

## [PP 1.7]

### Speciation of Copper and Iron Using Tangential Cross-Flow Ultra-Filtration Combined with Micro-Extraction in Small Sample Volumes

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The speciation of trace metals is of great importance for understanding the uptake and bio-geochemical cycling in natural aquatic systems. Copper and iron are essential metals for many aquatic species, but ionic Cu(II) has been shown to cause growth and reproduction inhibition at levels down to 3 µg/l for some sea-urchins.

The tangential cross-flow ultra-filtration technique can be used to separate the phases of metals between solid, colloid and ionic by filtration and ultra-filtration of water samples. After 0.45 µm filtration, the colloid concentration can thus be determined as the total copper and iron in the retentate of a 1-10 K Dalton ultra-filtration, and the ionic fraction as the concentration in the permeate of the 1-10 K Dalton ultra-filtrate (see for instance L-S. WEN et. al., 1996).

In this study, the ultra-filtrated samples were analysed for a number of different substances, e.g. nutrients and TOC, which left only minimal amounts of samples for the metal speciation work. This meant that only 10-100 ml of the samples was available for analysis, and micro extractions were therefore needed to concen-

trate and analyse the samples. The method of direct extraction in graphite furnace, autosampler cups (APTE and GUNN, 1987) was tested and modified for use with these samples, and applied to samples from oligotrophic as well as eutrophic waters.

Water sampling for this study was carried out under the MAST III EU project KEYCOP (<http://biologi.uio.no/keycop/home2.htm>), an interdisciplinary study of key coastal processes.

Results and discussion on the ability of the applied micro-extraction and ultra-filtration techniques to cope with the low-levels of metals in open seawater will be presented.

WEN, L.-S.; STORDAL, M.C; TANG, D.; GILL, G.A.; SANTSCHI, P.H. (1996): An ultraclean cross-flow ultrafiltration technique for the study of trace metal phase speciation in seawater. In: *Marine Chemistry* 55, pp 129-152

APTE, S.C. AND GUNN, A.M. (1986): Rapid determination of copper, nickel, lead and cadmium in small samples of estuarine and coastal waters by liquid/liquid extraction and electrothermal atomic absorption spectrometry. In: *Analytica Chimica Acta* 193, pp. 147-156

## [PP 1.8]

### Determination of some Arsenic Compounds in Aqueous Extracts

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The toxicity and bioavailability of an element are not dependent on its total concentration, but are strongly dependent on its chemical form. In the case of arsenic, the inorganic forms are orders of magnitude more toxic than the organic forms. The toxicity of arsenic compounds decreases in the following order: Arsenite ~ arsenate >> methylarsonic acid ~ dimethylarsinic acid >> arsenobetaine, trimethylarsine oxide, arsenocholine, tetramethylarsonium ion.

Thus, to estimate the risk to humans, animals and other organisms, the chemical forms of arsenic have to be determined. To determine the chemical form of an element a chromatographic separation (liquid chromatography, gas chromatography, capillary electrophoresis) is employed to separate the compounds and element-specific detectors are used for their quantification. Most commonly used element-specific detectors are the atomic absorption spectrometer (flame or flame-less), inductively coupled plasma atomic emission spectrometer (ICP-AES) or inductively coupled plasma mass spectrometer (ICP-MS).

In this work, a Hamilton PRP-X100 anion exchange column was used to separate arsenous acid, dimethylarsinic acid, methylarsonic acid, and arsenic acid. Potassium hydrogen phthalate solution saturated with nickel hydroxide was used as a mobile phase when the graphite furnace atomic absorption spectrometer (GFAAS) served as arsenic-specific detector. The best separation of all four arsenic compounds in a reasonably short

time of about 30 min was obtained with 0.003 M potassium hydrogen phthalate solution at pH 5.5. With ICP-MS as an arsenic-specific detector, a 0.030 M phosphate buffer solution at pH 6.0 was used as the mobile phase.

Arsenic compounds were identified and determined in mushroom samples, because mushrooms may be used as biological monitors for trace elements. Among several mushrooms accumulating arsenic, arsenic compounds were determined in aqueous extracts of *Laccaria amethystina*, *Laccaria laccata*, *Thelephora terrestris* and *Boletus cavipes*. In the edible *Laccaria amethystina*, 97% of the arsenic (~26 mg As/kg dry mass) was found to be dimethylarsinic acid and 3% arsenite. In the related *Laccaria laccata* (~26 and ~32 mg As/kg dry mass), the predominant arsenic compound was arsenate (~80%) and the minor arsenic compounds were arsenite (~14%), and dimethylarsinic acid (~3%). In the *Thelephora terrestris*, an inedible mushroom with woody structure, only inorganic arsenic compounds were determined (~70% arsenite and ~30% arsenate). In the *Boletus cavipes*, 50% of the arsenic (~12 mg As/kg dry mass) was found to be arsenate, 40% arsenite, and 10% in the form of dimethylarsinic acid.

The quantitative results for the four mushrooms obtained with the two systems agree reasonably when the concentrations of arsenic compounds in the aqueous extracts are sufficiently high. Minor arsenic compounds could only be detected with HPLC-ICP-MS.