



Development and application of solid phase microextraction to the measurement of methylamines in seawater

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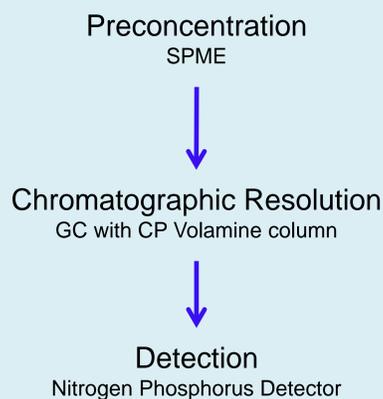
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Introduction

The methylamines (MAs) are ubiquitous in the marine environment and thought to be atmospherically active. Produced primarily by the degradation of glycine betaine (GBT), the MAs can, as neutral species, diffuse across the air-sea interface. Here, they potentially form cloud-condensing nuclei which can affect cloud cover. The chemical properties of the MAs mean that their determination presents a particular analytical challenge.

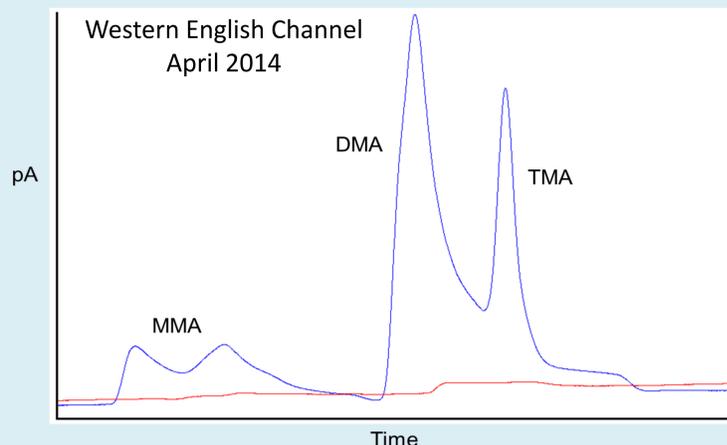
Analytical Approach



Methodology

- 1) Filtered seawater samples (0.7 µm GF/F) were spiked with MAs (natural samples filtered but not spiked).
- 2) Water samples were adjusted to pH 13.4 with NaOH solution.
- 3) The SPME fibre (PDMS/DVB) was exposed to the sample headspace while the sample was stirred and heated (60°C) for 2 hours.
- 4) The fibre was retracted then thermally desorbed in a GC injector at 270°C
- 5) MAs were resolved on a Volamine GC column (Agilent) and detected using a nitrogen-phosphorus detector.

MAs successfully quantified in seawater



MMA
6 nM

DMA
3 nM

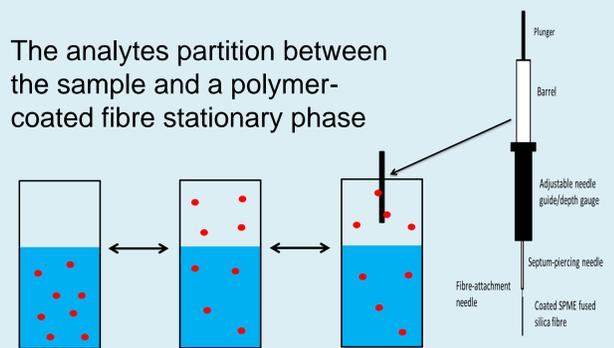
TMA
20 nM

In range of previous reported concentrations for WEC coastal waters

Solid Phase Microextraction

Solid phase microextraction (SPME) is a solvent-free extraction process that simultaneously extracts and preconcentrates analytes from aqueous samples or sample headspace

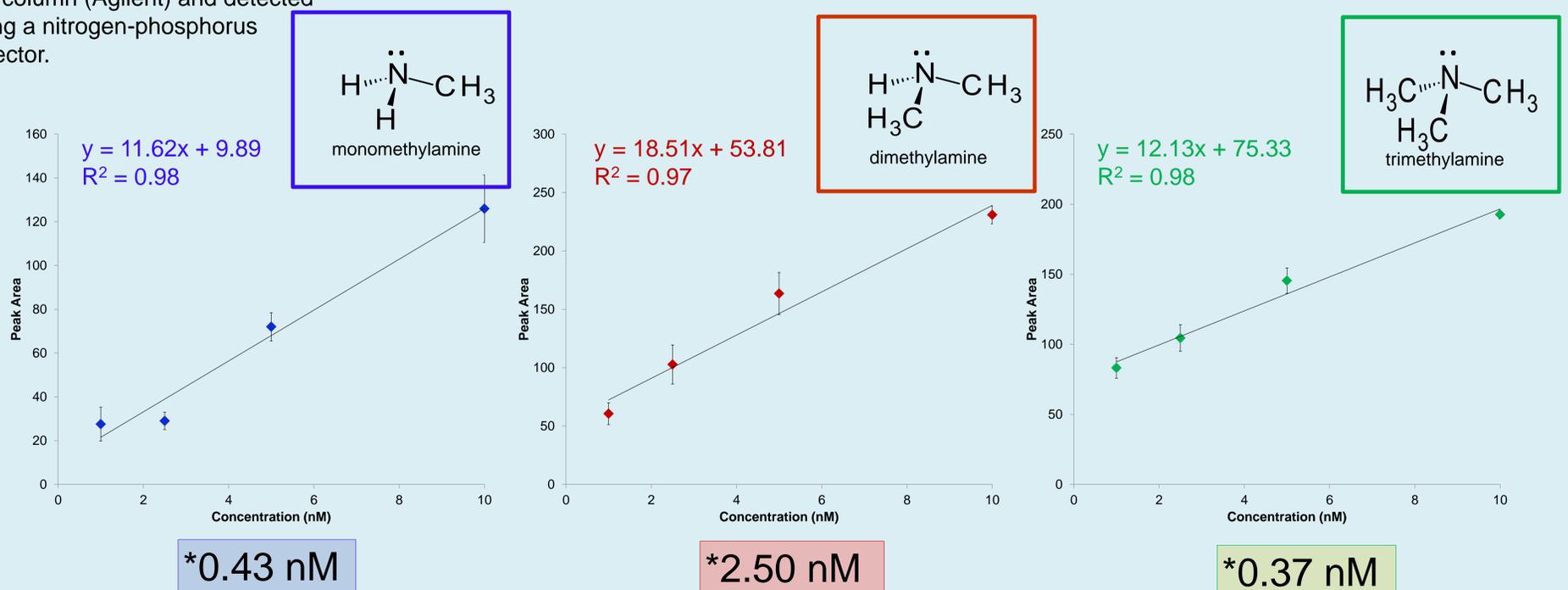
The analytes partition between the sample and a polymer-coated fibre stationary phase



Headspace SPME involves two mass transfer steps:

- Between the sample and the headspace
 - Between the headspace and the fibre coating
- The analytes are then thermally desorbed from the fibre in the GC injector.

The fibre selected for pre-concentration of the MAs was polydimethylsiloxane/divinylbenzene (PDMS/DVB).



*Limit of Detection (calculated as $3\sigma/S$, where σ = standard deviation and S = slope of calibration line of best fit).

Conclusions

The high volume SPME-GC-NPD approach we have developed represents an accurate and precise method for the analysis of the MAs in seawater at environmentally relevant concentrations.

This work represents a significant step forward in our ability to understand MA cycling and its importance in the marine environment.