

Flow-injection-ICP-MS method applied to benthic flux studies of San Francisco Bay

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ABSTRACT

An automated low-pressure flow-injection (FI) sample introduction method for use with an inductively-coupled plasma mass spectrometer (ICP-MS) has been applied to determine trace-element benthic fluxes in the San Francisco Bay. Due to metal concentrations of the order of 10 nM and lower, dilution is not an applicable method for circumventing the high ionic-strength (up to 0.7M) of the samples, which inhibits accurate analysis. Due to low volume constraints (as low as 60 ml per sample) presented by the design of the benthic flux experiment, high-throughput concentration methods are not viable. Using the FI method, small (~4 ml) aliquots are buffered on-line to pH 5.2 and are passed through a chelating resin. Following a deionized water flush, the sorbed metals are eluted with 1M quartz-distilled HNO₃, and carried into the plasma. This process represents advancement over the previously employed method involving off-line preconcentration followed by graphite furnace atomic absorption spectroscopy (GFAAS) analysis. Improvements are observed in detection limits, confidence intervals, viable analytes, reduction of contamination sources, and analysis time. For copper and nickel, metals whose estuarine transport mechanisms in the Bay are presently of much interest, detection limits are <0.2 nM, which are less than those for similar samples by GFAAS (<2 nM). Whereas GFAAS allows for effective analysis of only copper and cadmium under our experimental constraints, the FI method has thus far been found appropriate for analysis of Cu, Cd, Ni, Zn, Pb, Mn, Co and V. The FI-ICP-MS method, while still in its relative infancy, represents an invaluable addition to our analytical capabilities, and could benefit any study requiring multi-element analysis in low-volume samples of high ionic strength.

INTRODUCTION

To more effectively model the benthic fluxes of the San Francisco Bay (Wood and others 1995, Kuwabara and others 1996), more efficient methods for trace metal determinations in estuarine waters are required. Analysis of dissolved organic carbon and dissolved sulfide can be performed within a week of the benthic flux experiment. However, GFAAS trace metal analysis, with appropriate replication and quality control, requires 3 months to effectively complete. This process involves excessive handling, which can contribute to inconsistent results due to contamination. Only copper (Cu) and cadmium (Cd) data have been consistent and reliable using this method, inhibiting a more comprehensive study of solute benthic fluxes.

New methods involving chelating resins for trace metal analysis have recently been developed (Sturgeon and others 1981, Akatsuka and others 1992). Unfortunately, since these were

designed for seawater studies, they typically require large sample volumes (>1L). McLaren and others, 1993 provided the outline for an inductively coupled plasma mass spectrometry (ICP-MS) based method using on-line preconcentration of small-volume, high-ionic strength on chelating resin. In later work (Willie and others, 1998), the method was applied to a commercially available flow-injection autosampler (FIAS), with the sample volume required for each replicate less than 5ml. In addition to the low-volume, high-salinity conditions under which it could operate, this method allowed for simultaneous multi-element analysis. The goal of this study is to validate this method so that it can be applied to the benthic flux studies, thus improving both the scope and efficiency of the project as a whole.

MATERIALS AND METHODS

Analysis is performed on a Perkin-Elmer Sciex Elan 6000 ICP-MS. The instrument is optimized daily and operated as recommended by the manufacturer. The on-line preconcentration is performed with a Perkin-Elmer FIAS-400MS. Both the ICP-MS and the FIAS are controlled by Elan software, version 2.0.

All fittings, non-metallic and acid-washable, were selected to minimize metal contamination, mostly ETFE (Tefzel), with some polyetheretherketone (PEEK). Acid-washed PharMed tubing is used on the peristaltic pumps of the FIAS. All other tubing applications are performed with acid-washed fluoroethylene polymer (FEP) tubing. The chelating resin, Toyopearl AF-Chelate-650M (Tosohaas, Montgomeryville, PA), is packed into an FEP Perkin-Elmer column. The column has frits on each end and is push-fit into a threaded sleeve.

The buffer, ammonium acetate, is made with quartz-distilled acetic acid (Fisher Optima) and double-distilled ammonium hydroxide (Aldrich). The pH is adjusted to 5.6 \pm 0.2. The elutant, 1M HNO₃ is made with quartz-distilled nitric acid (Fisher Optima). MQ water is used for all dilutions and reagents, as well as for a rinse step. High-purity 10ppm standards are diluted in 0.1% nitric acid to create the calibration curve. The National Research Council of Canada certified estuarine reference material SLEW-2 (St. Lawrence Estuary) is used for quality control and to assess the accuracy of the method.

All sample types (samples, standards, reference materials, and blanks) are passed through the FIAS. Due to the pH sensitivity of the resin, the pH for all must be equal. Software-calculated linear regressions of the calibration curves are used to derive all final concentrations.

A four-step sequence program, designed to optimize the system, controls two pumps and two different valve settings on the FIAS. First, the sample is mixed on-line with the buffer and pumped over the resin column. This is followed by a DI water rinse to remove salts. The elutant passes over the resin, removing the analytes and carrying them to the instrument for analysis. A fourth step rinses the resin again with DI water, removing any acid and neutralizing the pH.

The use of trade names within the text is for identification purposes only and does not constitute

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DISCUSSION

Eight different elements (Cu, Cd, Ni, Zn, Pb, Mn, Co, and V) are linear throughout the desired range of concentrations (Figure 1). The calibration curves are set to encompass the values of the certified reference material SLEW-2 and the expected values of our samples. Each range covers nearly three orders of magnitude, allowing for a wide range of unknown concentration levels. This also creates data for six additional elements besides Cu and Cd, which were performed using the GFAAS method. Moreover, the simultaneous analysis of all of these, combined with efficient sample throughput, allows for the trace metal determinations required for each experiment to be completed within a month.

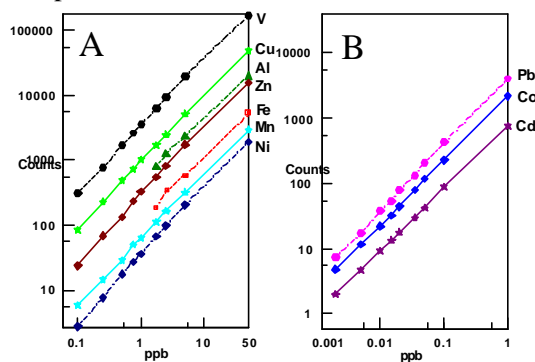


Figure 1. Standard curves for 10 elements using the FIAS-ICP-MS method. Note concentrations are ppb, not nM.

Unfortunately, iron (Fe) and aluminum (Al) (Figure 1A) are inaccurate at concentrations <10 ppb. While Al is ineffective due to inconsistent values, the interferences for Fe are mostly created by argon (Ar). Ar is the carrier gas for the ICP-MS. It mixes with the sample in the nebulizer and forms polyatomic species with oxygen, nitrogen and hydrogen in the plasma. The mass values of the interferences overlap those of Fe. This creates a massive background signal through which it is difficult to isolate the Fe signal. A recently acquired, but as yet untested, ultrasonic nebulizer promises to significantly reduce this background signal.

Cadmium, cobalt (Co), and lead (Pb) (Figure 1B) show method detection limits on the order of 1 ppt (parts per trillion). Although not necessary for

our needs, other elements show better method detection limits than those shown, including Cu and vanadium (V) (~1ppt), and Ni and zinc (Zn) (~10ppt).

To confirm the method's effectiveness in analyzing salt waters, SLEW-2 is used as a measure of recovery for each element. (Table 1) The recoveries are derived from a ratio of the determined value and the certified value. Al and V are not certified, and Fe is certified at a concentration that is too low to be measured effectively due to interferences explained above. Also, manganese (Mn) must be diluted at least three-fold to be accurately measured. Mn seems to be suppressed above 10 ppb (SLEW-2 Mn is 17ppb) in high-ionic strength solutions. The overall results are very good, allowing for reliable analysis of our own estuarine samples.

	% Recovery		
Cu	96.5	+/-	1.5
Ni	102.6	+/-	4.0
Zn	106.8	+/-	4.1
Mn	100.5	+/-	6.4
Co	110.4	+/-	3.2
Pb	82.3	+/-	9.4
Cd	92.4	+/-	7.0

Table 1. Percentage recoveries with error (average of six analysis dates) for seven elements certified in SLEW-2.

A comparison of benthic flux curves derived from the GFAAS method and the FIAS method is shown to indicate that it is prudent to continue with the development and implementation of this method. (Figure 2). The general trends for the benthic fluxes are similar. The FIAS method shows significant improvement in confidence intervals, especially for Cd.

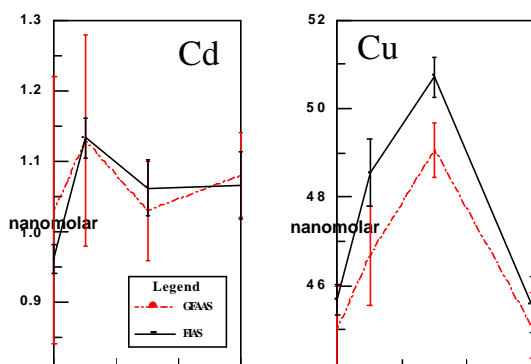


Figure 2. Comparison of concentrations using GFAAS method and FIAS-ICP-MS method for analysis of benthic fluxes. Error bars are 95% confidence intervals.

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