Molecular characterization of natural organic matter using non-discriminating flash pyrolysis

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A substantial fraction of natural organic matter (NOM) consists of complex mixtures of macromolecular compounds. Consequently, high-molecular-weight fragments liberated during the pyrolysis of NOM often carry the most significant structural information. Their diagnostic value, however, is commonly limited by the preferential transfer of lower-boiling pyrolysis products to the GC column.

Non-discriminating pyrolysis is an upcoming technique [1] that minimizes transfer losses of fragments such as long-chain alkanes and alkylated aromatics. In addition, the novel technique allows a range of sample sizes from less than a microgram for bacterial biomass up to 15 mg for the study of samples of low organic carbon content, such as soils and sediments (0.1-1.0%C), which eliminates pretreatment requirements. In this study, non-discriminating pyrolysis-GC/MS performed on a wide range of NOM sources allowed the observation of large molecular fragments, enabling a better understanding of the overall macromolecular structure of the NOM present. When comparing the results obtained with non-discriminating pyrolysis to those obtained by conventional Curie-point pyrolysis for Tertiary sandy aquifer sediments [2], the significance of macromolecular structures within NOM was stressed in the former technique by the strong presence of various polyaromatic and long-chain aliphatic compounds that were underexposed by the latter technique. Overall, non-discriminating pyrolysis promises to be a useful tool for the characterization of the macromolecular part of NOM.

References

[1] Z. Parsi, T. Górecki, J. Poerschmann, J. Anal. Appl. Pyrolsis 73 (2005) 89–96

[2] N. Hartog, J. Griffioen, P.F. van Bergen, Chem. Geology, http://dx.doi.org/10.1016/j.chemgeo.2004.11.006

Mass spectrometric investigation of thioarsenate formation in waters

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Introduction

Arsenic (As) mobilization in ground water aquifers has been linked to reducing geochemical conditions. Recent studies have suggested that As may form soluble sulfur species in sulfidic waters, but no spectrometric proof of this hypothesis has been produced at ambient As concentrations.

Methods

The four thioarsenates mono-, di-, tri- and tetrathioarsenate were synthesized in solution following previously published procedures. All members of the homologue series were characterized mass spectroscopically (MS) using electrospray ionization (ESI) with either quadrupole-quadrupole or quadrupole-time-of-flight MS detection in the negative ion mode. Fragmentation patterns of major ions were obtained by collision-induced dissociation. Geochemical model experiments were conducted by mixing 10 mg/L arsenite or arsenate with equimolar amounts of sulfide or elemental sulfur in deionized water in an inert atmosphere, and withdrawing sub-samples at certain time intervals. These model samples were either analyzed by ESI-MS directly, or subjected to analysis by anion exchange chromatography-inductively-coupled plasma-MS (AEC-ICP-MS).

Results

All members of the homologue series (including arsenate itself) show the same general types of major ions in ESI-MS: the molecular ion in the form $H_2AsO_xS_{4-x}^-$ (x = 0-4), fragments where this molecular ion loses H_2O or H_2S (where possible), and clusters of the molecular ion with Na^+ and/or H_2O. Although certain fragments of different thioarsenates are either identical or have the same nominal mass, the molecular ions are characteristic of each compound and are not overlapped by fragments from other As species.

Of the four possible combinations of As and S species, only the reaction of arsenite and sulfide yielded thioarsenates fast; within 24 h reaction time, significant amounts of these species were observed. Although this reaction would be expected to yield thioarsenites, (AEC)-ESI-MS proves unequivocally that thioarsenates are the only reaction products. We will attempt to provide a geochemical explanation for this apparent contradiction.