

Annual Report Summary

Period Covered by the Report: January 1, 2001 through December 31, 2002

Date of Report: January 25, 2003

EPA Agreement Number:

Title: Methods Comparison Between Stripping Voltammetry and Plasma Emission Spectroscopy for Metals in Mobile Bay

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Research Category: Small Grant for Exploratory Research

Project Period: July 1, 2000 through December 31, 2003

Objectives of the Research Project: The primary objective of this work was to assess whether or not stripping voltammetry would yield comparable data as ICP-AES for Mobile Bay water and sediment samples. Stripping voltammetry equipment is substantially cheaper and far less complex to operate than ICP-AES equipment. A secondary objective of this investigation was to determine if the voltammetric method might also be used to identify the manner by which a specific metal is partitioned in naturally occurring sediment samples. This is particularly valuable to an environmental scientist because it provides information with respect to the actual bioavailability of the metal and its potential for remobilization. The final objective of this work was to accomplish field measurements with the voltammetric equipment and compare them to laboratory measurements.

Progress Summary/Accomplishments: The primary objective was accomplished during project year 2001. Metal standards, National Bureau of Standards whole rock samples, and 24 partitioned samples from 12 sites in the bay were analyzed with stripping voltammetry and plasma emission spectroscopy. Seventy-six additional sites in Mobile Bay were also sampled in order to obtain complete bay coverage and these were analyzed using plasma emission spectroscopy only. For each sample analyzed by stripping voltammetry, concentrations were calculated using calibration curves generated from standards. Metals analyzed in all samples include Cu, Pb, Cd, and Zn. Preliminary analyses were also carried out for iron and bismuth. The results of these analyses are summarized below:

1. Detection limits for both the SV and ICP-AES methods were found to be comparable. These limits are approximately in the upper parts per billion range when averaged over all elements analyzed. It is therefore possible to use the SV procedure to obtain data at the sub part per million level
2. Comparisons between the ICP and SV methods on whole sediment (unpartitioned) analyses were quite good for Cu, Pb, and Cd. Most sediments contained levels in the low ppm to upper ppb range for these elements. The table below lists results from one sampling site in the bay and

gives a “feel” for the variation between the two methods. The two methods are seen to yield very similar values.

	Total Cu (ppm)	Total Pb (ppm)	Total Cd (ppm)
ICP-AES	24.90	21.00	0.67
SV	20.68	21.75	0.52

The secondary objective was partially accomplished during 2001 and 2002. Reasonable agreement between the two methods for results from the ion partitioning analyses was obtained. All of the values obtained for the different phases for copper, lead, and cadmium were within the same order of magnitude. This was especially encouraging and confirmed that the SV procedure can be used (at least for certain metals) for this critical type of analysis.

Although a number of attempts were made to use the method to measure barium, no results were obtained. This metal does not appear to be amenable to the stripping voltammetry technique.

It was difficult to ascertain how sample treatment might have affected the results. One step in the ion partitioning procedure requires the addition of a strong oxidizing agent. This substance would be electroactive if present at the end of the chemical treatment and might lead to distorted results for the SV method. pH control was not carried out for any of the samples. Highly acidic samples typically show interference from proton reduction when using stripping voltammetry.

Whereas 20 metal species were analyzed for each sediment sample by ICP-AES, only four were analyzed by SV. In general, this fact simply reflects the time necessary to carry out analyses using a “new” method (SV) as opposed to an established method (ICP-AES), but it also reflects the fact that SV is a much slower technique (requiring rinsing, cleaning, and blank conditioning between every sample run).

It is important to stress here that the SV procedure performed well beyond expectations. For the metals tested for which no interferences were observed (copper, lead, and cadmium), the SV method produced sensitivities and detection limits that were comparable to systems costing 5 to 8 times as much. Complete results for these metals from the 12 sampling sites in the bay can be displayed graphically by maps and in tabular form. Of all the analyses performed, all differences were less than one order of magnitude in size and only two of the samples produced questionable values. These data clearly attest to the importance and potential of stripping voltammetry as a low cost alternative for environmental analysis. Additional testing and evaluation will, hopefully, show that this technique can be applied for a wide range of elements and can consistently attain detection levels appropriate for most environmental applications.

The final objective was attempted in year 2002. We attempted to take the voltammetry equipment into the field using a laptop computer. Unfortunately, the equipment as designed at present is cumbersome and requires AC power which we attempted to provide using a generator. The electrical power provided was much too noisy and completely obscured any voltammetric signal.

Publications/Presentations: To date, two papers have been presented at scientific meetings; (1) “Determination of Cadmium, Copper, and Lead in Mobile Bay Sediments Using Plasma Emission Spectroscopy and Stripping Voltammetry”, M.S. Martin, S.C. Dorman, J.A. Cordi, and W.C. Isphording, 53rd Southeast Regional American Chemical Society Meeting, Savannah, GA, September 23-26, 2001.

(2) “Analysis of Natural Water and Sediments Using Electroanalytical Methodology”, J.A. Cordi, S.C. Dorman, W.C. Isphording, and M.S. Martin, American Chemical Society, 223rd National Meeting, Orlando, FL, April 7-11, 2002.

Future Activities: Work continues on testing stripping methodology for additional metals such as iron, chromium, nickel, manganese, and titanium. We also plan for field testing in natural waters using a laptop computer and a battery powered potentiostat. This should eliminate some of the problems previously encountered.

Supplemental Keywords: sediments, estuary, chemical transport, heavy metals, environmental chemistry, geology, measurement methods, southeast

Relevant Web Sites: none