

# Mass SURFER: a Low-Power Underwater Mass Spectrometer for Monitoring Dissolved Gas, Solutes and Large Organic Compounds

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**Abstract-** We are currently developing two low-power, miniature mass spectrometer-based field-sampling systems-- a "standard" and CE (capillary electrophoresis)-enhanced version-- with an aquatic-based sensor head, vacuum system, pressure case and associated electronics, called Mass SURFER (Mass Spectrometer Using Rotating Fields for Exploratory Research). The units incorporate the Rotating Field Mass Spectrometer (RFMS) developed at JPL, and are capable of 2000+ m deployments. Seawater-soluble gas samples are either admitted through an osmotic membrane boundary into a gas-based field ionizer, or the seawater liquid with its load of dissolved gases can be directly injected into a submersible vacuum chamber via a nano-electrospray nozzle (liquid/vacuum interface). The gas-sampler (first type) incorporates a hydrophobic, silicon-coated membrane. The membrane allows dissolved gases to enter the vacuum interface where small aliquots are sampled. The second interface is an on-line capillary nano-electrospray interface (ESI) capable of high-sensitivity mass spectrometry at nanoliter per minute flow rates. Mass SURFER vacuum levels need only be at the milli-torr level for a quality measurement, and the complete system nominally draws <10 watts when active. The RFMS mass resolution of 1 part in 1000 is comparable with the best of other small mass spectrometers. Its extremely large analytical mass range (from 1 to >100,000 amu) coupled with "soft" ionization techniques make it capable of analyzing practically anything from H<sub>2</sub> and He gas to large dissolved organic compounds such as proteins, peptides and DNA.

## I. INTRODUCTION

As analytical instruments, mass spectrometers have the capability of extremely high sensitivity, isotopic resolution, and wide dynamic range. Field-portable units incorporating mass spectrometers could therefore revolutionize the ocean and earth sciences. However, useful, low-power and compact instruments capable of long-term field applications, especially autonomous units capable of operating in the deep ocean, have been slow in arrival. This delay results from three basic problems of a mass spectrometer-based instrument in earth and similar-density planetary field applications: sample introduction, vacuum maintenance and power consumption. We have largely overcome these obstacles and are currently building and testing miniaturized mass spectrometer-based field sampling systems under contract to the State of Hawaii's Center of Excellence for Research in Ocean Sciences (CEROS).

These systems incorporate the Rotating Field Mass Spectrometer (RFMS) developed at JPL by Steven J. Smith and the JPL Technology Affiliates Program [1], which has very wide dynamic range and operates at modest vacuum levels. The Mass Spectrometer Using Rotating Fields for Exploratory Research (Mass SURFER) is housed within a 6.5-in. OD pressure vessel, 5.5 feet long that is capable of 2000+ m deployments (Fig. 1). Liquids such as seawater with their load of dissolved gases are either directly injected into the vacuum chamber via a nano-electrospray nozzle (liquid/vacuum interface) or soluble gas samples can be admitted through an osmotic membrane boundary into a gas-based field ionizer. The latter inlet approach is the state-of-the-art for most field mass spectrometer instruments, e.g., [2, 3]. The gas-only sampler incorporates a hydrophobic membrane that we have successfully used in the laboratory to 200 bars hydrostatic pressure and in field deployments on Loihi Seamount off Hawaii Island to 1300-m water depth. The direct liquid sampler uses an on-line capillary nano-electrospray interface (ESI) capable of high-sensitivity mass spectrometry at nanoliter per minute flow rates. The challenge for this type of interface is clogging by fine suspended particles (coarse particles can be screened) and salts build-up. Preliminary direct seawater injections have produced no significant deleterious effects. We are also incorporating an on-line capillary electrophoresis column to aid in sample spectral resolution.

## II. DESCRIPTION OF THE INSTRUMENT

### A. The Rotating Field Mass Spectrometer (RFMS)

The RFMS uses "rotating" RF electric fields. It consists of an ionizer, a mass spectrometer and an ion detector (Fig. 2). Each component is briefly described here. The sample flow output is introduced into a liquid nanospray ionization stage. The resulting sampled ions are focused into a beam (50 eV energy with 1 eV energy width) that enters a cell-like region with sinusoidal RF fields that are in the x- and y-direction and differ in phase by 90 degrees. The ions of a particular mass travel in a helix and impact an ion detector at the end of the cell. The ions generate a pattern which appears as a set of concentric circles, much like the lissajou figures generated by a dual channel oscilloscope driven at the same frequency but with the channels differing by a 90 degree phase angle. The choice of RF frequency and amplitude determines the particular ion mass to be selected.



Fig. 1. Mass SURFER prototype prior to pool test. JPL scientist for scale. The pressure housing is 6.5 in. OD by 5.5 feet total length.

RF potentials on the sidewalls of the cells were scanned from 1 to 12 MHz, with a constant amplitude of 20 volts, which are easily generated with simple one "chip" electronics. One intriguing novelty about this method is that clusters, or arrays of cells could be easily fabricated to cover a large area. One cell could be tuned to one specific RF frequency appropriate for one mass, and an adjacent cell could have a different RF frequency that would preferentially select a different mass. Thus simultaneous measurements over several mass ranges are possible. The ion trajectories for both the ionizer and the TOF/RFMS have been extensively modeled using SIMION [4], a commercially available, accurate computer-modeling program which can calculate ion trajectories for ions traveling in an oscillating electric field.

The prototype ionizer, the mass spectrometer cell, and the ion detector (a Faraday cup collector) are mounted in a 2.75 inch vacuum "tee" (Fig. 2). An 8 liter/sec ion pump provides sufficient vacuum pumping, as the system is rough-pumped before a mission and shock-resistant miniature leak valves and a capillary delivery line provide for very small conductance of sample into the RFMS. Since the ions travel helices rather than straight lines, flight tubes can be made short. Unlike the quadrupole, no pole pieces or apertures have to be accurately positioned. The rotating field mass spectrometer does not need a magnetic field and does not require apertures to be precisely placed, nor does it require the precision micro-machining requirements of a

comparable sized miniature quadrupole. The RFMS is a 2 x 2 x 20 mm (and in theory much, much smaller) cell. This represents a technological breakthrough in state-of-the-art miniaturized mass spectrometer design. In general, increasing the aspect ratio (the length to width ratio) increases the resolution accordingly.

### B. The Ionizer

Electrospray ionization (ESI) of analytes is due to charge buildup on the solvent droplets as they evaporate during transport through the ESI interface in a liquid flow. ESI is a "soft" ionization technique that yields abundant molecular ions. Multiple charging of molecules (in particular for peptides and proteins as seen in Fig. 3) is clearly evident and identification of a molecular ion species is made due to different mass-to-charge ratio. The normal electrospray is adapted by two important changes. First, the ESI is directly admitted into the vacuum chamber. Second, the spray is covered by an "anode cap", which is a pinhole aperture held at the desired electric potential of the beam. *This aids greatly in defining the precise energy of the "beam" of ions that are produced.* The now well-established microscale electrospray ionizer design similar to the one by [5] is used. An on-line capillary ESI capable of high-sensitivity MS has been established. Average-sized samples in solution generate ion currents on the order of 0.1 to 1.0 pA, which are easy to measure with a small commercial electrometer. The ESI is optimized for gradient elution of protein samples, but is fully capable of analyzing biologically and geochemically relevant inorganic compounds in solution. Observed flow rates of less than 1 nano-l/min are observed. The drawn fused silica needles have tip inner diameters of 5 micro-meter. This means that only very small samples are needed, and that ESI ionization techniques will allow most of the sample to enter the first vacuum region, with only modest vacuum pumping loads. We have found the nanospray nozzles to be remarkably robust if care is taken to firmly seat the nozzles in a compact polypropylene sleeve. Months of stable operation without serious breakage or clogging of the tips have been accomplished by the JPL nanospray prototype. Similar robust performance has been observed by many groups [6-8].

### C. Experimental Results of the RFMS

Our JPL nanospray tip has run with seawater solutions, and with organic compounds saturated in ethanol solvent and does not clog up, due mainly to the unique vacuum-ion technique that also serves to "vacuum out" the column.

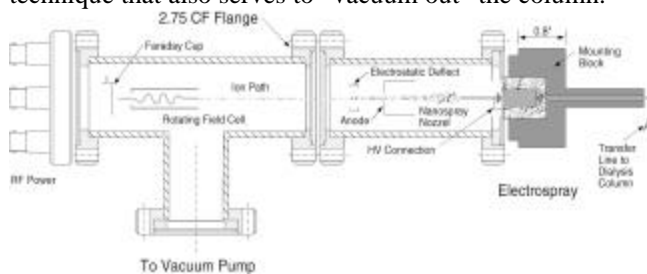


Fig. 2. Diagram of miniature Rotating Field Mass Spectrometer and Nano-Electrospray Interface.

A JPL laboratory version generated a mass spectrum for a variety of materials with better than 1 part in 1000 mass resolution. The RFMS has measured argon and large organic compounds ( $C_6F_{12}$ , mass 300 amu, lysozyme with mass greater than 14,000 Dalton, as well as adenosine, angiotensin, and seawater liquid samples where various mineral solutes are clearly seen. Fig. 3 shows a recent spectrum. The ions that were formed in the ionizer were launched into a 2x2x20 mm sized TOF/rotating field cell. The RF potentials on the sidewalls of the cells were scanned from 2 to 12 MHz, with a constant amplitude of 20 volts.

#### D. Proven Sensitivities

On-line analysis at JPL is performed at the 2 femtomole or less concentration level for peptides like angiotensin. Since the instrument uses a very efficient electrospray (ESI) ionization technique, this corresponds to approximately 1 kHz to 10 Hz of final signal assuming very conservative ion efficiency and mass analyzer transmission efficiencies (i.e.  $10^{-3}$  efficiency for the ionizer, and  $10^{-5}$  transfer efficiency for a low resolution of 1/100 amu). The current minimum detection levels for angiotensin, for example, are in the sub-femtomolar ( $<10^{-15}$  M) range.

For large organic compounds detection, we ran lysozyme, a common protein of formula weight 14,300 amu (see Fig. 3 for a sample spectrum), over a concentration range from  $10^{-4}$  to  $10^{-10}$  molar, recording seven charge states at the various mass to charge ratios. The response of the RFMS is very linear ( $r^2 = 0.988$ ) over five orders of magnitude and proves the sensitivity of detection for large dissolved organics to  $10^{-10}$  molar (sub-nanomolar) concentration levels. We present similar ESI- RFMS response curves for  $Na^+$  and  $Fe^{2+}$  using our inorganic standards set (Fig. 4).

#### E. Natural Spectra

We have made several runs of natural seawater solutions for the CEROS project. Runs using positive electrospray show major peaks for water, dissolved gases such as nitrogen, oxygen and carbon dioxide, and the major dissolved cations (Fig. 5). Negative electrospray produces major peaks for anions such as chloride, sulfate and carbonate ions (Fig. 6).

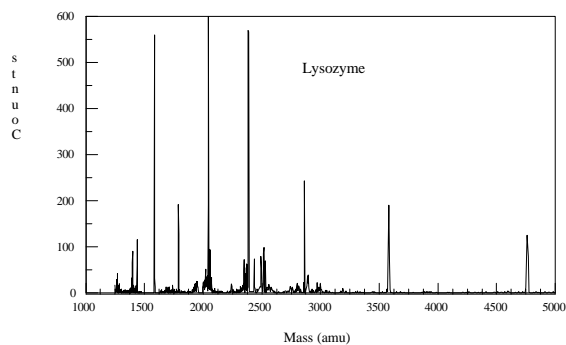


Fig. 3. Lysozyme run with a launch angle of 65 degrees.

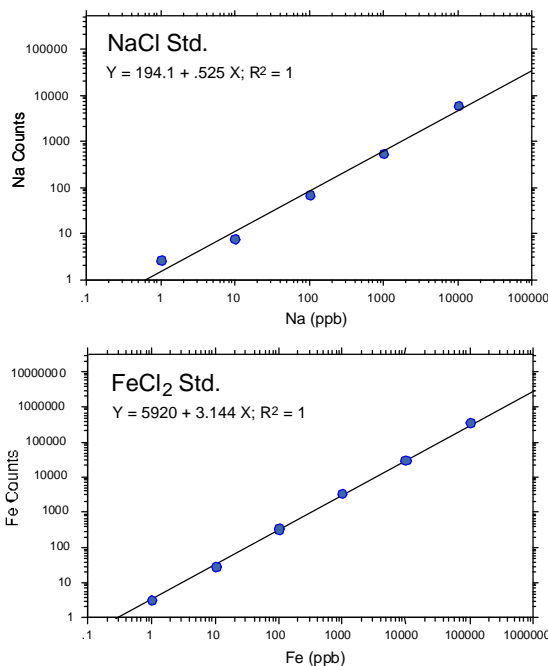


Fig. 4. Plots of  $Na^+$  and  $Fe^{2+}$  concentration versus RFMS signal. Estimated errors are within the data points. Solutions were Fisher AAS standards diluted with 18-megaohm DD water acidified with ultrapure nitric acid to pH 2.

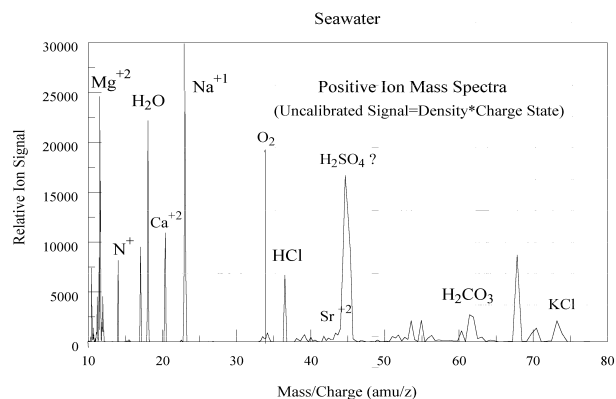


Fig. 5. Positive ion ESI-RFMS spectrum of a seawater sample collected at 1000-m depth from the hydrothermal plume over Loihi Seamount, Hawaii.

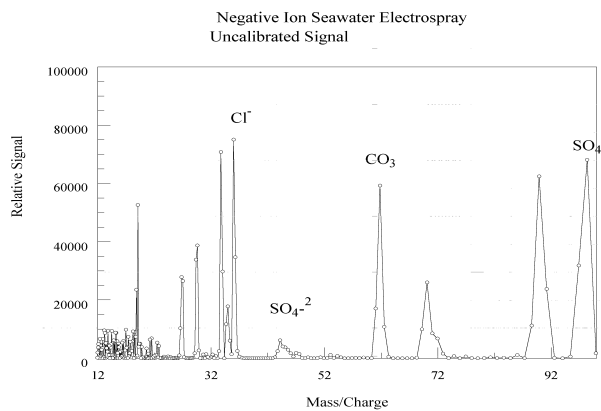


Fig. 6. Negative ion ESI-RFMS spectrum of a seawater sample collected at 1000-m depth from the hydrothermal plume over Loihi Seamount, Hawaii

### F. Power Budget

We conducted a power budget for the Mass SURFER while running in automatic program mode. Peak power is briefly 38 watts, which corresponds to the high frequency end of the RF scans, and abruptly drops (Fig. 7). Main power consumption occurs during the RF scans (averaging 20 watts), whereas most other SURFER operations consume no more than 11 watts, including an external water pump. Sleep or stand-by mode consumes about 4 watts. Most of this power is attributed to the CPU, power distribution board, and the ion pump, which is on continuously. Therefore, the total power budget for a 7.5-minute period conducting two ion scans (positive/negative) per standard/sample pair is approximately 8 watts. It is instructive to compare this power level to the *continuous* power levels of a “field” quadrupole mass spectrometer described by [2] which draws 1500 watts and to another, more recent quadrupole mass spectrometer-based instrument used for in situ marine deployments that draws 250 watts [3]. At approximately 13 V DC, the average current draw per standard/sample pair is approximately 600 milliamps. This sampling rate will produce about 4 sample/standard pairs per hour, or 96 samples per day. Our 12 amp-hr internal sealed Pb-acid battery will last 20 hours and the optional 172 amp-hr external Pb gel-cell batteries (see below) will last 12 days at this sampling rate. At 4 samples per hour, this would generate nearly 2400 spectral scans (+/- ion) for each sample and standard. Use of lower sampling rates and/or higher energy-density batteries will extend these deployment times.

### G. Field Deployment Capabilities

We recently completed the design and fabrication of the shallow-water deployment frame. The frame is completely modular and is composed entirely of light-weight, strong, corrosion-proof materials (Fig. 8). We used fiberglass-reinforced epoxy struts and a fiberglass-reinforced gridded sheet to enable instrument attachments. The frame is bolted and banded together with 316-stainless steel hardware. Four padded feet are used to keep the instruments off the bottom and from moving in any currents. For most field deployments, we will utilize either a Seabird or an Ocean Sensors CTD to measure water temperature, conductivity, pH and dissolved oxygen in tandem with the Mass SURFER. We use two filtration cartridges, a 75 micron pre-filter and a 10 micron filter that allow flow of <10 micron water over the instrument

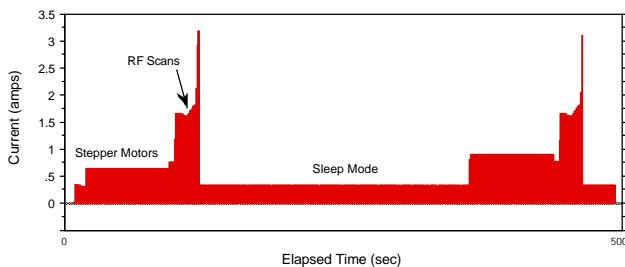


Fig. 7. Graph of Mass SURFER power consumption (as current draw in DC amps) vs. time during a recent bench test.



Fig. 8. Photograph of Mass SURFER, OS 200 CTD, Seabird pump, filtration cartridges and two 86 amp-hr external deep-sea batteries. The deployment frame is designed for a single-point lift.

plenums (Mass SURFER and OS 200 CTD) by the Seabird impeller pump without clogging. A pressurized water test of the external plumbing found no significant leaks. We have also configured two custom 86 amp-hr Pb gel-cell batteries in Deep Sea Power & Light boxes for a combined 172 amp-hr external battery. These can be banded onto the frame for use in long-term monitoring deployments (Fig. 8).

### III. FUTURE BENEFITS

Now that appropriate lab testing of the interfaces and the pressure housings are nearly complete, we plan shallow and deep water field tests of the instrument package in coastal waters off Oahu, Hawaii. Once built, lab- and field-tested, the miniaturized mass spectrometer-based sampling system will have a wide variety of useful applications. Its extremely high sensitivity and low power requirements will allow automated, quasi-continuous, in situ monitoring of chemical pollutants (hydrocarbons, dissolved gases, metals, nutrient solutes, etc.) and microbial populations (via protein profiling) in streams, rivers, wells, coastal waterways and harbors. It can also be used in exploration and in portable surveying mode, especially where real-time data analysis is paramount. Presently, most sampling and monitoring activities involve manipulations by trained field personnel with samples sent to distant, centralized laboratories where the analyses are performed by skilled analysts using conventional, state-of-the-art instrumentation and techniques, including mass spectrometry. Adaptation of the real-time, in situ instrumentation envisioned here will allow elimination of much of the sample handling, thereby limiting potential contamination issues, and will allow for more frequent sampling and rapid indications of rising toxicant levels in waters at key sites where these units are installed.

The goal of the upcoming field-testing program is to establish situations in which this novel instrumentation can

be “road-tested” by acquiring scientific data. The instrument can potentially perform extremely useful environmental surveys both in the deep ocean and in shallow offshore areas, and the technology developed and demonstrated here could be applied to similar environments both nationally and internationally. For example, environmental surveys by the U.S. Navy of explosives and other chemical contaminants could greatly benefit from this ocean sampling system. The U.S. Environmental Protection Agency and various state and county government agencies mandated to monitor groundwater and offshore seawater quality (Depts. of Health and Land & Natural Resources, County Boards of Water Supply) could measure contamination levels at the parts per billion level within minutes with this device.

#### IV. CONCLUSIONS

We have completed a working prototype of a low-power, miniature mass spectrometer-based field instrument that can perform under ambient pressures ranging from 1 to 200 atmospheres (bars), or greater than 2000-m water depth, and we are presently working upon a second, enhanced version. The Mass SURFER vacuum levels need only be at the millitorr level for a quality measurement, and the complete, active system draws only 8 watts. Samples can be directly injected into the RFMS or they can be admitted through an osmotic membrane boundary into a gas-based field ionizer. The RFMS mass resolution of 1 part in 1000 is comparable with the best of other small mass spectrometers. The extremely large analytical mass range of the RFMS (from 1 to >100,000 amu) coupled with “soft” ionization techniques make the Mass SURFER capable of analyzing light gases such as H<sub>2</sub> and He as well as large dissolved organic compounds such as proteins, peptides and DNA fragments. Its extremely high sensitivity and low power requirements will allow automated, quasi-continuous, in situ monitoring of the chemical composition of natural waters, hydrocarbon and other chemical pollutants, and microbial populations in streams, rivers, wells, coastal waterways, harbors, and the deep ocean.

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