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**A DEEP-OCEAN MASS SPECTROMETER TO MONITOR HYDROCARBON SEEPS AND PIPELINES****Gary M. McMurtry**  
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University of Hawaii**ABSTRACT**

New developments in instrumentation for ocean environmental engineering are allowing unprecedented levels of trace contaminant measurement in the deep ocean. With funding from the U.S. National Science Foundation (NSF), our engineering design team constructed a new mass spectrometer-based *in situ* analysis system for work in the deep ocean environment over prolonged deployment periods. Our design goals were a depth capability of up to 4,000 m water depth (400 bars hydrostatic pressure) and autonomous operation for periods of up to six months to a year, depending upon the type of external battery system used or other deployment circumstances, e.g., availability of a power cable or fuel cell power source. We chose a membrane introduction mass spectrometry (MIMS) sampling approach, which allows for dissolved gases and volatile organics introduction into the mass spectrometer vacuum system. The MIMS approach and the hydrophobic, silicon-coated membrane chosen both draw upon our previous experience with this technology in the deep ocean. The membrane has been tested to 400 bars in a series of long-term hydrostatic pressure tests, which extend the 200-bar working depth rating of this membrane by a factor of 2. Long-term deployment capability of the moderately powered, approximately 100 W system, was accomplished by power management of the embedded computer system and custom electronics with Windows-based and custom software now fully-developed and bench tested.

The entire system fits within a 6.5-inch outside diameter pressure housing that is approximately five feet long. It consists of a 1 to 200 amu range quadrupole mass spectrometer equipped with Faraday and electron multiplier detectors, compact turbo-molecular and backing diaphragm vacuum pumps, internal rechargeable batteries, and internal waste vacuum chamber. Sample routing past the MIMS is accomplished by computer-controlled solenoid valves. We designed the pressure housings of both 6AL4V and type 2 titanium alloys that are rated to working depths of >4,000 m

and are essentially corrosion proof over long-term deployments. We designed and integrated a fail-safe valving system for both rapid response to high-pressure MIMS failure and a pressure-switch circuit and high-pressure solenoid valve to detect and protect against slow leaks of the MIMS. To route sample waters to the MIMS-based instrument, we also designed and built a rugged plastic plenum that couples to the face of the sampler head, the latter of which consists of the MIMS inlet and a full-ocean rated thermister temperature probe with an operational range from -5 to 50°C. These instrumentation innovations will be described in the paper.

**Keywords:** Mass spectrometer, hydrocarbon, monitoring, deep-ocean instrumentation.

**INTRODUCTION**

While mass spectrometry has been around for more than 100 years, it has been rarely used to monitor the deep ocean environment. Furthermore, a deep-water instrument needs a good membrane-introduction interface and an efficient high-vacuum system to work at very high pressure. Being able to solve these problems could greatly improve scientific work that requires long-term monitoring of the environment (geology, biology, oceanography). The traditional deep water sampling method usually involves collection of water samples via a rosette and the delivery to a laboratory for analysis. This approach can result in sample quality degradation over time and inaccurate results. Also, the limitation in duration of sampling at a particular location does not provide a long-term solution. *In situ* measurements by an underwater mass spectrometer can eliminate many problems intrinsic to traditional sampling methods and provide data with temporal resolutions that are difficult to obtain by other means. In the case of a 6-12 month study of a particular location, it is the only means to get a time series for simultaneous monitoring of a broad suite of analytes. As a result, a single underwater mass spectrometer can be used in lieu of an array of single-analyte sensors (e.g. methane, oxygen or carbon dioxide).

This instrument use will almost be limitless. To name a few applications, for example, it could be used to monitor the effect of CO<sub>2</sub> disposal on the marine environment, environmental impact of a sewage plume, pollution monitoring, and to monitor oil or various chemicals seeping from a sunken ship. Also, networks of systems could be used for tracing chemicals, both natural and anthropogenic to their sources [1]. Some of the applications of an array of underwater mass spectrometers are: pollution tracking, geochemical profiling, algal bloom/plume diagnostics, chemical source material discovery, oil leaks (natural and anthropogenic), methane gas discovery, advection/diffusion studies, shipping channel and point source pollution localization. One of the most useful applications for an underwater mass spectrometer mounted on an AUV (Autonomous Underwater Vehicle) could be monitoring of the main discharge associated with offshore oil production. The main discharge is called “produced water” and is a combination of formation and injection water and can be a complex mixture of inorganic and organic compounds, which has the potential to be toxic to the ocean environment. The typical rates for produced water are very high and the quantity of discharge is typically 10 times as high as the volume of hydrocarbon produced [2]. Constituents of concern include metals, low molecular weight aromatic hydrocarbons, nutrients, radioactive isotopes, and treatment chemicals. Many of these are capable of detection with a 300 amu mass spectrometer.

Previous developments of underwater mass spectrometer systems include the “In-spectr” [3, 4, 5] and the NEREUS/Kemonaut [6, 7]. The In-spectr is based upon a linear 200-amu range quadrupole and uses a hollow-fiber type inlet for membrane introduction mass spectrometry (MIMS) [8]. Both the linear quadrupole and an ion trap-type mass analyzer have been successfully demonstrated in various shallow-water tests involving detection of dissolved gases and volatile organic compounds at the 1-10 ppb level [9, 10]. The instrument scans at a high rate of a few tens of seconds and has a working depth to about 250 m. The In-spectr draws about 100-150 watts of power continuously, and uses an AUV or ROV to supply power. NEREUS is based upon a compact, cycloidal 2-100 amu mass spectrometer and a hollow-fiber type MIMS, with a relatively low 25-watt power consumption. NEREUS can operate to water depths exceeding 300 m, and

uses AUVs such as the Kemonaut for power and mobility. Recent shallow-water deployments have proven its capability to map dissolved gases in the ocean [6, 7].

## OPERATIONAL PRINCIPLES

Since its early stages about 100 years ago, mass spectrometry has become a virtually omnipresent research tool. Amongst the techniques used in analytical chemistry, none surpasses mass spectrometry by having such a broad molecular detection range. Mass spectrometers are therefore the most multipurpose of all chemical sensors. Among the group of analytical capabilities provided by a mass spectrometer is very fast analysis of compounds ranging from small molecules to large biomolecules with high sensitivity. However, the utilization of mass spectrometry underwater is new. In deep water, it has been unavailable until now. Mass spectrometry is well matched to the needs for hydrocarbon leak monitoring, but until recently its *in situ* applications have been problematic. The challenges involved are related to sample introduction, vacuum control, and power consumption. The biggest challenge encountered by submersible systems is that they must operate over a considerable range of external hydrostatic pressures (very high for deep water) while the system is maintained at high vacuum [6]. The high vacuum is necessary because the principle of operation of most mass spectrometers, such as quadrupole or time-of-flight types, are based on the kinetic energy of ions produced in an ionization chamber. Since this kinetic energy is relatively low, the vacuum range needs to be in the high-to- ultrahigh range (10<sup>-4</sup> to 10<sup>-14</sup> Torr). If the pressure is too high, low energy ions will collide with target ions and will be diverted to collide with the quadrupole rods, thus never to be collected at the detector.

The basic components of the MIMS deep water mass spectrometer are the membrane-introduction head, a pressure reducing inlet composed of a capillary and an aperture, the vacuum pumping system, the ionization chamber and the electron source, the focusing lens, the quadrupole analyzer, the detector, the data/control system, and a waste vacuum isolation chamber. Next is a description of each of those components in the order encountered by the flow path, starting with the membrane-introduction head and finishing with the waste vacuum (Fig. 1).

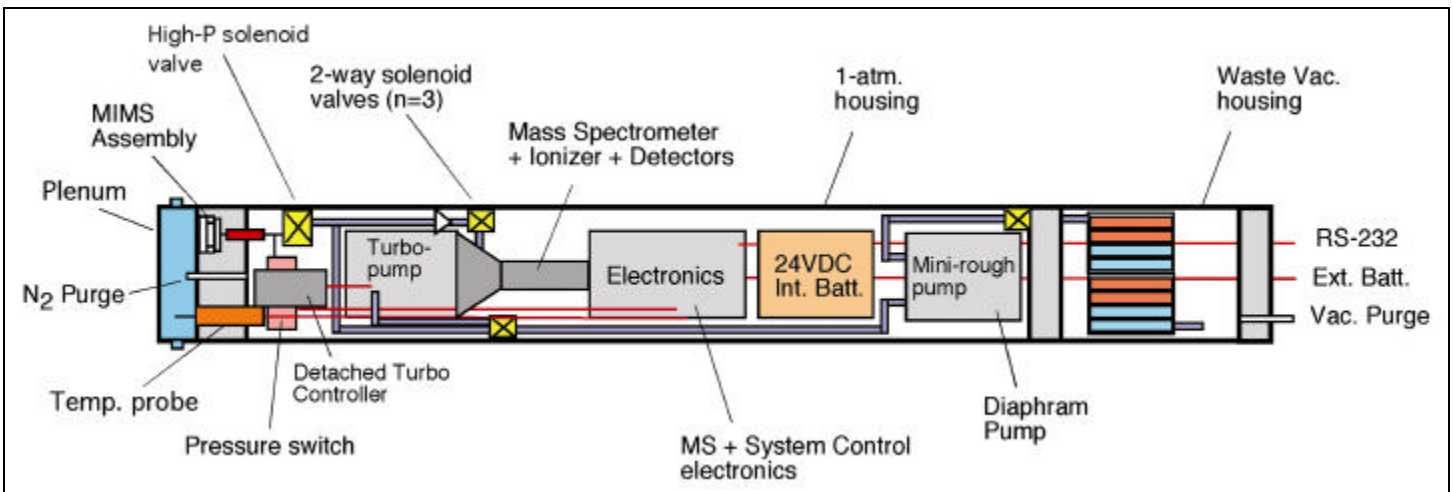


Figure 1. Schematic drawing of the Deep-Ocean Mass Spectrometer (DOMS)

Membrane introduction is a convenient technique for transporting organic vapors and dissolved gases from the solution phase to the gas phase [11]. MIMS was first introduced in 1963 [12]. Membrane introduction is based on solubility principles involving membranes, such as polydimethylsiloxane (PDMS also known as silicone), which selectively transport non-polar volatile compounds. It is installed between the sample and the ion source of a mass spectrometer. Highly polar compounds, such as liquid water, do not migrate through the membrane. As a result, small membranes provide an effective interface between the water column and the vacuum system of the mass spectrometer. Because the flow of the analyte matrix, usually water, through the membrane is proportionally smaller than the flow of the desired analytes, analyte enrichment is obtained. This facilitates very sensitive levels of detection as low as  $\text{ng l}^{-1}$  levels in water. This concentration enhancement provides very low detection limits for many low-relative-molecular-mass volatile compounds using membrane introduction mass spectrometry [13]. Other important advantages offered by MIMS are: (i) the method is fast; (ii) pretreatment of samples is not necessary; (iii) the cost per sample is low; (iv) solvents are not used, and (v) most importantly, MIMS can be used for long-term continuous monitoring of environmental, biochemical and chemical processes. The two major drawbacks are: compounds with relative molecular masses in excess of 300 amu do not pass through the membrane with enough efficiency to be detected, and membrane inlets cannot operate at temperatures much higher than  $70^{\circ}\text{C}$  at 1 atm. pressure before bubble formation in front of the membrane causes highly unstable signals. At temperature above  $100^{\circ}\text{C}$  the signals fall almost to baseline because of the large volumetric expansion of water as it starts to boil [14]. However, in the deep sea at the high pressures at which we are operating, boiling water should not be a problem.

The components in line behind the MIMS assembly are the pressure-reducing inlet coupled with a series of high-pressure and vacuum valves. The sample flow is choked down to  $10^{-1}$  Torr with a capillary line coupled with the aperture. An efficient pumping system providing high vacuum ( $<10^{-5}$  Torr) is critical to the operation of most mass spectrometers. The vacuum for mass spectrometry is established in two stages: a fore pump takes the vacuum down to about  $10^{-1}$  Torr, then either an oil diffusion pump or a turbomolecular pump drops the analyzer pressure to  $10^{-5}$  to  $10^{-7}$  Torr. Most often, the fore pump is a diaphragm pump. Diaphragm pumps use a diaphragm that moves back and forth to transport gas from one place to another. Diaphragm pumps are highly reliable because they have no internal parts that could rub against another part. The turbomolecular pump is basically a turbine or molecular fan. It has a series of vaned blades on a shaft rotating at speeds up to 90,000 RPM between an alternate series of stator plates. Only a small amount of gas is moved each time, but the number of blades and the high rotary speed rapidly move gas from the analyzer chamber to the exhaust into the rough pump. We are using a compact model provided by Pfeiffer Vacuum (TMU 071 P, Asslar, Germany). The turbo pump brings the analyzer pressure down to  $10^{-5}$  to  $10^{-7}$  Torr. The TMU 071P pumping capacity is 60 L/s. Its biggest drawback is potential mechanical failure and high power requirement to get it spinning at full

speed. The choice of the mass spectrometer is reduced to either a linear quadrupole mass filter or a quadrupole ion trap mass spectrometer for a practical underwater mass spectrometer. This is because they are robust, compact and relatively inexpensive. They are also both very well characterized. The ion trap mass spectrometer system has a wider mass range (up to 650 amu) than the linear quadrupole mass spectrometer and an increase in sensitivity, however, it requires the introduction of helium buffer gas (collision gases). Even though its use could be feasible by employing neutral water vapor and dinitrogen passing through the membrane as carrier gas [4], the gains are very small since the transmission characteristics of the silicone membrane have an upper limit of 300 amu. It is therefore simpler to use a 300 amu linear quadrupole fitted with an electron multiplier detector to increase sensitivity. Furthermore, as the power requirement of the ion trap is much higher than the traditional linear quadrupole, it would greatly impede the deployment duration and therefore be more of a handicap than a benefit.

The linear quadrupole mass spectrometer has three basic sections: an ionization chamber, the analyzer, and the ion detector. The quadrupole is the heart of the mass spectrometer. It consists of four cylindrical rods clamped in a pair of ceramic collars. Both an oscillating direct current (DC) and radio frequency (RF) signal are applied across opposite rods with adjacent rods having opposing charge. The ion stream entering the quadrupole is forced into a corkscrew three-dimensional sine wave by the quadrupole electromagnetic field of the analyzer. The combined DC/RF field applied to the rods is swept together at higher (or lower) field strength by the DC/RF generator, upsetting this standing wave for all but a single fragment mass to charge ratio at a given frequency. This single mass follows a stable path down the length of the analyzer and is deflected onto the surface of the detector. Any ion fragments not passed at a given frequency follow unstable decaying paths and end up colliding with the walls of the quadrupole rods. As the DC/RF fields are swept up or down, larger or smaller masses strike the detector. The linear quadrupole mass spectrometer can be equipped with a Faraday cup detector and/or an electron multiplier detector.

## DESIGN HURDLES

There are four major challenges to design a compact, low power, deep-water mass spectrometer. The primary challenge is linked to the great hydrostatic pressure associated with a deep water system (4,000 m). The introduction silicone membrane has to keep pressurized liquid water from entering the apparatus but needs to let dissolved gases in. If the membrane is too thick, gases will not come in, if the membrane is too thin or scratched or otherwise punctured, pressurized water will come in and possibly ruin the system. Presently, a high-pressure membrane-introduction probe has not been pressure tested to a depth greater than 250 m [4]. The next challenge, also associated with high pressure but with the system being enclosed in a pressure housing, is vacuum system management. Mass spectrometry typically requires a vacuum of the order of  $10^{-5}$  Torr or less. Maintaining such a high vacuum with pumps exhausting into a closed pressure housing is a real engineering problem that requires careful design. On a traditional system most vacuum pumps compress the pumped gases and exhaust them into the

atmosphere. With a closed system, the pressure at the pump exhaust port will undeniably increase above atmospheric pressure and will eventually corrupt the vacuum generated by the pumping system. This will result in an insufficient vacuum for the ionization and mass filtering process. The next challenge is related to power consumption. Since the biggest advantage of using a mass spectrometer over a traditional sampling method is the number of samples that can be taken *in situ*, remotely over an extended period of time, one of the most important requirements to this design is relatively small power consumption (limited by the weight that can be deployed, therefore limiting the amount of batteries). One very important problem is related to background noise attributed to the residual gas in the ionization chamber. The vacuum system and the chamber will remain contaminated with some previous sample load for an undetermined period of time. One way to clean up the apparatus is to run the vacuum pumps for an extended period of time. Once the chamber is cleaned of previous sample, the ionization process can start again. The latency between pumping the old sample out of the tubing and ionization chamber and taking a new sample will have to be determined in the laboratory. The problem with this method is that some gases will dissipate very quickly while others will take a longer time to be removed completely, and yet other gases may never completely disappear.

## DESIGN SOLUTIONS

This field system has to be able to operate for long periods (months to a year) with relatively moderate power consumption (~100 W) during brief sampling periods and very low power most of the time when the instrument is in “sleep” mode. This has yet to be accomplished by anyone, so it is both novel and useful. This analytical instrument will function at great depths (very high pressures) and at low temperatures (2-4°C). It should sample low-temperature hydrothermal vents and cold seeps on the ocean floor, as well as do hydrographic profiles and tows. No one has accomplished this deed to date. The entire system fits within a 6.5-inch outside diameter housing that is approximately five feet long (without the external battery package). It consists of a 1 to 200 amu range quadrupole mass spectrometer equipped with Faraday and electron multiplier detectors, compact turbo-molecular and backing diaphragm vacuum pumps, various valves, internal rechargeable batteries, and internal waste vacuum chamber.

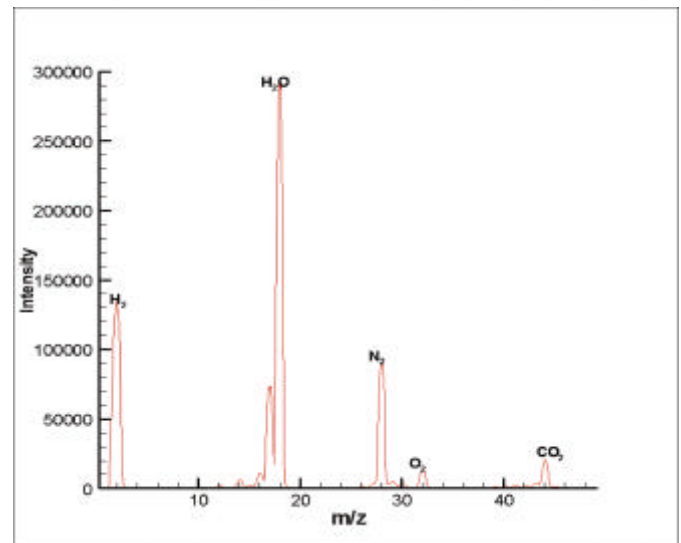
In order to route waters to the MIMS-based instrument, we also designed and built a rugged plastic plenum that couples to the face of the sampler head, the latter of which consists of the MIMS inlet and a full-ocean rated temperature probe with an operational range from -5 to 50°C. The system also uses an additional Ti pressure housing that will contain the battery package. We designed and built the pressure housing of both 6AL4V and Type 2 titanium alloys that are rated to working depths of >4,000 m and are essentially corrosion-proof over long-term deployments. The design solution is shown in Figure 1.

We designed a fail-safe valving system for rapid response to high-pressure MIMS failure and a pressure-switch circuit and high-pressure solenoid valve to detect and protect against slow leaks of the MIMS. The fast leak is stopped by an excess flow valve: a spring-loaded slotted poppet remains in the open

position during normal system operation. If the membrane lets water leak because it is cut or ruptured, the poppet moves to the tripped position, closing the slot and therefore blocking the flow. A slow leak, which is probably more likely to happen (i.e., a scratched membrane silicon surface will generate a very slow leak), can be contained with the use of an electrical pressure switch and a high-pressure solenoid valve. The high-pressure solenoid valve will be closed at all times except when sampling. Therefore, even if there is a small leak, the water will not get inside the system and damage the instrument. Before and during sampling, the high-pressure switch will close off an electrical circuit if the preset pressure is not exceeded. The closed electrical circuit will send a signal to the onboard embedded system that will open the high-pressure solenoid valve (via a solid-state relay) to allow sample to come into the system. If the switch trips due to a pressure exceeding the preset pressure, the high-pressure solenoid valve will remain closed.

The vacuum system has been tested with a residual gas analyzer (RGA) using Windows-based software sold with the RGA. It has also been tested with custom software installed on the embedded system. Data were successfully recorded on flash memory, then retrieved and post-processed on a personal computer. Spectra were successfully plotted (Fig. 2).

A series of pressure tests up to 6,000 psi were made in order to check the membrane for leaks. During those tests, the



**Figure 2.** A filament degassing spectrum in a closed system loaded on the memory of the embedded system.

membrane inlet showed the first sign of failure. It appears that the silicone on the membrane was initially scratched. New membrane stock was used and successfully tested up to 6,000 psi for an extended period of time. Figure 3 shows the results of the membrane test as a time series histogram.

We are currently bench testing the response of the system to various standard gas saturation partial pressures in water, including helium, nitrogen, argon, methane and propane. A vacuum cylinder 12 inches long by 5.5 inches inside diameter (same capacity as the waste vacuum housing to be used in the

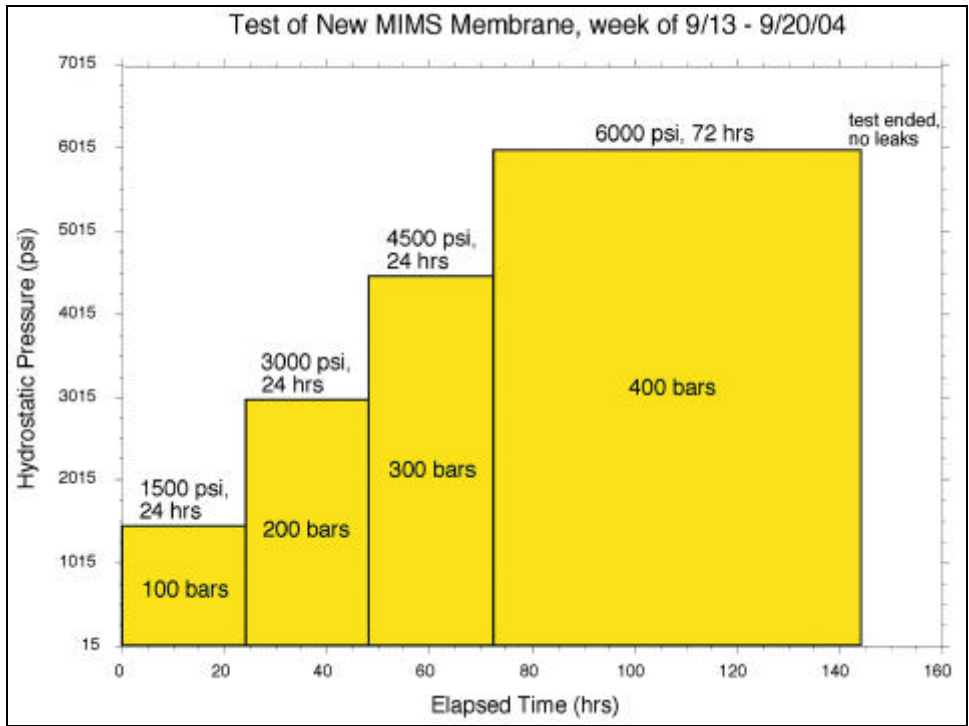


Figure 3. Pressure test of the MIMS membrane and assembly, September 2004.

mass spectrometer) was tested as a waste chamber. It was first evacuated to 150 Torr. Then the bench-top diaphragm and turbo pump were started with the waste gases evacuated into the waste housing. The experimented system was run continuously for 216 hours until the backpressure attained 750 Torr. The experiment allowed us to determine that the waste vacuum capacity was not a serious issue if vacuum conditions

can be maintained on long deployments.

Power management is a major issue on long-term deployments. Power consumption has been judiciously reduced for every system to the bare minimum. Table 1 illustrates how this has been done to maximize battery life.

instruments (in order of operation)	Voltage (V)	Current (A)	Power (W) peak	time(sec) peak	Watt.sec peak	Power (W) steady	time(sec) steady	Watt.sec steady	Watt.sec total		
Seabird (temperature probe)	9	0.01	0.09			0.09	10	0.9	0.9		
By pass SV (vacuum valve)	24	0.50	12.00			12.00	600	7200	7200		
Hi. Vac. SV (behind aperture)	24	0.50	12.00			12.00	600	7200	7200		
Waste SV (vacuum valve)	24	0.50	12.00			12.00	600	7200	7200		
Diaphragm Pump	24	0.63	15.00			15.00	600	9000	9000		
Turbo Pump	24	3.90	93.60	150.0	14040.0	21.60	390	8424	22464		
RGA (quadrupole MS)	24	2.50	60.00			60.00	360	21600	21600		
								60624.9	74664.9		
								<b>Watt.hr.</b>	<b>20.7</b>		
								<b>total battery</b>	<b>Watt.hr.</b>	<b>alkaline</b>	3000.0
									<b>7" dia. X 24" # samples</b>		144.6
									<b>lithium</b>		6000.0
									<b># samples</b>		289.3

Table 1. Power budget



## INSTRUMENT TESTS

Two major at-sea tests are planned for the deep water mass spectrometer. One of these will involve a one-day test on a deep diving submersible. The University of Hawaii operates the 2,000 m deep submersibles *PISCES IV* and *PISCES V*. In 2005, the mass spectrometer will be strapped to the submersible's sample basket on one of several dives on wrecks. These wrecks include a sunken aircraft and a World War II Japanese midget submarine. The wrecks leak oil and provide an excellent test case for the mass spectrometer. Samples will be taken at different distances from the wreck and compared to water samples collected from the submersibles' CTDs and measured for hydrocarbons in the lab.

The second instrument test will be a long-term deployment on some natural hydrocarbon seeps off Costa Rica. This will be a six-month deployment. The deployment will involve the submersible *ALVIN*. The instrument deployment site is shown in Figure 4.

Recently there has been a surge in interest in the Costa Rica margin because it represents a predominantly non-accretionary convergent margin and there are large lateral

changes in the chemical signatures in the arc that appear to relate to both changes in sediment input and basement topography and hydrology. Numerous mud volcanoes have been imaged at mid-slope depths during swath bathymetry mapping of Nicoya Peninsula. We have chosen one of these located at a depth of 1,919 m as a primary target. This approximately 1,000 m diameter mud volcano hosts massive accumulations of chemotrophic biological communities indicative of active expulsion of methane-rich fluids with values as high as 94 nmol/l in bottom water. The sources of these methane-rich fluids is unknown and may be of both near-surface microbial and deeper thermogenic origin. Our proposed objective is to test our ability to separate these different sources by *in situ* and laboratory measurements and to test the level of hydrologic activity and fluxes through features such as the mud volcanoes and natural hydrocarbon seeps.

The mass spectrometer will be part of a larger bottom station to be deployed by submersible and positioned with a specialized collector at a natural seep site. The instrument will be released acoustically for pick up by an oceanographic vessel of opportunity. The full station design is shown in Figure 5.

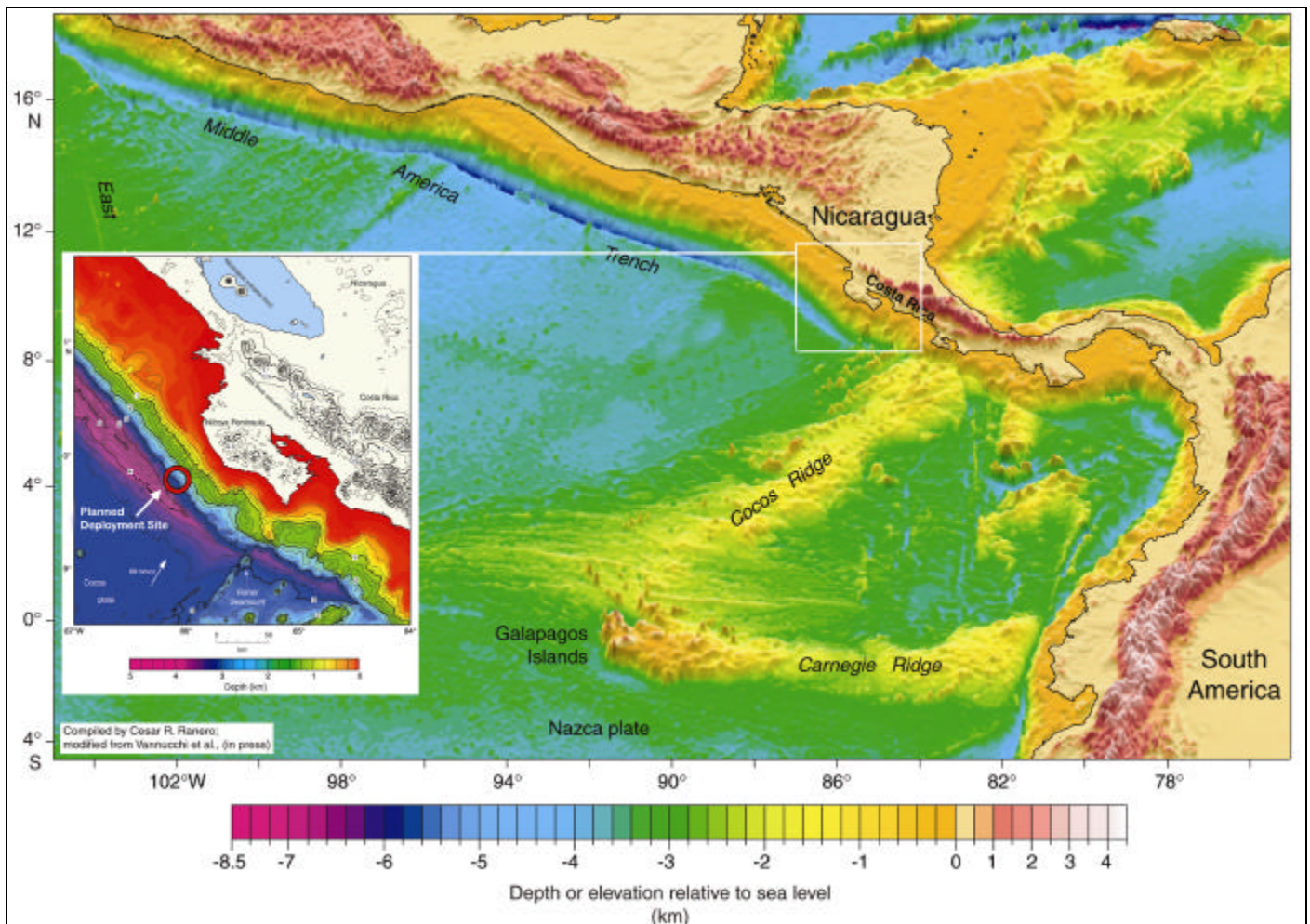
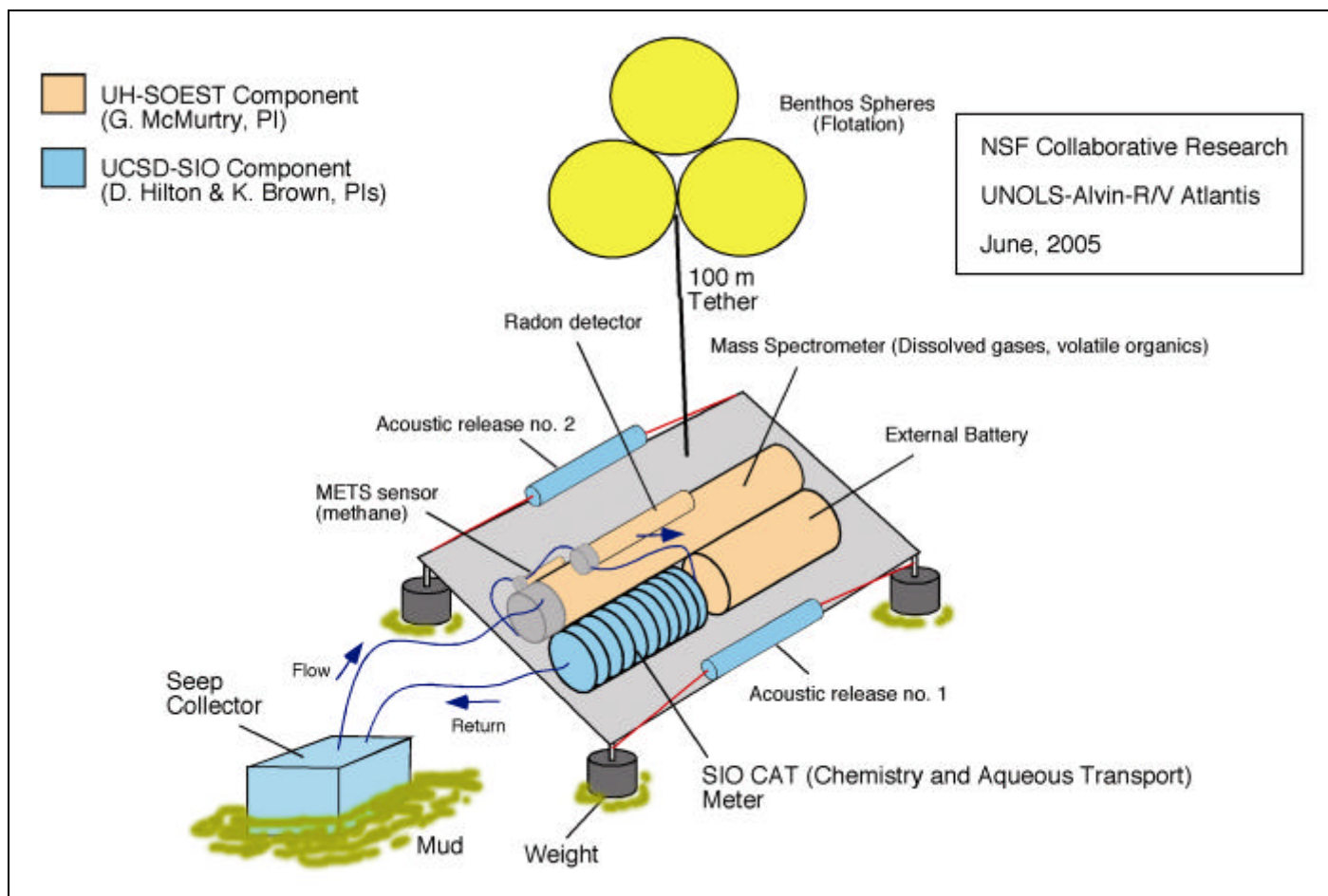


Figure 4. Location of the Costa Rica margin seeps.



**Figure 5.** Drawing of the planned Costa Rica Margin Deployment Unit

## CONCLUSIONS

Conventional strategies for ocean sampling involve the collection of water samples and biological specimens using equipment that is usually deployed over the side of the ship, and return of these samples to shipboard or land laboratories for later analysis. This approach can result in degradation of sample quality over time and provide inaccurate results as volatile chemicals can transform quickly, but mostly, this approach limits an *in situ* monitoring capability. Thus *in situ* chemical analysis of samples is desirable in order to keep the quality of samples high. *In situ* measurements can eliminate many problems intrinsic to traditional sampling methods and provide temporal resolutions that are difficult to obtain by other means. In the case of long-term study of 6-to-12 month periods at a particular location, the mass spectrometer provides a means to obtain a time series of a broad suite of analytes for simultaneous monitoring. As a result, a single mass spectrometer can be used in lieu of an array of single-analyte sensors. High sensitivity and the ability to measure multiple species (e.g. hydrogen, helium, methane, oxygen or carbon dioxide) with the promise of isotopic resolution are its major features. For these reasons, mass spectrometry is arguably the most diverse measuring machine in the world, one that can be used repeatedly on projects measuring all types of chemical species.

A deep-water mass spectrometer is challenging due to a lack of an effective membrane-introduction interface and an efficient high-vacuum system that will work remotely for long periods at very high ambient pressure. This oceanographic instrument should eventually allow the measurement of dissolved gases (i.e., CO<sub>2</sub> and methane) and volatile compounds in a variety of ocean environments, e.g., cold seeps on the continental margins, deep-sea hydrothermal vents, submarine groundwater discharge, and pollution in coastal areas. We are developing a field system that can operate for extended periods (months to a year) and needs relatively moderate power (~100 W) for brief sampling periods. This analytical instrument will function at great depths (4,000 m) and at low temperatures (2 to 4°C) for extended periods without any sort of human operation. This will give the ability to monitor both natural hydrocarbon seeps, as well as leaks from pipelines. The innovations in this instrument allow monitoring in deep water for multiple chemical species over long time periods. This is critical to establish baseline information and represents a new step forward in marine monitoring of hydrocarbons.

## ACKNOWLEDGEMENTS

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