

## Category III - Water Quality

### *Development of a Liquid Membrane Technique to Measure the Temporal Variation in "Bioavailable" Copper and Nickel in the South San Francisco Bay*

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#### Executive Summary:

South San Francisco Bay has been designated as an impaired water body under the Federal Clean Water Act because the "total concentration" of dissolved copper and nickel in the water often exceeds the numerical limits set in the water quality objectives. There is strong evidence, however, to suggest that most of this nickel and some of the copper is complexed to anionic hydrophilic ligands such as ethylenediamine tetraacetic acid (EDTA) that are not directly assimilated by microorganisms. Copper is also strongly bound to natural organic ligands in a form that is not directly available to the plankton community. The aim of this project is to measure the concentration of "bioavailable" copper and nickel in South San Francisco Bay. The bioavailability of trace metals to phytoplankton (with respect to both toxicity and biolimitation) is generally correlated to the free or inorganic metal ion concentrations rather than the total metal concentration of the water.

In order to determine the free or labile fraction of copper or nickel, the total dissolved concentration of these metals has to be determined first. The concentrations of alkali and alkaline earth ions and dissolved organic matter (DOM) are rather high in estuarine waters. Because of the interferences by these substances, it is difficult to accurately measure trace amounts of Ni and Cu present in the estuarine water. A separation and concentration step to remove the trace metals of interest from the complex background chemical matrices of the water is therefore necessary. Solvent extraction has been the most common sample concentration method used for this purpose. Solvent extraction methods although very reliable, are time consuming and difficult to automate because they are not readily adapted to flow injection systems of the instruments commonly used in elemental analysis.

The first task of this project was to develop an automated flow injection method for determination of total copper and nickel concentration in estuarine water. This method employs a chelating resin packed in a mini column to partition and concentrate the trace metals in the water sample from the interfering alkali and alkaline earth ions prior to on-line determination by inductively coupled plasma mass spectrometry (ICP-MS). The performance of this new on-line ICP-MS method was compared to outcomes of the well established solvent extraction graphite furnace atomic absorption spectrometry (SE-GFAAS) method..

An on-line chelating resin column partitioning Inductive Capillary Plasma – Mass Spectroscopy method was developed to determine the dissolved nickel and copper in South San Francisco Bay estuarine water.

To obtain total dissolved copper concentrations comparable to those measured by the SE-GFAAS, it was necessary to destroy the DOM in the acidified water samples prior to on-line chelating resin column partitioning ICP-MS determination.. The discrepancy was especially pronounced in samples from South San Francisco Bay, which had high concentrations of dissolved organic carbon.

To determine the free copper and nickel concentration in South San Francisco Bay, we have developed a membrane-based separation technique that employs an automated on-line flow system consisting of a peristaltic pump, electrically actuated valves and a membrane filtration unit. The membrane holder was custom-machined in our machine shop. It consists of two circular Teflon blocks each with circular grooves like an Archimedes spiral.

The entire set-up is computer controlled via a digital I/O card to switch valves and start or stop the peristaltic pump. Copper and nickel concentration is determined off-line by GFAAS after membrane extraction.