Medusa-Aqua System: Development of Analytical Techniques for Novel Halogenated Transient Tracers in the Ocean

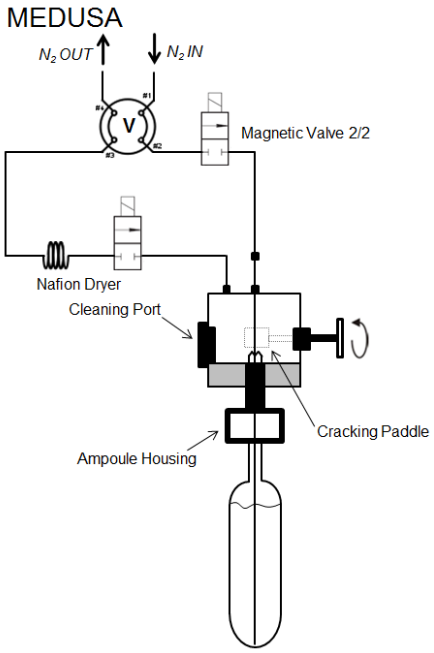
Pingyang Li[1], Toste Tanhua[1]

[1] GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany
[Corresponding author: pli@geomar.de]

Chlorofluorocarbons (CFCs) and SF_6 are widely used oceanic transient tracers for the determination of oceanic circulation, mixing and for estimating oceanic uptake of anthropogenic CO_2. However, the utility of CFCs is increasingly restricted by their negative atmospheric growth rate. There is a need to explore other transient tracers with positive growth rates. Utilization of multiple transient tracers facilitates empirical determination of the transit time distributions (TTDs) in the ocean, a fundamental property of transport.

A proven analytical technique based on a pre-concentration step followed by GC-MS analysis, the Medusa system [*Miller et al.*, 2008], enables the reliable and fast simultaneous determination of a large number of relevant transient trace gases. The goal of this study is the analysis of ocean waters in order to obtain depth profiles of a suite of potential oceanic transient tracers, such as HCFC-22, HFC-134a, HFC-125, HFC-23, CF_4 and C_2F_6. This will be performed by modification of the "Medusa" analytical system (the Medusa-Aqua system) to be able to measure seawater.

The Medusa-Aqua system consists of a Medusa system and a seawater sample pretreatment system. The Ampoule-Cracker-System (see figure in right-hand side) was developed as the seawater sample pretreatment system to degas the samples from gaseous tracers before injecting into the Medusa. This method is used for off-line seawater samples in 1.1L ampoule that are flame sealed at sea and measured in the lab in Kiel. This method is based on purge-and-trap technology, where the Medusa system serves as the trap unit and chromatographically separates the sample for detection on a mass spectrometer.



The Medusa-Aqua system has measured over 20 seawater samples from two research cruises to the tropical Atlantic Ocean in 2011 and 2016. It can detect over 25 species in seawater samples. Except C_2F_6, HCFC-22, HFC-134a, HFC-125, HFC-23 and CF_4 can all be detected. The purge efficiencies for HCFC-22 reach 98.3±1.2% after purge three times. For other compounds, they can reach 100%.

Here we will show results from seawater measurements and discuss the potential for some compounds as oceanic transient tracer in view of their atmospheric history, feasibility of analysis and stability in sea water.

References

B. R. Miller, R. F. Weiss, P. K. Salameh, T. Tanhua, et al., Medusa: A sample preconcentration and GC/MS detector system for in situ measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, Analytical chemistry, 80, 1536-1545, 2008.