NBC detection in air and water

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Abstract

California Institute of Technology's Jet Propulsion Laboratory (JPL), in collaboration with **Ionfinity** and **Pacific Environmental Technologies (PacTech)**, is participating in a Navy STTR project to develop a system capable of the 'real-time' detection and quantification of nuclear, biological and chemical (NBC) warfare agents, and of related industrial chemicals including NBC agent synthesis by-products in water and in air immediately above the water's surface. This project uses JPL's Soft Ionization Membrane (SIM) technology which totally ionizes molecules without fragmentation (a process that can markedly improve the sensitivity and specificity of molecule composition identification), and JPL's Rotating Field Mass Spectrometer (RFMS) technology which has a large enough dynamic mass range to enable detection of nuclear materials as well as biological and chemical agents. This Navy project integrates these JPL technologies into a system that is small enough to fit in the 6" diameter nose cone of a Remote Environmental Monitoring UnitS (REMUS) an autonomous underwater vehicle (AUV). It is anticipated that the REMUS AUV will be capable of "real-time" detection and quantification of NBC warfare agents.

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Autonomous underwater analysis system

Working with the Navy Remote Environmental Monitoring UnitS (REMUS) team, Pace Tech designed an autonomous underwater analysis system that incorporates JPL's Soft Ionization Membrane (SIM) and Rotating Field Mass Spectrometer (RFMS) and fits within the dimensional constraints of the REMUS autonomous underwater vehicle (AUV). Figure 1 illustrates Pace Tech's design. Pace Tech's design enables REMUS to sample both air and water.

While the AUV is submerged, the REMUS snorkel is raised automatically to enable sampling of ambient air. A compact hybrid diaphragm-turbo molecular pump within REMUS creates a vacuum that serves to draw an air sample down the snorkel and through a hydrophobic silicon-coated membrane (the membrane removes moisture). The air sample is then drawn through the SIM for molecule ionization and to the RFMS for analysis.

Pace Tech's unique environmental sampler, labeled as "sampler head" in Figure 1, introduces small, discrete water samples at essentially any water pressure (to 4000 m water depth equivalent) into a nano-electrospray ionizer system (or alternatively via a low pressure manifold into the SIM) and the RFMS. A plenum located within the nosecone of the AUV utilizes the forward motion of the AUV to introduce water samples into the environmental sampler.

PaceTech and JPL developed the **Mass** Spectrometer **U**sing **R**otating **F**ields for **E**xploratory **R**esearch (**Mass SURFER**) system that operates down to 2000+ m of seawater. PaceTech is deploying the **Mass SURFER** (Figure 2) in underwater studies of hydrothermal activity to

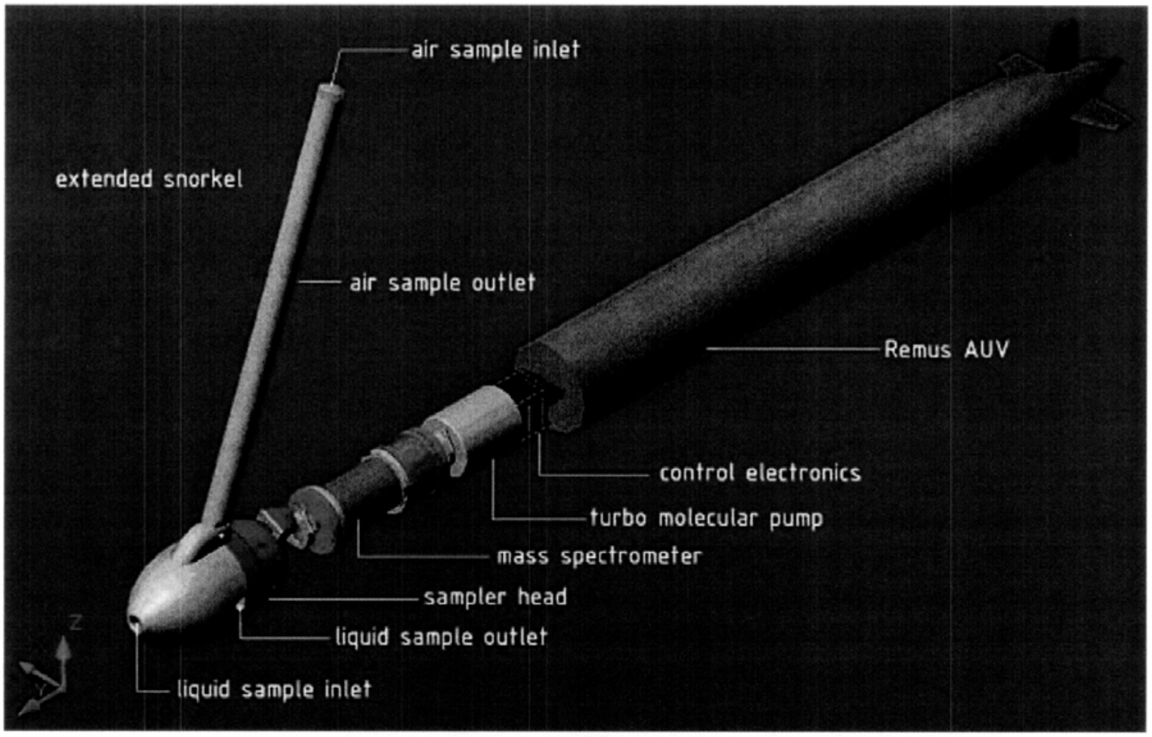

*Fig 1. CAD diagram of the **autonomous underwater analysis system** that incorporates the SIM and RFMS.*

provide in-situ monitoring of ocean chemistry (hydrocarbons, dissolved gases, nutrient solutes) and microbial populations (via protein profiling).

The REMUS autonomous underwater analysis system involved the miniaturization of the Mass SURFER and the incorporation of JPL's Soft Ionization Membrane (SIM) to enable mass spectroscopic measurements to detect low levels of chemical warfare agents and nuclear materials in both air and water.

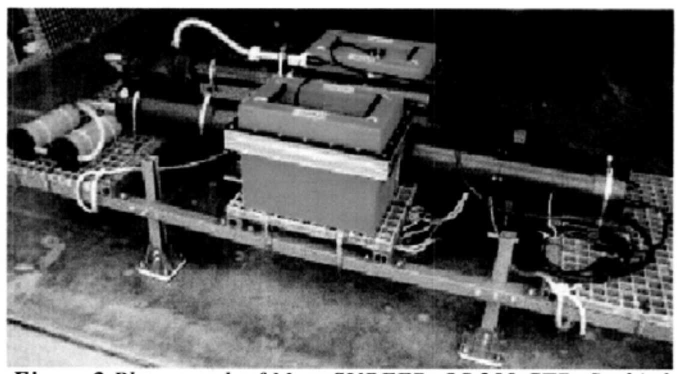

***Figure 2** Photograph of Mass SURFER, OS 200 CTD, Seabird pump, filtration cartridges and two 86 amp-hr external deep-sea batteries.*

Rotating Field Mass Spectrometer

Rotating Field Mass Spectrometer (RFMS) systems are different from traditional MS approaches in that ions spiral from one end to the other in a radio frequency field. Mass is determined by both time of flight and impact position at the ion detector. A focused beam of ions (600 eV ions, with 1 eV energy width) admitted into sinusoidal radio frequency fields cause ions of a particular mass to travel in a helix and impact an ion detector placed at the end of the cell. The frequency and amplitude of field determines which particular ion mass will be in resonance. Lighter ions impact the detector at larger radial distances for a given frequency, while heavier ions impact in the center of the detector. The RFMS is a 2 x 2 x 20 mm cell (which possibly can be made much smaller), the sweep frequency range is 200kHz to 5 MHz, the ion detection is with an electrometer-grade operational amplifier capable of measuring 0.01 nanoamps. This RFMS was used in the MassSURFER with an electrospray ionization (ESI) system (where charge builds up on a suspended material as the solvent evaporates during transport through a nanospray tube). The MassSURFER was miniaturized and modified to integrate the ion optics with the SIM holder (to ensure that incoming gas could not enter the RFMS without passing through the SIM), to enable the rotating field element to be set at either of two angles to the ion beam (facilitating easily changing the resolution of the analyzer) and to make all the spectrometer elements self-aligning during assembly.

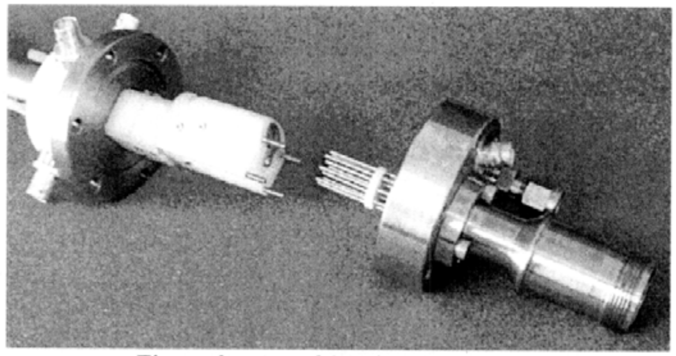

Figure 3 *– Actual SIM/RFMS assembly*

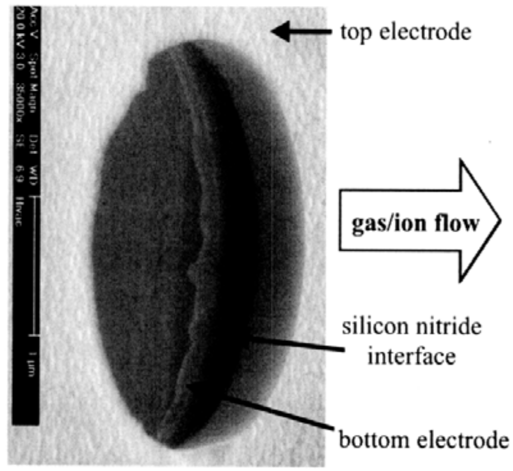

Figure 4 – SEM of one membrane elementwith a 2-μm hole through it

Figure 3 shows the actual SIM/RFMS assembly with the various elements aligned on four rods attached to the inlet flange where the gas flow enters from the left side and passes through the SIM holder into the RFMS (the flanged 1.5" OD tube surrounding the RFMS elements is not shown). The ion optics consist of an Einzel Lens to focus the ions at a precise spot aperture, an X-Y deflector element that steers the beam from the aperture into the rotating field, the Rotating Field elements and an off-center 'wire' cathode to collect the ions.

Soft Ionization Membrane (SIM)

The patented SIM is fabricated on a 200 μm thick silicon wafer coated with a 300nm (0.3 μm) silicon nitride (SiN) membrane. A lithographic mask is used to define an area on the backside of the wafer where the silicon is etched anisotropically to provide free standing SiN membranes in which a pore is produced that allows a gas sample to pass from one side to the other. Thin metal coatings on both sides of the membrane provide narrowly spaced electrodes (300 nm) that provide extreme electric fields for small, applied voltages. The distance that a neutral gas molecule or ionized electron and ion have to travel in the high electric field is at most 300 nm, which, at operational pressures, is less than the

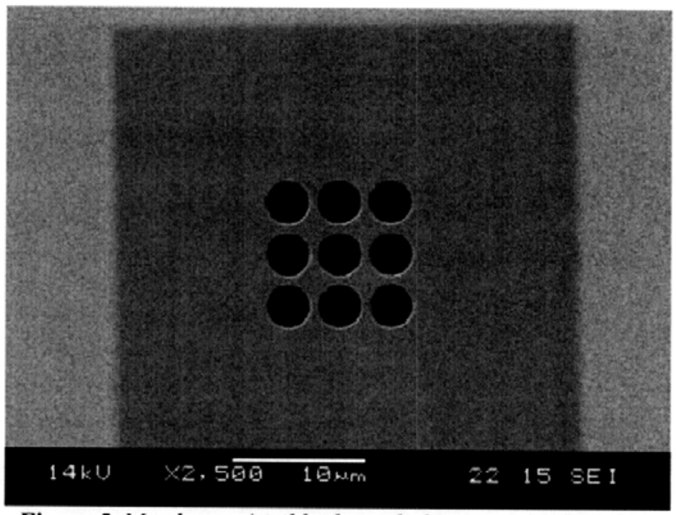

Figure 5 *Membrane (visible through the titanium layer) with 9 pores of 2.8- μm diameter.*

mean free path for collisions with neutral sample molecules. Therefore, ionized particles do not collide with and ionize neutral molecules and thus the arcing or avalanche breakdown usually associated with high electric fields doesn't occur.

This is the fundamental physical principle of the Soft Ionization Membrane. It is efficient because most sample molecules are ionized. It is soft because the electrostatic ionization does not fragment the sample. Further, it does not require high vacuum (10^{-6} Torr) as does filament ionization. It can operate effectively up to 10 Torr, which allows use of a small vacuum pump thus enabling miniaturization of the entire mass analysis system.

Figure 4 is a micrograph of a single hole in one membrane element that was produced by 'maskless' focused ion beam ablation. Figure 5 is a SEM image of a single SIM membrane, produced using standard lithography, anisotropic wet etching and reactive ion etching, that illustrates its 40 µm x 40µm size (visible through a thin Titanium layer) and the nine 2.8 µm diameter pores at its center. The complete SIM is of 6mm x 6mm dimension with a roughly circular 89-membrane array at its center.

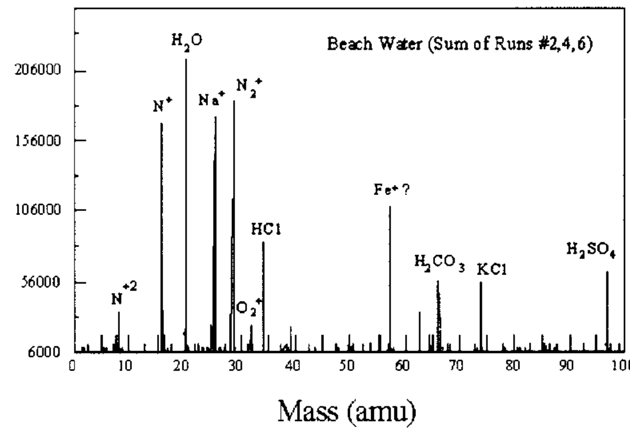

Figure 6 *Seawater Mass spectra from test deployment in Maunalua Bay, Oahu taken by Pace Tech*

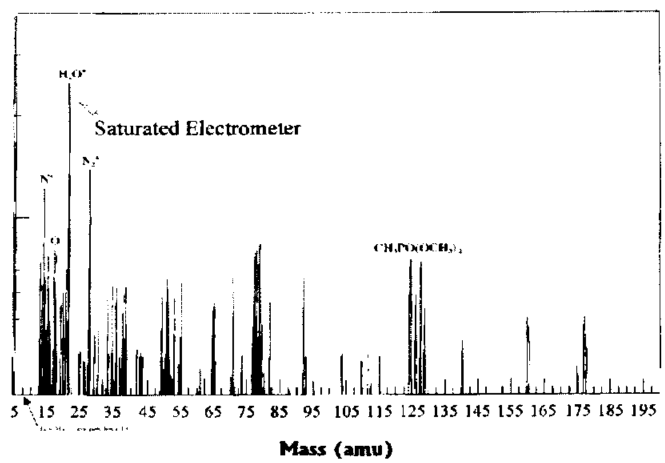

Figure 7 *Soft Ionization Membrane with RFMS – DMMP in unknown dirty gas background*

Measurements

The Mass SURFER was deployed in about 2-3 feet of water in Maunalua Bay, Oahu and the resultant seawater spectrum is presented in Figure 6 showing major peaks for water, nitrogen, oxygen, Na^+ and Fe^+, with further peaks for molecular HCl, KCl, H_2CO_3 and H_2SO_4.

Initial testing of the measurement capabilities of the SIM/RFMS system in response to the presence of a chemical warfare agent (CWA) stimulant and related industrial chemicals in aqueous solution and in vapor phase was done at JPL by Dr. Steven Smith.

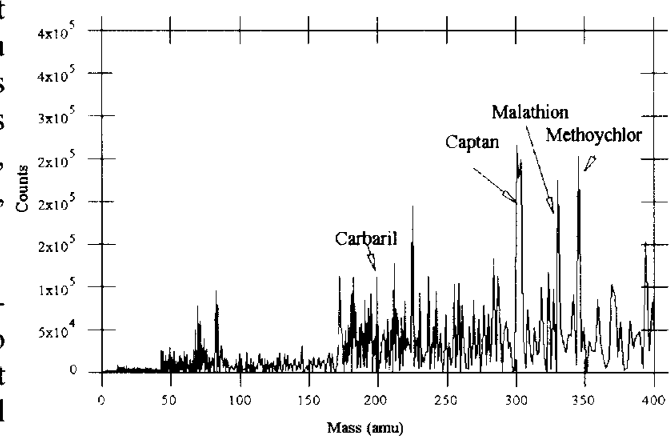

Figure 8 *Mass spectrum of "Liquid Fruit Tree Spray" containing neurotoxins*

The RFMS data below was taken with both nanospray and SIM ionization (original SIM). One CWA stimulant analyzed was the Sarin gas analog Dimethyl Methane Phosphonate (DMMP - $C_3H_9O_3P$ - 124.1 amu), at 1 ppm concentration in a "dirty" air background (Figure 7). Another CWA analyzed was a commercially available neurotoxin called "Fruit Tree Spray." Analysis of this insecticide and fungicide, consisting of Methoxychlor (12% - $C_{16}H_{15}C_{13}O_2$ - 345.65 amu), Malathion (6.0% - $C_{10}H_{19}O_6PS_2$ - 330.36 amu), Carbaril (0.3% - $C_{12}H_{11}NO_2$ - 201.22 amu) and (Captan (11.4% - $C_9H_8C_{13}NO_2S$ - 300.59 amu) in a petroleum base similar to kerosene, is presented in Figure 8. Figure 9 presents an example of the 'soft' ionized mass spectrum for toxic industrial chemicals - specifically BTEX, an EPA reference standard containing Benzene, Toluene, Ethylbenzene, and o-Xylene in a balance of nitrogen. Figure 10 presents an example of the 'soft' ionized mass spectrum of a biological species – 20 mer DNA with a mass of ~ 6000 amu. Nuclear agent analysis by isotopic mass spectroscopy was not demonstrated but the sensitivity and mass resolution of the SIM/RFMS ensure that it is measurable.

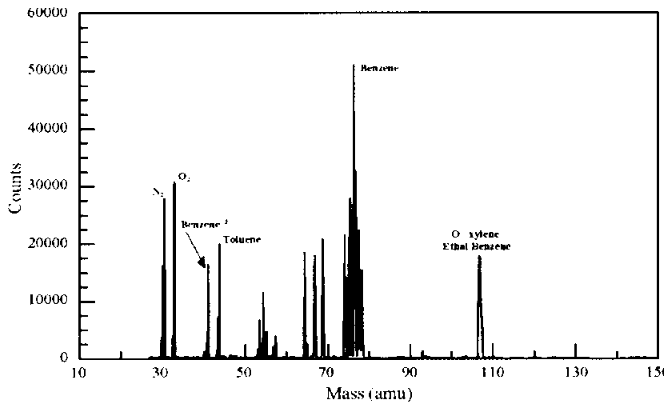

Figure 9. *Uncalibrated mass spectrum for 'soft' ionized BTEX in a balance of nitrogen*

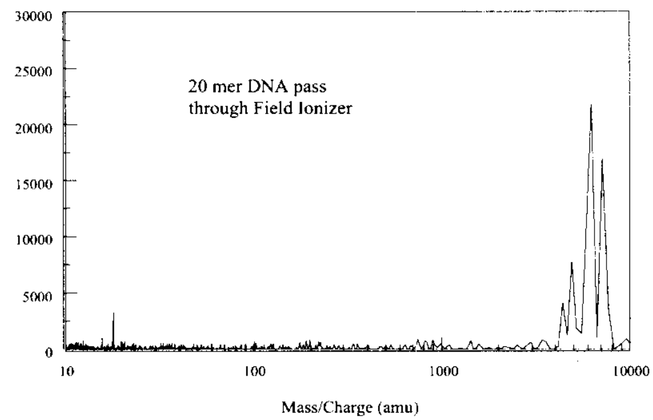

Figure 10. *– 20 mer DNA Fragment*

These analyses clearly demonstrate the effectiveness of the SIM-RFMS in detecting and identifying chemical and biological agents and industrial chemicals in air and water.

On-going work

The Navy is satisfied with the REMUS design and the demonstration of the SIM/RFMS capabilities in detecting NBC warfare agents and industrial toxins in air and water. Thus the Navy has commissioned Ionfinity, together with its partners Caltech/JPL and Pacific Environment Technologies, to undertake Phase II of the STTR entitled 'Autonomous Underwater Sensing of Weapons of Mass Destruction'.

Future Opportunities

Traditional analytical mass spectrometer instruments with high sensitivity, isotopic resolution, and wide dynamic range are housed and operated in centralized laboratories necessitating remote sample collection and transport of materials there for analysis. However, this approach prohibits the production of in-situ or continuous temporal records due to the discrete nature of the sampling strategy and latency of transport. Therefore, field-portable mass spectrometer systems which are capable of producing, storing, and analyzing data remotely could revolutionize ocean and earth sciences.

The REMUS is a portable system capable of 'real-time' analysis and quantification of practically anything from H_2 and He gas to large dissolved organic compounds such as proteins, peptides and DNA. It is a sensitive nose and tongue analog that possesses smell and taste sensitivities below ppb concentrations.

Besides the Navy and Coast Guard interest in NBC detection, a wide variety of other environmental applications are envisioned for the REMUS including monitoring of military and municipal water supplies, coastal and ground water pollution, off shore oil exploration and production and natural hazards. Additionally, the SIM/RFMS approach can address many land-based applications ranging from forensic monitoring of chemical and biological agents, forensic analysis of food, homeland security assessments, to law enforcement and environmental testing. Further, the SIM/RFMS approach is capable of detecting 1) pesticides and other environmental chemical residues or contamination, 2) narcotic-processing chemicals, 3) indirect volatile metabolites from flora exposed to CW agents and pesticides, 4) industrial toxins, and 5) environmental protection applications in the monitoring of exposure to pesticides, herbicides and other organic chemicals of neuro-physiological importance.

Summary and Conclusions

The REMUS is about the size of a shoebox, weighs only a few Kgs, consumes very little power and is moderately priced (~ $2,500 in quantity). The REMUS is a field-portable (even man-portable) Mass Spectrometer that could revolutionize ocean, earth and space science. JPL and PaceTech already have developed the MassSURFER that promises to revolutionize ocean science. Further, JPL has proposed the SIM/RFMS elements for a spacecraft instrument that could revolutionize planetary science.

These earth, ocean and space science revolutions may materialize slowly if waged only by academia and federal laboratories alone – industry needs to be encouraged to join the fray. It is conceivable that this technology could be scaled down by an order of magnitude to yield a Mass Spectrometer of only a few cubic centimeters, small enough to be installed inside a cell phone. Imagine a future consumer product acting as a "personal guardian" that could monitor one's food and immediate environment to provide a personal medi-cosm.

Acknowledgments

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