NEREUS/*Kemonaut*, a mobile autonomous underwater mass spectrometer

R. Camilli, H.F. Hemond

NEREUS is a self-contained underwater membrane-inlet mass spectrometer (MS) based on a cycloidal mass analyzer. Designed for autonomous operation, with a mass of 22 kg and a power consumption of less than 20 W, a NEREUS prototype was demonstrated in freshwater and marine environments to a depth of 25 m. The instrument was operated in both tethered and towed operation, as well as aboard *Kemonaut*, an Odyssey-class autonomous underwater vehicle (AUV) modified to accommodate the NEREUS instrument. The *Kemonaut* AUV greatly expands the range of environments that can practicably be investigated. NEREUS was demonstrated to measure many important metabolic gases, such as oxygen, methane, and carbon dioxide, at levels encountered in natural waters; it also responds to light hydrocarbon pollutants. Important goals for future instruments are increased capability to self-calibrate *in situ* and lowered detection limits that enable measurement of trace metabolic gases, such as hydrogen and nitrous oxide.

Keywords: AUV; Cycloid; Mass spectrometer; Methane

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1. Introduction

Water resources are increasingly challenged as the global population of people exceeds 6 billion. Knowledge of the water environment is required for pollution mitigation, sustainable use of natural aquatic resources, and identification and forecasting of hydrospheric processes affecting the Earth system. While understanding of the hydrosphere is concentrated at the near-surface, the chemistry, biology and physics of deeper regions are equally important. However, the submarine environment is inhospitable to humans. Thus, advancements in sensor and delivery platform technologies are essential for comprehensive exploration and analysis of the sub-surface aquatic environment.

Many chemical species of concern are present as dissolved gases and volatile fractions. MSs have several advantages for *in situ* aquatic chemical analysis, being able to quantify multiple species, at low concentrations, and without exhaust or consumable reagents. They are amenable to automated control and data processing, which is a significant advantage because conventional water-analysis methods are typically labor-intensive, time-consuming and involve manual collection and transport of samples to a laboratory. Additionally, error often arises because of chemical and physical changes affecting samples during transport, including degassing and biological or photochemical degradation. *In situ* devices, such as dissolved oxygen probes, can avoid the drawbacks encountered with off-site analysis, but they are commonly limited to detecting one or a few gas species [1], with separate sensors required for each species and sensitivities typically about 1 ppm. Continuous sampling techniques, such as the Weiss equilibrator, are generally limited to shipboard use with modest sampling depths, and have equilibration times that vary with gas species and range from minutes to hours [2,3]. The resulting sparseness of data may lead to temporal aliasing (translating into spatial aliasing on a moving platform), which can mask important chemical and biological features in an aquatic environment.

Autonomous, *in situ* MSs have the potential to overcome many of the limitations described above. Coupling of a MS with a mobile instrument platform, such as an AUV, provides a further multiplier of effectiveness, potentially enabling meaningful three-dimensional, transient mapping of chemical conditions in the underwater environment. The resulting datasets will make possible much more

Figure 1. NEREUS MS with upper glass-pressure hemisphere removed.

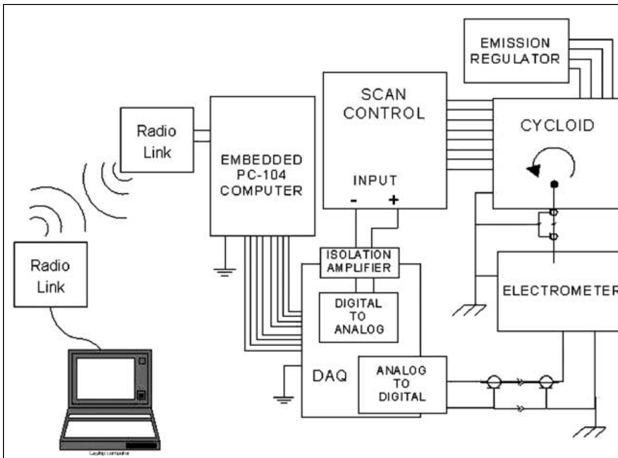

Figure 2. Functional diagram of the NEREUS instrument and optional remote interface.

effective monitoring of natural waters, as well as greatly enhanced ability to carry out scientific investigations. However, use aboard an AUV does impose several critical constraints on the design of the instrument payload, including: autonomous operation; limited size; and, exceptionally low power consumption [4]. To date, relatively few underwater MSs have been built [5–7].

We describe here the NEREUS submersible MS (Fig. 1) for operation aboard variants of Odyssey-class AUVs as well as with stationary moorings, towfish, and remotely operated vehicles. The fundamental design concept of the NEREUS membrane-inlet MS was to develop an in situ instrument that is fully autonomous, robust, capable of rapid data collection, and highly optimized for operation onboard a variety of platforms. To address the constraints of operation aboard an AUV:

- the NEREUS system is completely self-contained within a 17-in.-diameter glass pressure sphere,
- its mass (with battery) is only 22 kg,
- power demand is less than 20 W, and
- it is provided with an autonomous control system.

The *Kemonaut* AUV is an Odyssey-class platform built specifically for the NEREUS instrument. Essential characteristics of this instrument and vehicle system are described in the following sections.

2. Design overview

NEREUS comprises five major component groups, namely: inlet, vacuum system, mass analyzer, electronic hardware, and, software. Fig. 2 shows a functional diagram. The instrument is mounted a 17-in., glass, pressure sphere by a lightweight (~0.5 kg), composite laminate, support frame with an inverted quadripartite geometry designed to resist shock load and damp vibration. Its layout permits batteries to be housed within the lower hemisphere volume, while securely holding the instrument in the upper hemisphere. The support frame is bonded to the base of the lower glass hemisphere via a composite disk. The battery pack comprises two (12 V, 7 A h) sealed lead-acid batteries wired in parallel but they can be replaced with other higher energy-density primary and secondary cells for increased endurance.

2.1. Inlet and vacuum system

Any successful *in situ* marine sensor must survive the hydrostatic pressures encountered at depth and the corrosive effects of seawater. In addition to such considerations, *in situ* MS design must also allow for adequate introduction of analyte gases into the vacuum chamber while maintaining an internal pressure no greater than $\sim 10^{-5}$–10^{-6} Torr and, in the case of a magnetic analyzer, maintaining the appropriate magnetic field throughout the analyzer region. Therefore, the vacuum system components were fabricated from non-magnetic #304 stainless steel, and high vacuum is maintained by an 8 L/s ion pump operated from a 3000 V dc-to-dc converter.

Dissolved gases are introduced via a semi-permeable membrane-inlet, similar to that described by Hoch and Kok [8]. The inlet is positioned outside the pressure sphere and connected to the analyzer with a 6-mm-diameter stainless steel inlet tube. The membrane is supported by a stainless steel micro-etched backing plate, constructed using a material commercially manufactured for the construction of ''aperture masks'' in cathode ray tubes, and secured by a Teflon washer in series with an annular stainless steel cap that is threaded onto the stainless steel inlet body.

2.2. Mass analyzer

A cycloidal mass analyzer was chosen for NEREUS, based in part on its successful use in an earlier instrument designed for backpack portability [9]. The cycloidal analyzer, using crossed magnetic and electric fields to impart trajectories to sample ions, has the inherent property of perfect direction and velocity focusing [10], making for a relatively compact analyzer at a given resolution. The NEREUS cycloid is slightly modified from the cycloid tube used in a CEC 21-620 analyzer, described by Robinson and Hall [11]. The NEREUS instrument has a mass range of $\sim$2–150 amu, and a mass resolving power of 100 [12], permitting analysis of dissolved biogenic gases, atmospheric gases, light hydrocarbons, and the differentiation of many isotopes.

To help minimize power consumption, a permanent magnet is used to generate the required B field. With an air gap of 1 in. and pole-piece diameters of 3.5 in., the yoke of the magnetic circuit is constructed of low carbon steel, while coercive force is generated by two cylindrical NdFeB magnetic elements, each residing between a pole piece and the yoke. Pole pieces are shaped to minimize fringing effects, and the yoke itself is aggressively trimmed in low-B regions to minimize size and mass. The NeFeB elements are nickel plated to protect the brittle magnetic material from cracking and to minimize exposure to damaging hydrogen gas that could be vented by the instrument's internal battery pack during recharge.

2.3. Electronic hardware

DC control potential for the cycloid is produced by a high-voltage operational amplifier, which supplies an adjustable potential of the magnitude required to select a given m/z value to field-shaping plates within the analyzer. Samples are ionized at 70 eV by a standard tungsten-filament, electron-emission source. The emission regulator was designed to minimize power usage by employing a high-frequency, duty-cycle modulated filament supply. The ion current generated by the ion beam at the selected m/z value is collected by a Faraday cup and sent to the electrometer. Electrometer output is converted to 16-bit digital signal and transmitted to an embedded computer for interpretation and storage.

An embedded PC-104 computer is used to control instrument power, data collection and handling, systems diagnostics, and communications with auxiliary systems, such as radio transceivers, remote viewing terminals, or vehicle navigation computers. A 100 MHz 486DX PC-104 core module is used, with memory storage provided by a Compact Flash disk, which has the advantages of extremely small form factor, low power consumption, tolerance to vibration, impact, and pressure fluctuation, low cost, and ease of data transfer from the NEREUS computer to a laptop computer, when desired.

The computer interface to the mass analyzer and electrometer is via a digital-to-analog (D/A) and analog-to-digital (A/D) controller, referred to here as the DAQ, permitting a sampling frequency of up to 1500/s while adhering to a power budget of less than 5 W. The DAQ permits simultaneous output to the high-voltage operational amplifier and digitization of the electrometer output. In addition to carrying out D/A and A/D conversion, the DAQ also operates a relay controlling the on/off state of the emission regulator, thus permitting a computer-selectable, low-power sleep mode.

The PC-104 computer also sends data or receives commands from either of two RS232 serial ports, providing an optional link to AUV control computers or a half-handshake protocol to a radio transceiver via a tethered surface float, thereby allowing communication with a remote computer on the surface. The radio transceiver receives power from the internal NEREUS power system, with a total power requirement of $\sim$150 mW, and operates using a 418 MHz FM frequency with an effective range of $\sim$150 m when the companion laptop transceiver is within clear line-of-sight. Communications with either radio transmitter or standard wired serial link are performed at 9.6 kbit/s and may be routed through an optional 9-pin wet-pluggable, waterproof, marine cable. This cable also permits remote battery recharging and hard computer resets while the instrument is submerged.

2.4. Software

The NEREUS operational code is a stand-alone executable file that auto-loads during the computer boot sequence from a 128 MB flash disk configured as a fast IDE drive. Data files are also stored on this drive and specified by a time code name [hh-mm-ss] and .NDF (nereus data file) extension. The operating system and instrument code together require $\sim$500 KB, allowing the remaining 127 MB to be reserved for data storage. Because NEREUS employs signal averaging, memory requirements are decreased to less than 2 MB/h of operation, thus permitting at least $2\frac{1}{2}$ days worth of data storage when the instrument is in continuous operation. Error-correction algorithms are incorporated into the operation code to increase conversion accuracy. A signal-averaging regime is included in the operation code to further increase signal-to-noise ratio.

Functionality is enhanced through a supervisory control architecture, via a remotely linked GUI (Fig. 3) and a suite of embedded behaviors onboard the instrument that allows for external input or assimilated data to direct NEREUS operation adaptively in real time. These behaviors minimize the power and time required to

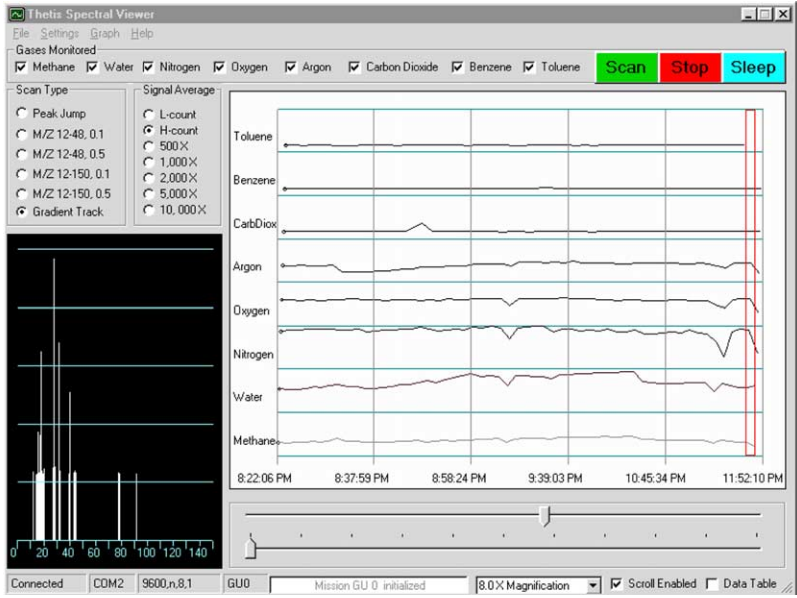

Figure 3. Graphical user interface for real-time analysis and supervisory control of the NEREUS instrument.

gather relevant data at an appropriate resolution by controlling the sleep/wake state, type of scan undertaken, and amount of signal averaging that is performed. Execution times vary from seconds to tens of minutes, depending on the scan-mode and signal-averaging combination that is executed. Six scan modes are available to the instrument, four of which are spectral sweeps in the ranges m/z 12–48 or m/z 12–150 with step intervals of 0.5 or 0.1 amu. The remaining two scan modes make use of a peak-jumping strategy, which allows the instrument to monitor rapidly 15 separate ion peaks by evaluating only the peak regions and thereby omitting

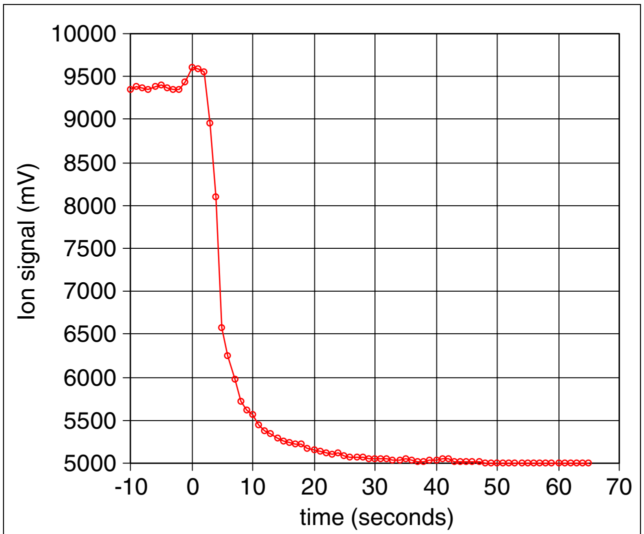

Figure 4. Time response of the NEREUS instrument to carbon dioxide.

m/z spectral regions of minimal interest. Gradient tracking, one of the peak-jumping modes, permits the instrument to adjust the time interval between successive scans according to absolute value of amplitude changes in the m/z peaks that are being monitored. The instrument can assume seven different signal-averaging intervals, two of which involve variable signal averaging. The five fixed signal-averaging routines are 500, 1000, 2000, 5000 and 10,000×, thereby decreasing statistical error to 4.5%, 3.2%, 2.2%, 1.4% and 1.0%, respectively. The variable signal averaging conducts repeated sampling until the absolute value of the integrated electrometer voltage relative to baseline exceeds either 50 or 100 V, and, to avoid baseline clipping, it relies on a baseline determination derived from the ion current sensed at $m/z = 11.5$ amu. This dependency on the number of samples averaged to the integrated voltage causes the same relative magnitude of statistical error to be generated for each data point, thus avoiding excessive sampling of large signals, or insufficient sampling of smaller signals.

3. Instrument performance

Quantitative models of instrument-response time and sensitivity were developed prior to construction of the NEREUS instrument [13], based on measurements of the response of the cycloidal MS to inputs of argon from a calibrated leak. Estimates for detection limits of individual gases were projected to be in the sub-ppm range for the major atmospheric gases and methane, and correspond well with observed sensitivities (e.g., 60 mV/ppm for methane at room temperature, and total pressure of 1 atm).

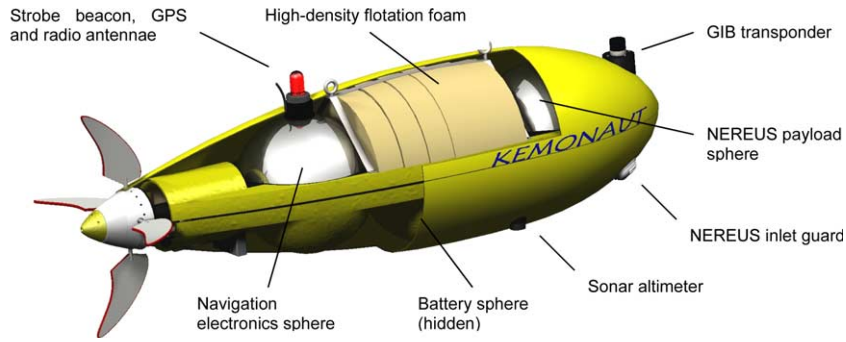

Figure 5. Cut-away view of the *Kemonaut* AUV.

Calculated instrument-response time ranged from 2 s for helium to ~15 s for light hydrocarbons (e.g., methane) and atmospherically abundant gases, including nitrogen, oxygen, argon and carbon dioxide to over 1 min for heavier hydrocarbons, such as toluene and benzene [13]. Measured time response to a step change in carbon dioxide – defined as the time required for the ion-current signal to decrease by 95% from its initial value – was observed to be ~15 s (Fig. 4).

3.1. Kemonaut AUV platform

NEREUS is designed to be compatible with Odyssey-class AUVs. However, because Odyssey II-class AUVs hold only two pressure spheres, both required for vehicle operation, the *Kemonaut* variant was developed to accommodate the NEREUS instrument. The *Kemonaut* AUV is largely based on the Odyssey II design, incorporating a free-flooding hull with three internal glass pressure-sphere housings, allowing the NEREUS submersible membrane-inlet MS to be carried as payload in its forward bay. The vehicle-payload combination weighs ~200 kg in air and is designed for operation to a depth of 300 m. Composite structural components, including carbon–fiber laminates and high-density structural foam, are used throughout the vehicle to minimize weight while maintaining adequate strength and vehicle stability. Stability is further increased through asymmetric positioning of the glass pressure spheres relative to the vehicle centerline. This design permits vehicle payload capacity to be greatly expanded while preserving the hull shape of the Odyssey II and allowing for the use of existing propulsion and control systems. The *Kemonaut* requires minimal support equipment, specifically a small boat as a tender, and a GIB-hydrophone array for real-time tracking of the AUV. Fig. 5 shows a cutaway diagram of *Kemonaut*.

4. Field tests

NEREUS was deployed on a mooring in Boston's Inner Harbor region, where several pollution sources remain, such as combined sewer overflows (CSOs) that are known to discharge quantities of hydrocarbons and organics during storm events [14], and as a tow-body within the Upper Mystic Lake, a metals-polluted lake [15], north of Boston.

Tethered deployments were executed by lowering the instrument in parallel with a Hydrolab sonde and attached depressor weight from a line through the water column. NEREUS ion peaks were displayed in real time via the radio transceivers and a ship-based laptop computer. Dissolved oxygen, salinity, oxidation–reduction potential, and temperature data from the Hydrolab sonde was stored and viewed via a cable connection to its Surveyor 4 logger at the surface. Although the Hydrolab dissolved oxygen data can be cross correlated with NEREUS oxygen peak data, there was no absolute *in situ* calibration scale for the other gases. The fact that instrument response is affected by temperature, and probably by pressure, implies that a means of *in situ* calibration should be provided in future instruments.

The Boston Harbor deployment area, located at N42° 22.23′ W71° 03.42′, experiences a diurnal tidal cycle typically of 3.5 m amplitude and has a mean low-water depth of ~9 m, causing the water column to be well mixed. Trials were conducted during high tide at depth intervals corresponding to 1.5, 3, 4.5, 6, 7.5, 9, 10.5 and 12 m. Scans were made across a spectral range 12–150 amu using a 2000× signal-averaging routine. The eight NEREUS spectra generated during this deployment indicated the expected well-mixed body of water. Increased carbon dioxide and the appearance of a small methane signal at 12 m was not unexpected, given the proximity to typically anoxic sediments. Concurrent decreases in oxygen were recorded at this depth by both the Hydrolab and NEREUS, supporting an anoxic bottom-sediment hypothesis.

NEREUS trials in the Upper Mystic Lake, located at N42°26′ W71°09′, were conducted using a tow-fish configuration, wherein box transects were conducted, covering the entire depth range (to 25 m). Hydrolab dissolved oxygen, salinity, and temperature data indicated the presence of two stratified water layers,

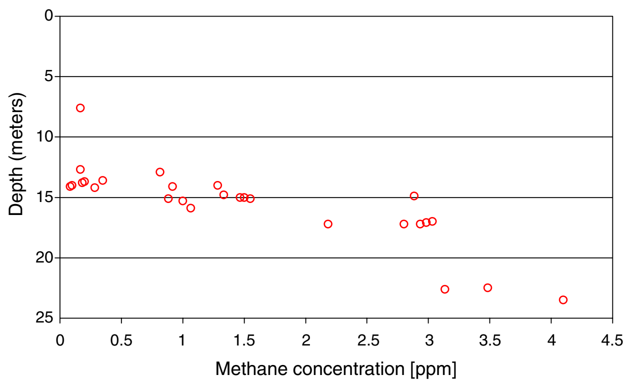

Figure 6. Methane concentration as a function of depth in Upper Mystic Lake (using $m/z = 15$ peak).

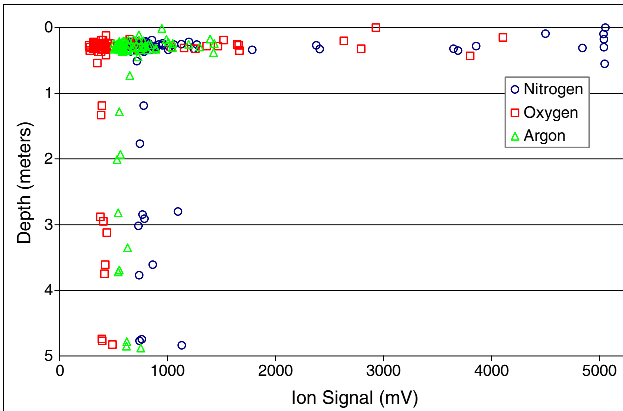

Figure 7. Depth record of dissolved gas ion signal from the NEREUS instrument during *Kemonaut* deployment in Boston Harbor.

interfacing at ~13 m depth. Fig. 6 shows a plot of NEREUS methane concentration versus depth. No temperature or hydrostatic pressure corrections were applied to the data.

Following tethered deployments, NEREUS underwent sea trials as payload aboard the *Kemonaut* AUV in Boston Harbor, demonstrating the ability of the NEREUS instrument to collect meaningful chemical data while operating onboard a moving AUV platform. The NEREUS instrument conducted spectral scans of volatile dissolved gases in the range 12–150 amu at a mass step interval of 0.1 amu to ensure that ion-peak shape could be clearly resolved. Signal averaging was 500 per data point, and the instrument was able to complete an entire 12–150 amu scan once every 98 s under these conditions. This wide scan mode was chosen so that high molecular weight hydrocarbons could be clearly identified in the event of the AUV encountering them.

The NEREUS instrument collected ~90 individual spectra over the course of eight AUV dive missions within a 3-h period. The data appeared to be largely unaffected by vehicle motion through the water or vibration from the propulsion and control system of the vehicle while underway. Spectra indicated the presence of only the expected dissolved atmospheric gases, principally nitrogen, oxygen, and argon. Due to the cold temperatures encountered on this day (an air temperature of −5 to −1 °C and a water temperature of 2–4 °C) the instrument's inlet membrane permeability was significantly decreased, causing all spectra to exhibit lesser peak heights than during the tethered deployment [16]. RMS noise was typically about 5 mV, but exhibited sudden increases, to hundreds of mV, apparently when the tender occasionally bumped into the AUV while being towed.

A time stamp synchronized merging of NEREUS chemical data with vehicle track log data (including depth). That revealed an apparent increase in dissolved gas concentration near the surface of the water (Fig. 7). This anomaly is likely to be the result of air-bubble entrainment from breaking waves generated by a +10 m/s wind that day. No hydrocarbon fractions or xenobiotic compounds were observed.

5. Summary

The NEREUS MS is capable of quantifying metabolic gases in aquatic systems at ambient levels in real time, and has completed numerous dives without failure aboard the *Kemonaut* AUV. The MS/AUV combination is capable of autonomously measuring chemical distributions in surface-water bodies in three dimensions, and the low power consumption of NEREUS makes possible missions lasting many hours.

We propose that future research efforts seek to:

- provide means of calibrating sensitivity *in situ*,
- increase depth capability,
- lower limits of detection to enable measurement of additional trace gases of interest (e.g., N_2O, H_2), and
- develop advanced vehicle-instrument behaviors for autonomously adapting mission strategy in response to observed chemical features.

Acknowledgements

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