Beaver Creek Analytical LLC

BCA Whitepaper: Underwater Mass Spectrometer, *In Situ Calibration*

In Situ Calibration Whitepaper V1.0

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Changelog:

Date	Whitepaper Version	Comment
Jan, 2025	V1.0	Initial Release

Underwater Mass Spectrometer, *In Situ Calibration*

UMS Analyte Calibration

Once operational, Beaver Creek Analytical's (BCA) Underwater Mass Spectrometer (UMS) can commence data collection immediately. However, the initial data will be limited to detect/no-detect results unless the UMS undergoes calibration. Pre-cruise and post-cruise calibrations provide a reliable measure of the actual concentrations found in the ocean, which are sufficient for many applications. This reliability is supported by the dynamic nature of the ocean, where dissolved gas concentrations vary significantly over time and space as water packets move and dilute. Consequently, sampling variability typically exceeds the variability between UMS calibrations.

To achieve accurate analytical and ratiometric results, in situ calibrations are required. This process involves transporting an external standard to the sampling site and using a stream selector valve on the UMS inlet to redirect the calibration solution to the UMS for a specific period. This method allows the system to collect the data needed to account for variations in pressure, temperature, salinity, and UMS residual gases that affect raw data results. Using this approach, real-time results can provide ratiometric data comparable to laboratory results from discrete samples.

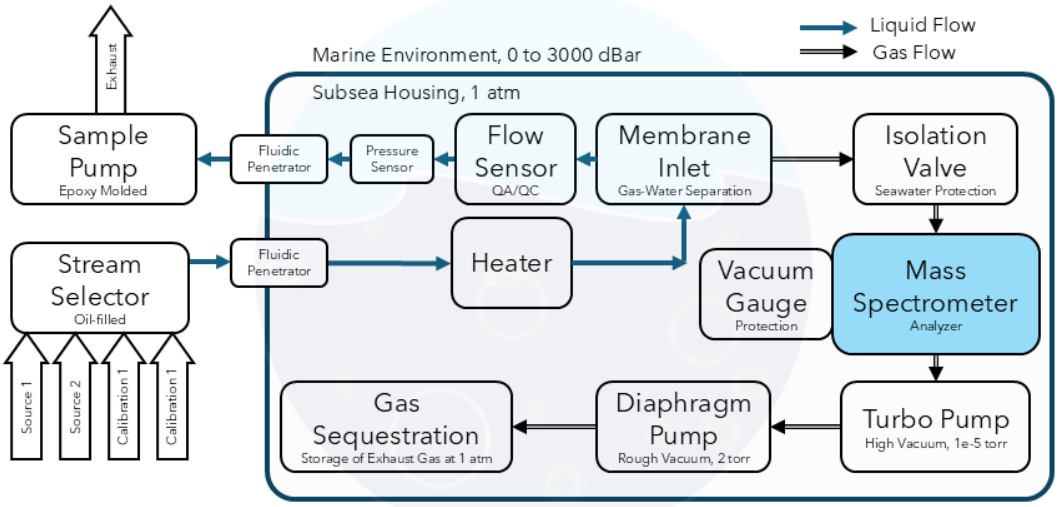

Figure 1. Simplified Schematic of the underwater mass spectrometer operational components. The stream selector enables automated calibration of the system's response to analytes and system timing.

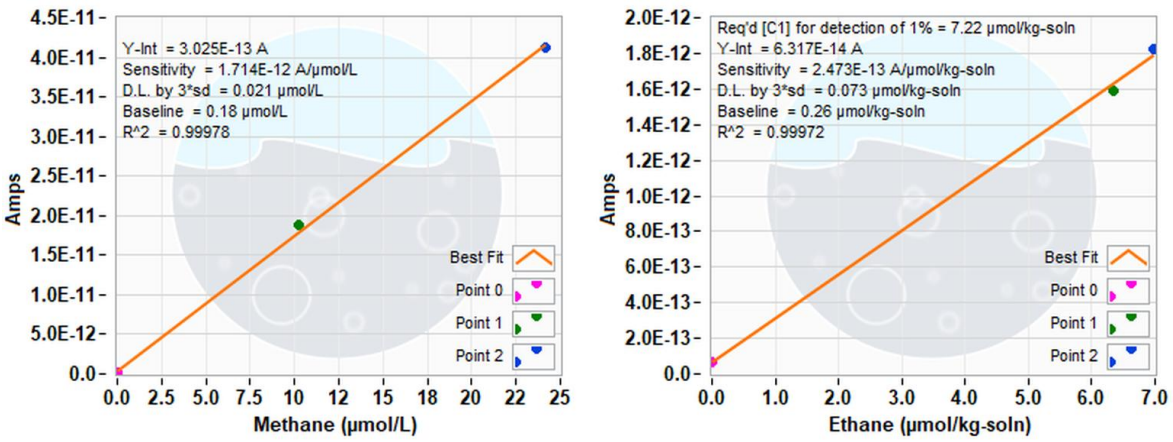

Figure 2. Analytical results collected using and in situ *calibration system.*

UMS Timing Calibration

The introduction of the external standard enhances the determination of system timing within the UMS. By analyzing the duration required for the sample impulse to generate a response in the UMS, the transfer function of the entire system can be accurately established. This approach is advantageous when there is a sampling time offset due to the transport of the sample from the system's inlet to the UMS location. Once determined, timing calibration results facilitate:

- Precise mapping by accurately correlating the UMS response to the platform's location at the moment of sample ingestion.
- Transfer function corrections that improve ratiometric quantitative results.
- The effective use of discrete sample collection methodologies.

BCA offers clients an effective solution for in situ calibrations by providing a subsea stream selector directly controlled by the UMS. This allows for the introduction of external standards also provided by BCA or a sample from a secondary inlet location (e.g. benthic chamber). The calibration process is initiated by the user via BCA software, with results automatically generated and uploaded to the UMS after user acknowledgment. BCA is currently integrating this intelligent self-calibration capability within the UMS firmware, enabling fully automated and user-free in situ calibrations for analyte concentration and system timing.

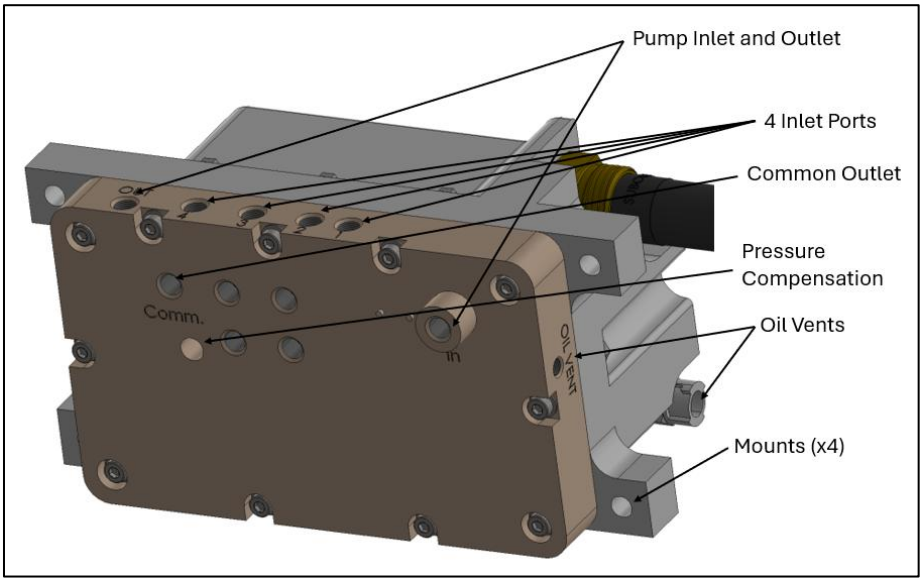

Figure 3. For ease of maintenance and enhanced flexibility, the oil-filled stream selector is positioned externally to the subsea vessel without impacting the critical aspects of the mass spectrometer. The above design features four sample ports and one common outlet as well as an integrated sample pump.