

Under Water Coded Aperture Miniature Mass Spectrometer for Measurements of Methane Content in the Ocean

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Abstract

Methane hydrates, solid complexes of water and methane, naturally occur in permafrost sediments and beneath the ocean floor[1]. Remarkably, under standard temperature and pressure, dissociation of one cubic meter of methane hydrate can yield up to 164 cubic meters of methane gas[2]. These hydrates remain stable within a narrow range of pressure and temperature conditions[3]. However, global warming can disrupt this stability, potentially leading to a catastrophic feedback loop between climate change and methane release from methane hydrate reservoirs. The exact pathways of methane release and its metabolism in the ocean water column remain unclear[1, 3], as *in situ* methane content measurements are still challenging. Currently, the most common method involves collecting seawater samples in canisters for laboratory analysis [4, 5], which is expensive, introduces potential errors, and does not provide the real-time data that can help guide sampling strategies. To address these challenges, we are developing an underwater coded aperture miniature mass spectrometer[6] for *in situ* methane measurements in the ocean water column. This instrument will not only be applicable to methane released from methane hydrates but also to other oceanographic and biogeochemical research questions. Our mass spectrometer integrates three key technologies: a

cycloidal mass analyzer, a capacitive transimpedance array detector, and a spatially coded aperture[6]. The gas content in the water will be sampled using a high-pressure membrane inlet[7]. The entire instrument, including control boards, pressure vessel, mechanical parts, cooling system, has been designed, simulated, and fabricated. We will present the design and fabrication of the instrument, including details of the control board[8] and preliminary calibration curves of low concentrations of methane/air in water.

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References

- [1]Ruppel, C.D. and J.D. Kessler, *The interaction of climate change and methane hydrates*. Reviews of Geophysics, 2017. **55**(1): p. 126-168.
- [2]Makogon, Y.F. and R.Y. Omelchenko, *Commercial gas production from Messoyakha deposit in hydrate conditions*. Journal of Natural Gas Science and Engineering, 2013. **11**: 16.
- [3]Ketzer, M., et al., *Gas hydrate dissociation linked to contemporary ocean warming in the southern hemisphere*. Nature Communications, 2020. **11**(1).
- [4]Boulart, C., D.P. Connelly, and M.C. Mowlem, *Sensors and technologies for in situ dissolved methane measurements and their evaluation using Technology Readiness Levels*. TrAC Trends in Analytical Chemistry, 2010. **29**(2): 186-195.
- [5]Magen, C., et al., *A simple headspace equilibration method for measuring dissolved methane*. Limnology and Oceanography-Methods, 2014. **12**: 637-650.
- [6]Aloui, T., et al., *Spectral Reconstruction Improvement in a Cycloidal Coded-Aperture Mass Spectrometer*. Journal of the American Society for Mass Spectrometry, 2024.
- [7]Schlüter, M. and T. Gentz, *Application of Membrane Inlet Mass Spectrometry for Online and In Situ Analysis of Methane in Aquatic Environments*. Journal of the American Society for Mass Spectrometry, 2008. **19**(10): 1395-1402.
- [8]Serpa, R.B., et al., *Control system for an underwater coded aperture miniature mass spectrometer*. Green Analytical Chemistry, 2025. **13**.

Biography - Rafael Bento Serpa

Rafael Bento Serpa is a Research Scientist at Duke University. He holds a Ph.D. in Physics, along with bachelor's degrees in Physics and Electronic Engineering. His scientific career began in the field of materials science, where he focused on electrochemical systems with applications in photocatalysis and organometallic solar cells. Since 2019, he has been working at Duke University on the development and application of mass spectrometry instrumentation for isotopic ratio analysis and the quantification of dissolved gases in oceanic environments.

Keywords

Under water MS, Methane measurement in ocean water, Depth profile of methane concentration, Cycloidal mass analyzer