

BCA Whitepaper: Discrete Sample Collection



Discrete Sample Collection Whitepaper V1.0

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Changelog:

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Jan, 2025	V1.0	Initial Release

Triggered Sampling

By providing real-time chemical data, the underwater mass spectrometer (UMS) system enhances opportunities for discrete sample collection upon detection of target analytes. The sniffing system, operated and sold by Beaver Creek Analytical (BCA), can be precisely timed to ensure accurate mapping using fast-moving platforms. This precise timing also allows for the redirection of the most relevant water samples from UMS effluent into collection vessels. The novel BCA subsea stream selector, used for calibrating the UMS, can also be employed on the outflow to achieve this redirection to take discrete water samples for further on board analysis. This method can target the most intense concentration transients, allowing for optimal use of shipboard or laboratory-based measurements and informing the laboratory operational decision-tree.

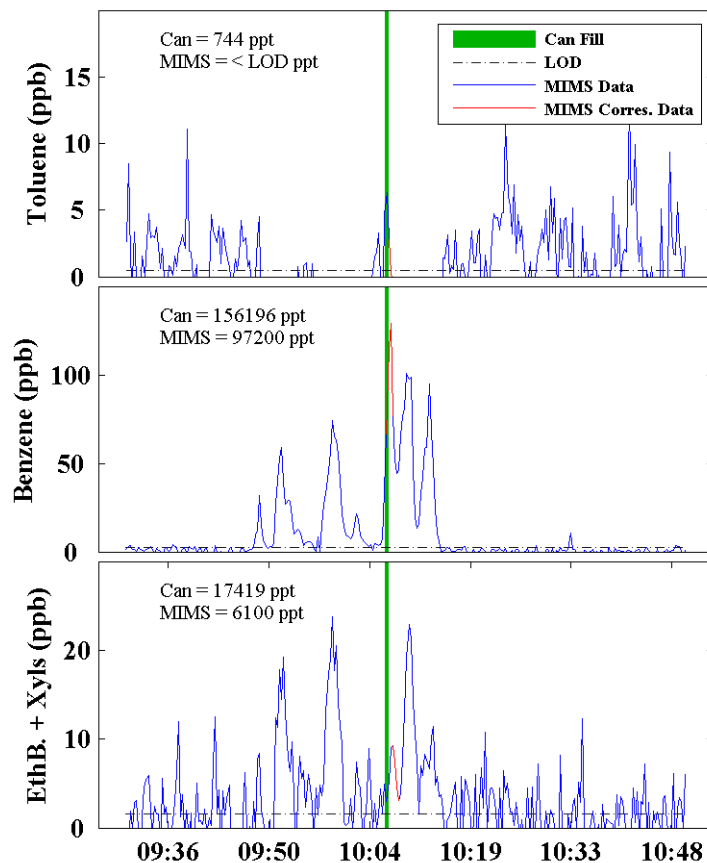


Figure 1. Intense and transient data captured by a discrete sampling cannister where sampling trigger was informed by membrane inlet mass spectrometer real-time atmospheric data (credit: AERL)

As demonstrated by our previous work with Davey et al, 2020¹, this approach captures momentary and transient data that would otherwise be missed in highly transient and turbulent environments. The sampling trigger may be a completely automated system using real-time results or rely on human-in-the-loop sampling decision; Hwang et al, offers a review of such methods including the use of a UMS². Further, sampling decision may rely on predetermined time of day or location-based triggers or be completely opportunistic^{3,4}. Perhaps the most useful aspect of this approach is that the UMS can simultaneously produce chemical gradient maps of the area that provide critical context. This

data can be used to provide unambiguous context for each sample to ensure the origin of the sample is known, for example, bubble ebullition.

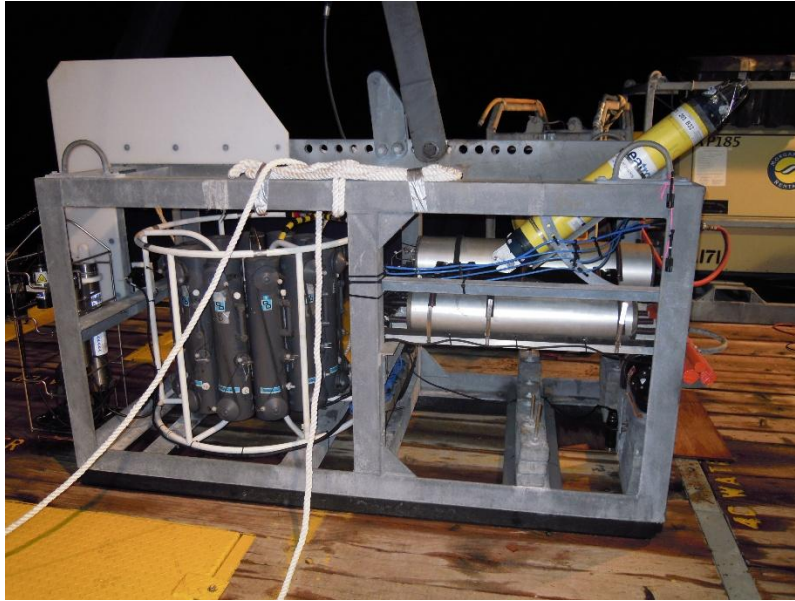


Figure 2. Towed system for tracking hydrocarbon signatures released from the Deepwater Horizon oil spill. The system used real-time data from an underwater mass spectrometer (among other sensors) to inform the timing for triggering the discrete Niskin samplers. (2010)

Discrete Sample Collection

BCA's system collects samples that are (30-500 mL) from the UMS outlet are collected in gas-tight and pressure compensated bags or syringes, guaranteeing lossless collection despite significant changes in temperature and pressure. Furthermore, immediate in situ preservation of samples prevents oxidation by omnipresent methanotrophs and simplifies transport by minimizing refrigeration needs.

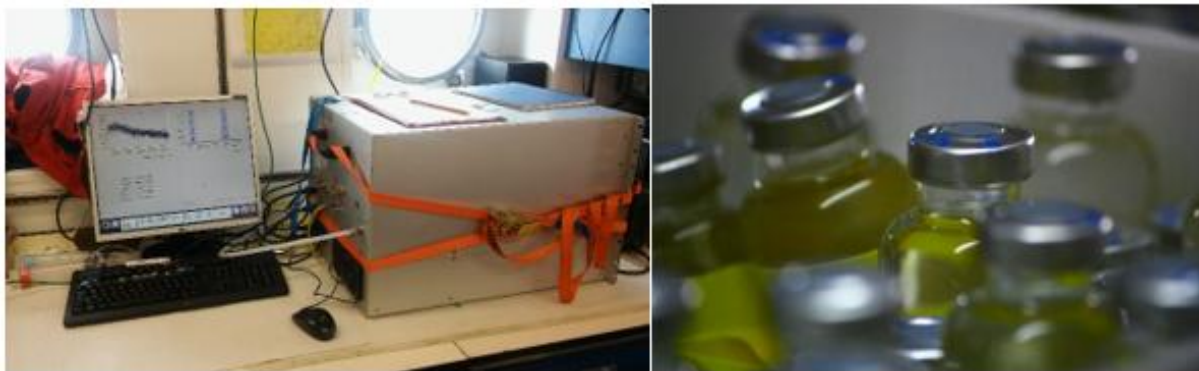


Figure 3. Shipboard dissolved gas analysis system

BCA offers shipboard compositional analysis via gas chromatography⁵ and shipboard isotopic analysis by cavity ring down spectroscopy. Our standard shipboard isotopic instrumentation offers $\delta^{13}\text{C}$ for CH_4 and CO_2 along with the contextual data collected in situ, we offer a complete dataset with cross-checked results that can be related directly to the source feature. Further, we are actively working on systems capable of 2H in CH_4 and $\delta^{13}\text{C}$ in C_2H_6 isotopic results, pushing the envelope even further on

unambiguous for geochemical conclusions. All together, we provide real-time and near-real time results that have the potential to save tens of thousands of dollars in ship-time through the use adaptive sampling to avoid null replicates and focus on the most meaningful sites.



Figure 4. Ship-capable cavity ring down and gas chromatograph systems for the isotopic and compositional analysis of dissolved gas hydrocarbons.

Additionally, samples can be sent to ISO/IEC 17025 accredited laboratories for comprehensive and legally defensible analysis. As they are preserved in situ, the samples can be refrigerated and shipped in cooler with no additional sample handling – a key failure point in many operations. Having associated UMS data will help inform the laboratory’s decision making during the pre-analysis process and prevent wasting both sample and time.

Data Product

Through detailed analysis of hydrocarbon isotopic and compositional ratios, the origins of hydrocarbons can be categorized by comparison to published literature⁶⁻⁸—potentially providing clear indications of a seep's source as either biogenic or thermogenic (or abiotic). The sampling method described above employs informed triggers and in situ mapping, allowing these results to be positively linked to specific seep sites. Consequently, the findings can be utilized for assessments of the underlying source reservoir and derisking infrastructure planning projects.

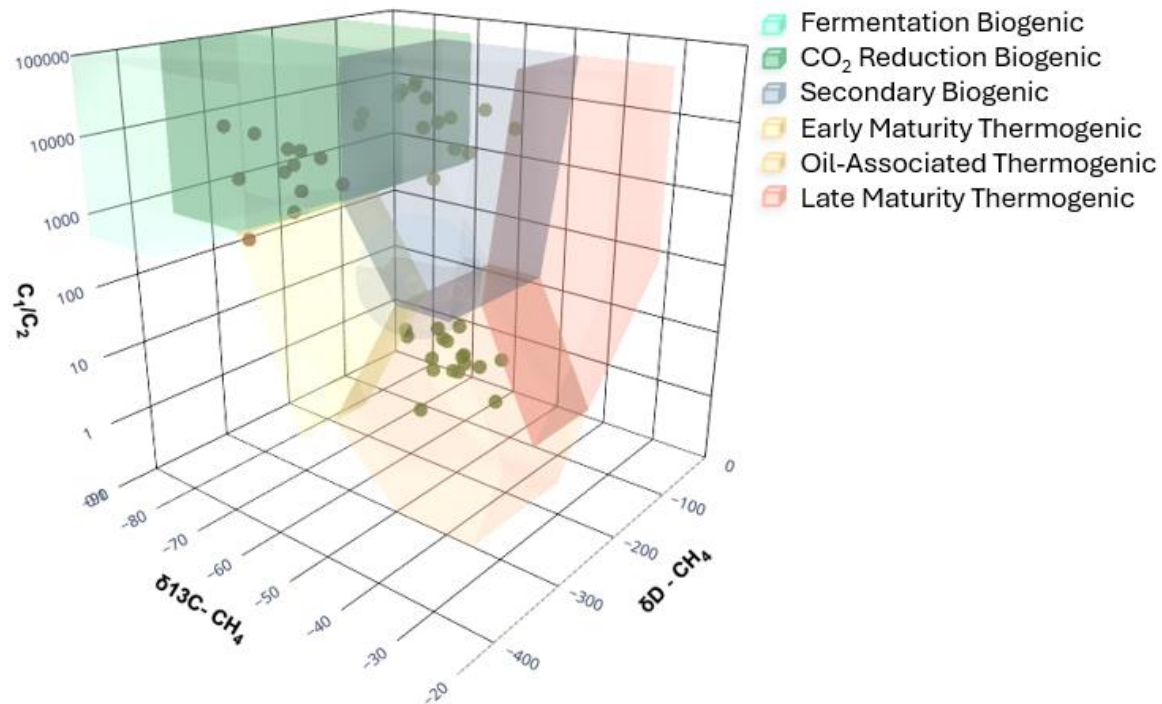


Figure 5. Categorization of hydrocarbon origins through isotopic and compositional ratios. Simulated example data.

References

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