycling through all 12 ion masses was complete in 6.1 s. The selected *m*/*z* values were appropriate to a range of common VOCs, including primary and secondary diagnostic ions for chloroform (*m*/*z* 83 and *m*/*z* 85), and primary and secondary diagnostic ions of toluene (*m*/*z* 91 and *m*/*z* 92).

Wastewater influent tank monitoring data are shown in Fig. 4. The ion plot for *m*/*z* 83, the primary diagnostic ion for chloroform, is shown in Fig. 4a. Chloroform is a byproduct of the chlorination of drinking water [18]. The presence of chloroform was corroborated by the strong similarity between Fig. 4a and a plot of the secondary diagnostic chloroform ion (*m*/*z* 85, not shown). Similarly, the primary diagnostic ion of toluene, *m*/*z* 91 (Fig. 4b), was corroborated by a plot of *m*/*z* 92, a secondary diagnostic ion of toluene. Although there are clear distinctions between the chloroform and toluene concentration patterns in the effluent (Fig. 4), there is also a good overall correlation. For example, both peaks exhibit a periodic daily maximum at approximately 5 pm local time. Based on laboratory calibrations the maximum intensities shown in Fig. 2 correspond to concentrations in the10–50 ppb range for both substances. This estimate is in general agreement with an independent laboratory analysis of samples taken from the influent tank earlier in the year.

Data acquisition was discontinued after 30 h due to clogging of the stainless steel intake filter and the membrane capillary. All other instrument subsystems functioned properly for the entire deployment period. This test demonstrates the robust character of the underwater quadrupole MS system. For long term sampling in waters with exceptionally high turbidity, it would be recommended that the MS inlet line included a filter that could be periodically replaced.

3.2. Analyses of dissolved gases at a submarine hydrothermal vent

The underwater quadrupole MS was used for investigations of gases in a submarine hydrothermal vent field in the Gulf of Mexico, approximately 12 miles south of Sanibel Island, Florida. The quadrupole MS, along with two lead–acid battery packs (sufficient for approximately 4 h of operation) were deployed on a PVC frame. The system was adjusted to neutral buoyancy and maneuvered by SCUBA divers into position at a principal vent of the spring. Unfiltered seawater or spring water was sampled continuously. The mass filter was programmed to cycle between 23 ion masses with a dwell time of 64 ms ion^{-1}. Sample water was not pre-heated for these measurements. Temperature at the sample inlet was recorded continuously.

Fig. 5 shows typical data obtained at Rusty Springs, a geothermal vent located at a depth of 17.5 m. The plot of

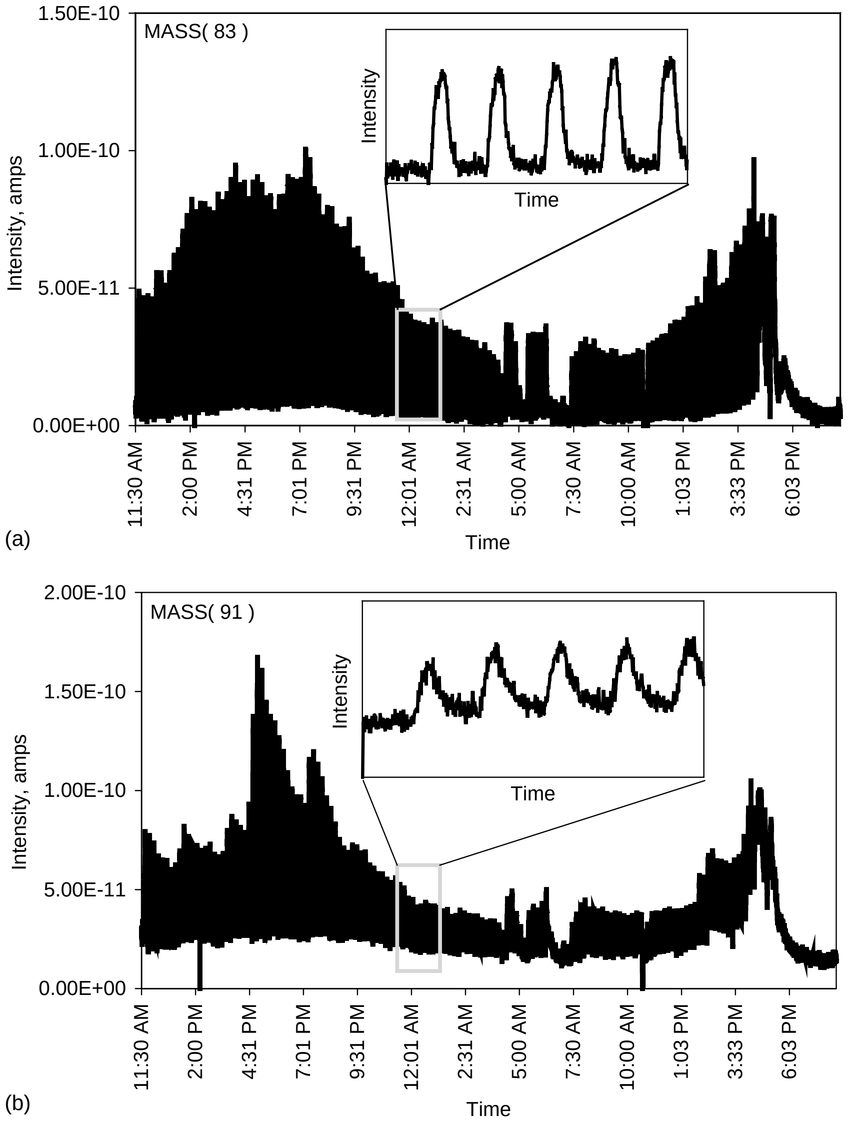

Fig. 4. In situ analyses by underwater linear quadrupole MS immersed in City of St. Petersburg influent wastewater tank: (a) time series intensity data for *m*/*z* 83, diagnostic for chloroform; (b) time series intensity data for *m*/*z* 91, diagnostic for toluene.

ion intensities (Fig. 5) corresponds to N_2 (*m*/*z* 28), O_2 (*m*/*z* 32), Ar (*m*/*z* 40) and CO_2 (*m*/*z* 44). While these ion intensities are nominally proportional to the aqueous concentrations of each gas, some degree of interference is expected at each *m*/*z* value. For example, the *m*/*z* 28 signal is principally due to $N_2{}^+$, but to some extent also CO^+ ions created by electron impact ionization of CO_2. The vent water was typically as much as 10 °C warmer than the surrounding seawater. Consequently, some of the variations in ion intensity in Fig. 5 can be attributed to differences in water temperature. Nevertheless, there are clear differences between vent water chemistry and the surrounding seawater that can only be attributed to the unique chemical signature of the vent waters. For example, it is evident that the hydrothermal water is highly depleted in *m*/*z* 32 (presumably O_2) and enriched in *m*/*z* 44 (presumably CO_2). Shipboard measurements of equilibrated samples taken from the vent and surrounding seawater corroborate these conclusions [19].

The membrane interface has been redesigned to allow exploration of vents at depths greater than 200 m. The redesigned interface is amenable to incorporation of a gas chromatograph (GC) column. Consequently we are exploring use of a GC and a small magnetic sector MS for real-time in situ isotopic analysis.

3.3. Monitoring VOCs in an urban marina

In an attempt to monitor VOC components attributable to motorized boat traffic, the underwater ion trap MS was deployed in a marina at the Port of St. Petersburg. The MS was protectively housed in an autonomous underwater vehicle (AUV) nosecone in an area of low-speed boat traffic. The sampling system operated by injecting 1 mL samples

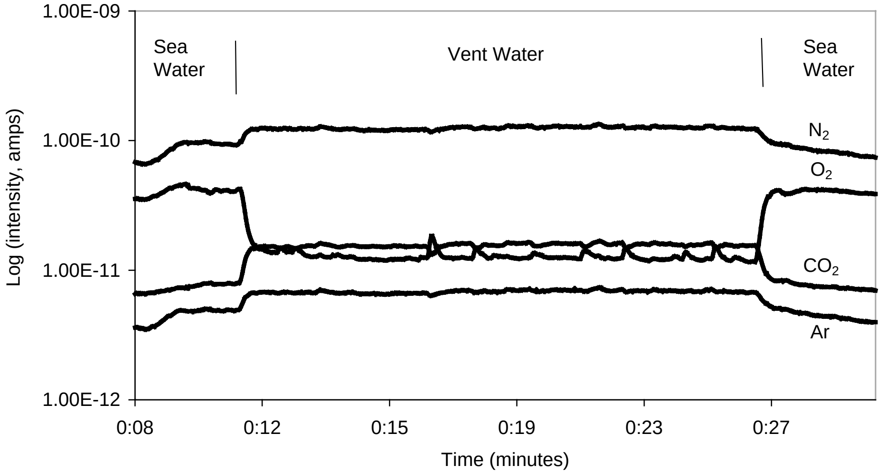

Fig. 5. In situ underwater quadrupole analyses of dissolved gases at a shallow marine geothermal vent in the Gulf of Mexico. Species identifications are N_2 (*m*/*z* 28), O_2 (*m*/*z* 32), Ar (*m*/*z* 40) and CO_2 (*m*/*z* 44).

of harbor water in a continuous stream of deionized water. Five samples were collected per hour, and each sample was heated to 35 °C. The ion trap was run continuously for 72 h on an external power tether, with a direct Ethernet link between the onboard computer and a laboratory PC at the University of South Florida College of Marine Science. Fig. 6 shows a typical example of the time series data in this deployment. The upper plot shows a time series plot of *m*/*z* 91 ion intensity (diagnostic of alkalated benzenes). The signal to noise ratio for these data is on the order of three. Based on laboratory evaluations of aqueous toluene solutions (Fig. 2), the *m*/*z* 91 intensities in Fig. 6 correspond to alkylated benzene concentrations less than or equal to 5 ppb. The observed intermittent signals for *m*/*z* 91 are likely attributable to small-boat traffic. The lower plot in Fig. 6 shows concurrent data obtained for the *m*/*z* 83 ion. This plot shows a pattern that is indistinguishable from random noise. As chloroform is not an expected fuel combustion product, the *m*/*z* 83 trace indicates that the instrument was stable while significant variations were observed for *m*/*z* 91. These observations demonstrate the capacity of in situ mass spectrometry for long-term chemical monitoring of VOC discharges in environmentally regulated harbors.

3.4. *Real-time mapping of chemical discharges*

The capability of MS instruments for identifying sources of anthropogenic chemicals in marine systems was exam-

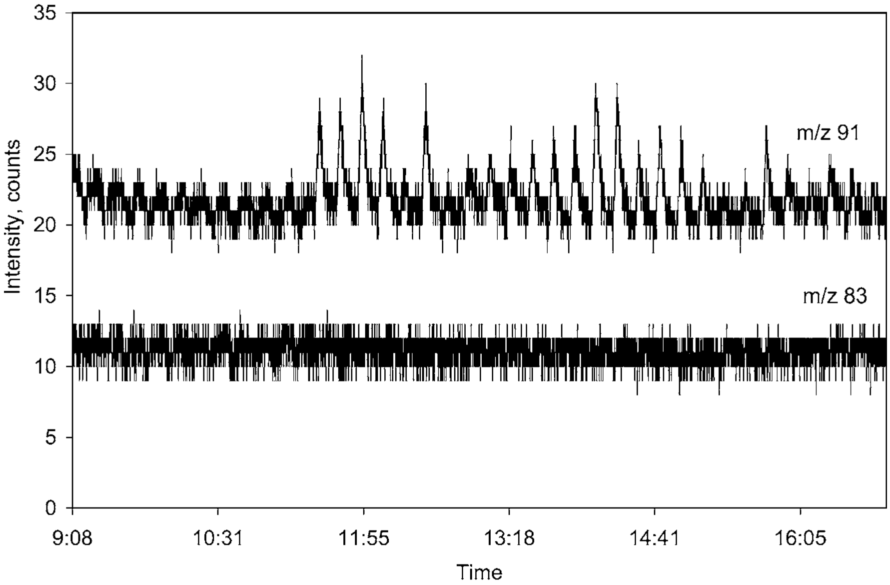

Fig. 6. Underwater ion trap MS analyses in a St. Petersburg Marina. The top trace is diagnostic of alkylated benzenes and the bottom trace, diagnostic of chloroform, demonstrates instrumental stability.

ined in deliberate discharge experiments. The experiment described here involved the underwater ion trap MS. An anchored boat was used to release two liters of dimethyl sulfide (DMS) into a steady tidal current over a one hour period. The MS was navigated through the DMS plume in multiple transects at varying distance from the source. Global positioning system (GPS) data were collected at the release point and on the mobile MS platform. The underwater ion trap MS was mounted in an autonomous underwater vehicle (AUV) nosecone and towed across the target plume in a series of 8 transects between 18 and 64 m from the DMS source. Seawater was pumped continuously into the membrane introduction probe at 4 mL min^{-1}. The sample was heated to 40 °C, and averaged mass spectral scans (40–250 amu) were recorded every 5 s. The MS was controlled from a laptop computer through wireless Ethernet while the towboat was maneuvered with an electric trolling motor.

The MS time series data were merged with GPS data to create DMS distribution maps. Fig. 7 shows ion intensity maps for *m*/*z* 62, the DMS primary diagnostic ion. The mapped area in Fig. 7 is roughly 80 m (latitude) by 250 m (longitude). MS position locations are accurate to ±1 m relative to the DMS discharge point. Fig. 7a shows the ion in-

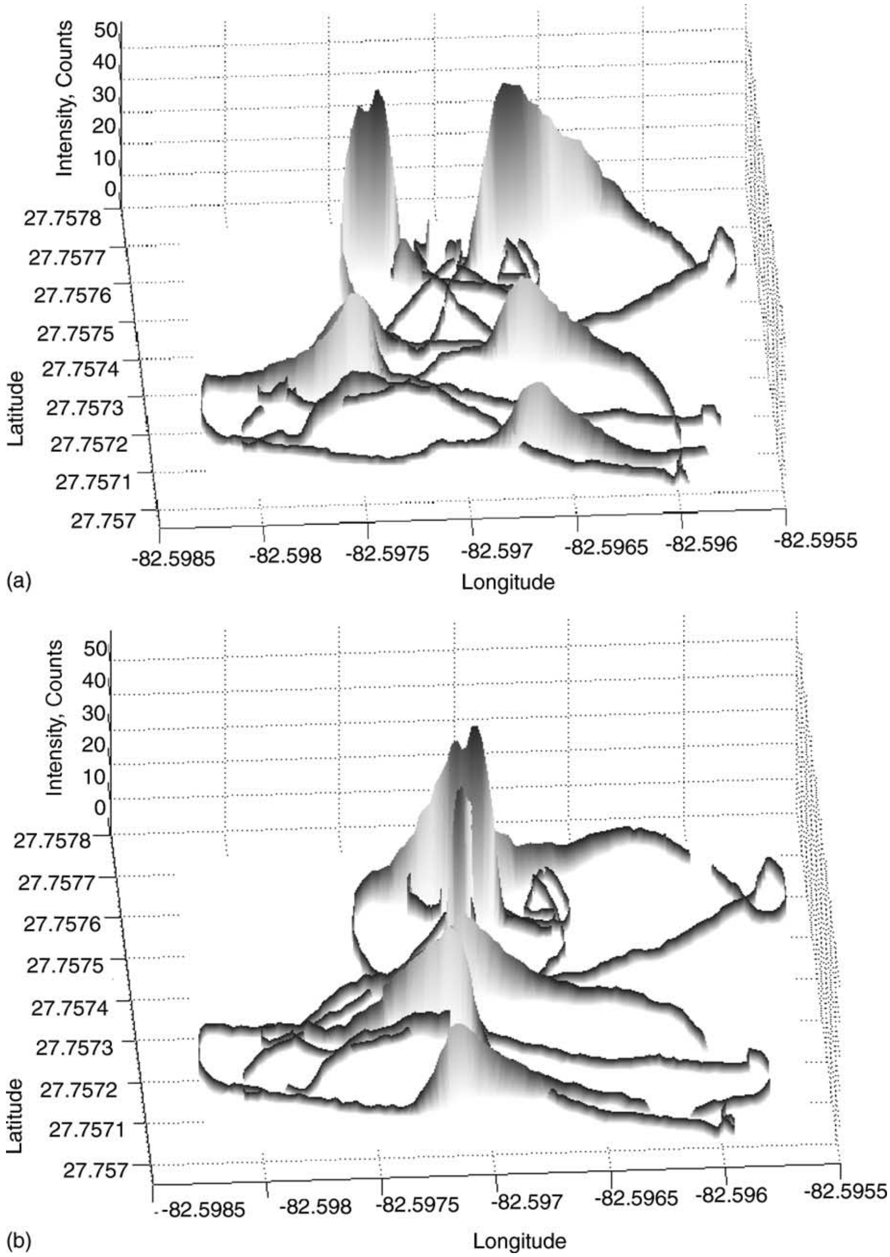

Fig. 7. Underwater ion trap MS analyses for *m*/*z* 62, primary diagnostic for DMS, in a Tampa Bay plume mapping experiment: (a) intensity data are directly recorded relative to MS position (latitude and longitude); (b) intensity data relative to MS position accounting for the 80-s lag between sample acquisition and analysis.

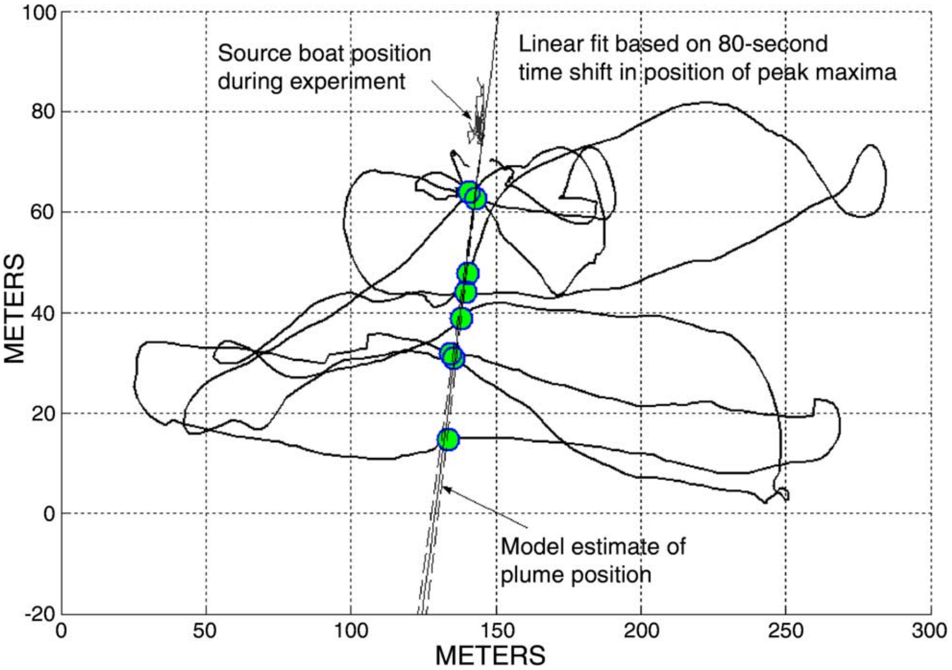

Fig. 8. Underwater ion trap MS plume mapping experiment: location of *m*/*z* 62 maxima after adjusting for 80-s difference in times of sample acquisition and analysis.

tensity data as a function of position in real-time. The figure exhibits an apparent bimodal dispersion due to an 80 s offset between sample acquisition and sample measurement. The observed lag was largely dependent on the length of the sampling tube and the flow rate of the sample stream. Fig. 7b shows a map of the DMS plume that accounts for the 80 s offset between sample acquisition and measurement. Observations of a colored dye released with the DMS indicated that the plume dispersion width was approximately 2 m at a distance of 64 m from source. Comparisons of plume width based on dye tracer observations and mass spectrometry observations demonstrated significant broadening of the estimated DMS distribution relative to the visual observations of the plume. This broadening is primarily due to the diffusion characteristics of the sample introduction membrane. One challenge in the development of highly resolved, chemical species maps is to significantly reduce this effect.

Fig. 8 is a two dimensional display of the results from the plume mapping experiment described above. The path of the mass spectrometer/AUV assembly is shown, along with the position of the dispense boat. The locations of the maxima of the peaks shown in Fig. 7 are also shown, after correction for the 80-s offset between sample intake and mass spectrometer response. The plume position can be readily estimated by a linear fit to the locations of these maxima as shown in Fig. 8. This procedure works well when the tidal current is fairly constant over the course of the experiment. In more turbulent conditions the plume behavior may be more complicated and would not be accurately described by a simple linear model.

4. Summary

Underwater mass spectrometry is especially useful in applications that require a very large throughput of samples. Such applications include detailed mapping of naturally occurring chemical distributions and tracing the dispersion of anthropogenic emissions. Synchronous real-time MS and GPS data can be used for adaptive sampling of complex chemical distributions.

Underwater mass spectrometry is particularly useful for observations of multivariate chemical distributions. The in situ instruments described here are capable of detecting gases and VOCs at low ppb concentrations. Although essentially any instrumental introduction system is susceptible to fouling, urban wastewater observations indicate that in situ membrane introduction systems are sufficiently robust to permit long term observations under relatively severe conditions.

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