Underwater Mass Spectrometry Advancements for Real-time Geochemical Analysis of Deep-sea Cold Seeps

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Abstract

Offshore oil and gas reservoirs commonly release fluids to the seafloor through hydraulic fracturing, caused by hydrostatic overpressure within the reservoir. This phenomenon is evidenced by associated blow-out pockmarks, seismic piping anomalies, and deep-sea hydrocarbon cold seeps. As a result, these seeps provide a means of characterizing fluids and brines transported directly from reservoir bodies. Integrating information from these fluids with other sensing methods offers profound insights into hydrocarbon risk, leakage, maturity, source, and migration. Modern laboratory geochemical seep data offers a wealth of information, but two simple parameters stand out: measurements of readily diffused or broken-down components, which indicate the presence of "live" seep fluids, and ratiometric alkane measurements. The latter are crucial for reservoir source assessment tools like Bernard diagrams, enabling quick discrimination between biogenic and thermogenic hydrocarbons.

In situ analyzers capable of determining multiple hydrocarbons simultaneously in real-time enable cost effective, adaptive, seep sampling strategies. To effectively characterize seeps, ratiometric determinations necessitate optimized analytical accuracy and detection limits across a wide concentration range. The Underwater Mass Spectrometer (UMS) developed at Beaver Creek Analytical, LLC (BCA) has been designed and commercialized for real-time, *in situ* ratiometric dissolved gas measurements at depths up to 3000 m. This technology has been deployed at over 200 deep-sea seeps, leading to the characterization of seep hydrocarbons and their associated dissolved gas plumes.

To enable these measurements, the UMS has undergone a number of upgrades in recent years. The inlet now uses a laser cut membrane support capable of sustaining hydrostatic pressure equivalent to 3000 m water depth. The vacuum transfer line is designed to include an optional water trap, which improves detection limits by freezing water between the inlet and the analysis chamber. Detection limits have been further improved through ion source optimizations. Each component, including mass spectrometer data collection and analysis, is performed by a single microcontroller board.

Subsea valves located externally to the mass spectrometer's subsea vessel have significantly improved subsea operations, leading to numerous analytical advancements. These include:

- **Steady State Analysis**: Recirculating seawater that has already passed through the analyzer enables the sample to achieve steady state with the UMS and provides quantitative conditions.
- **External Standard Introduction**: Stored in gas-tight syringes or bags, standard seawater solutions facilitate calibrations that effectively negate the influence of ambient temperature and pressure variability.
- **Sample Collection**: Pulses of the external standards enable precise timing calibrations. Knowing system timing allows BCA’s UMS to trigger the collection of target-positive discrete samples. These samples can then be analyzed in an accredited lab for complete compositional and isotopic analyses.

The BCA UMS embodies numerous analytical improvements while maintaining a focus on ruggedization and reduction in size and weight, making it uniquely suitable for field-portable applications. In addition to providing real-time geochemical data from specific fluid point sources using precisely controlled platforms (e.g., ROVs), it has successfully guided autonomous underwater deployment platforms (e.g. AUVs). Data from recent cruises, totaling over 26 weeks at sea, will be used to illustrate these advancements.

Biography - Ryan Bell

Ryan J. Bell, Ph.D., is a chemical oceanographer and engineer specializing in the design and deployment of chemical sensing systems for environmental monitoring in harsh conditions, with extensive experience in mass spectrometry, real-time data visualization, and data analysis, supported by academic teaching roles, professional appointments, patents, and numerous scientific publications. His work aids clients and partners in fulfilling adaptive sampling strategies to help make cost-effective campaign decisions. Ryan leads research, manages projects, and publishes papers on advanced instrumentation for geotechnical surveys. Survey targets have included seafloor hydrates, well-head blow-out plumes, fugitive emissions, anoxic basins, and cold-seep fields.

Keywords

Deep-sea cold seeps, Dissolved gas measurements, Ratiometric alkane measurements, Real-time geochemical analysis