Approaches to Metal Speciation Analysis in Natural Waters

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Abstract

Approaches to the separation and identification of metal species in natural waters are discussed.

Dissolved and colloidal metal species may be fractionated, on the basis of physico-chemical characteristics, by ion exchange, u.v. irradiation, resin adsorption, solvent extraction or strong acid digestion. Size fractionation techniques include filtration, centrifugation, dialysis, ultrafiltration and gel filtration chromatography. Suitable detection techniques, either before or after fractionation, are anodic stripping voltammetry, ion selective electrodes and atomic absorption. The bioavailable uptake rate of metal species may be determined by Dialysis with Receiving Resins.

The separation of particulate associated metal species into fractions is best achieved by a series of sequential chemical extractions. Metals may be partitioned between the exchangeable fraction (which is considered to be that which is available primarily and immediately for biological uptake) the carbonate fraction, the hydrous metal oxide fraction and the organic/residual fraction.

Additional approaches to speciation analysis include mathematical models and the product approach, as well as complexation capacity and conditional stability constant determinations.

Metal Speciation Analysis

Metal speciation analysis involves the fractionation of total metal concentration by physico-chemical methods (Florence 1986). The fractionation of metal species is recognised as an essential step in the assessment of the potential biological uptake and toxicity of metals in a water sample. As a consequence total metal concentrations may soon be replaced in water quality standards by an assessment of the bioavailable metal fraction.
Metal Species in Natural Waters

Heavy metals in aqueous systems may occur as organic and inorganic complexes of varying sizes, or be associated with colloidal or particulate material of a heterogeneous nature (Stumm and Brauner 1975, Steinnes 1983). An important problem, which relates to most natural aquatic systems, is the difficulty of distinguishing between dissolved (0-0.8 nm), colloidal (0.8-400 nm) and particulate (>400 nm) species using conventional physical methods, such as filtration.

Dissolved metal species, particularly those that are free and weakly complexed are potentially available to organisms (Morrison et al. 1984a). In addition, certain lipid soluble metal complexes, such as Cu xanthogenate, rapidly diffuse into biomembranes and are extremely toxic (Florence 1986).

Separation of Metal Fractions in the Dissolved and Colloidal Phase

Preliminary separation and instrumental techniques have been used to fractionate metals. Instruments which respond to certain metal species include Ion Selective Electrodes (ISE) and Differential Pulse Anodic Stripping Voltammetry (DPASV). Preliminary separation techniques include filtration and ion exchange resins. The different approaches are complementary to each other providing a wide range of information on metal speciation.

Anodic Stripping Voltammetry

DPASV is sufficiently sensitive, with a typical detection limit of about $10^{-9}$ M, for the direct determination of heavy metals in natural waters (Florence 1982a). This analytical technique can distinguish between the electrochemically available fraction, which may be toxic, and the bound or electrochemically inert fraction, which is less likely to demonstrate toxic properties.

DPASV has commonly been applied to the primary distinction between "labile" and "bound" metals in filtered water samples (Chau and Lum-Shue-Chan 1974, Duinker and Kramer 1977). The normal procedure for estimating the fraction of labile or electrochemically available metal involves a standard addition analysis of an untreated sample and is therefore dependent on the kinetics of the reactions controlling the assimilation of the metal spike (Whitfield and Turner 1979). However, Florence (1986) avoids metal spike complexation by calibrating using a blank solution containing standards.

Labile metal, as defined by the experimental conditions, includes ionic as well as some weakly complexed metal. Bound metal is identifiable as the non-labile fraction.