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Chemical characterization of dissolved organic matter from original seawater using LC-FT-ICR-MS

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Dissolved organic matter (DOM) is one of the most complex natural mixtures and thus poses the greatest challenges to chemical characterization using instrumental analytics. The characterization of marine DOM is further complicated by the fact that the salt concentration in the ocean exceeds the DOM concentration by a factor of 35,000. At the same time, the low DOM concentrations challenge the analytical sensitivity. To improve sensitivity and robustness, solid-phase extraction (SPE) is often used for DOM desalting and enrichment. However, SPE is not quantitative leaving more than half of the DOM analytically undetectable. The chemical composition of the extracts obtained is strongly influenced by the type and loading of the adsorbent.

Here we present a new method for characterizing DOM that allows direct injection of seawater samples with native salt and DOC concentrations. The method uses reversed-phase chromatography in combination with Fourier transform ion cyclotron resonance mass spectrometry (LC-FT-ICR MS). It allows effective salt separation and highly sensitive detection of organic compounds in as little as 100 µL of seawater. A post-column counter gradient quarantees a stable solvent matrix during electrospray ionization and internal standardization supports internal calibration and quantitative exploitation of the analytical data.

We determined analytical metrics such as reproducibility, robustness, sensitivity, and linear detection range. The method was tested with DOM samples of varying carbon and salt concentrations and applied to samples from the central Arctic Ocean with DOC concentrations as low as 20 µmol / L. Each ocean water sample yielded more than 10,000 molecular formulas with an average of about 20 C atoms per formula. Therefore, the average detected absolute amount of a molecular formula was in the low femtomole range, not considering structural isomers.

The method provided a quantitative DOC response, allowing initial quantitative estimates of DOM sub-fractions in seawater (such as terrestrial dissolved organic carbon) that are relevant for the global ocean carbon cycle. Moreover, liquid chromatographic separation opens an analytical window that supports separation of structural isomers based on polarity, a key for an improved understanding of the role of DOM in aquatic systems.