



Project Summary

Pre-Concentration Method for Inductively Coupled Plasma-Mass Spectrometry

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A semi-automated system is used to pre-concentrate Ti, V, Mn, Fe, Co, Ni, Cu, Cd, and Pb prior to analysis by inductively coupled plasma-mass spectrometry (ICP-MS). The pre-concentration system accepts digests with a broad range of acid concentrations, neutralizes them, and loads them onto a macroporous iminodiacetate resin. Alkali and alkaline earth metals, along with deleterious anions such as chloride, are washed off the resin before the concentrated analytes are eluted with nitric acid. Measurement of a total of 13 isotopes of the analytes, as well as two internal standard elements added to the eluent stream, indicates that the technique enhances the ICP-MS response of the target metals. Investigation of the nature of the blank signals suggests that the detection limits of several of the isotopes could benefit by much larger pre-concentration factors, while those of copper, cadmium and lead are currently limited by reagent purity. Method performance data is presented for several simple synthetic matrices, synthetic sea water, two waste waters and a natural surface water.

This report was submitted in fulfillment of contract number 68-03-3249 by Lockheed Engineering and Sciences Company under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from October 1, 1988 to September 30, 1989. Work is on-going.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings

of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The analysis of environmental samples for trace elements poses two major problems. First, the regulatory action levels of several metals are in the low part-per-billion range, and reliable quantitation requires analytical methods with detection limits 5-10 fold lower than these threshold levels. Second, the matrices encountered in environmental samples are extremely diverse and often highly complex. Because of the need for low detection limits, graphite furnace atomic absorption spectrometry (GFAAS) and, more recently, inductively coupled plasma-mass spectrometry (ICP-MS) have been employed in environmental analysis. ICP-MS has the advantage over GFAAS of being a multi-elemental technique, but there is incomplete performance data for ICP-MS analyses of target elements in all matrices of interest to the U.S. Environmental Protection Agency.

One of the major drawbacks of ICP-MS is the interferences often exhibited with the complex matrices encountered in environmental analysis. Pre-concentration can be used to separate analytes from interferences prior to analysis. Separation is effected by complexation of analytes to an immobilized form of an iminodiacetate chelating agent. The functional group is covalently bonded to a highly cross-linked divinyl benzene, polystyrene copolymer resin. The iminodiacetate strongly complexes transition metals and certain main group metal ions, such as lead, while showing very little affinity for alkali and alkaline earth metals which can

interfere with subsequent analyses. The analytes can then be released by changing the ionic form of the resin. This approach allows the development of semi-automated methods that make use of resin-packed columns.

Procedure

Acidified samples are buffered to pH 5.5 by on-line mixing with 2-M ammonium acetate and then fill a sample loop of appropriate volume for the degree of pre-concentration desired. Prior to the pre-concentration step, the resin is placed in the ammonium form using 2-M ammonium acetate. When the pre-concentration program is initiated, a high pressure pump sweeps the sample to the resin column with 2-M ammonium acetate at 3 mL/min, pre-concentrating the analytes, and passing the rest of the sample matrix, including alkali metals and anions, to waste. The ensuing wash-out with additional ammonium acetate replaces chelated Mg^{2+} and Ca^{2+} with NH_4^+ . The high pressure pump then switches to 1-M nitric acid, passing the eluted trace metals to the ICP-MS. After the analyte peaks have passed, 3 mL/min of 2-M ammonium acetate is passed through the column for 1 minute. This is followed by successive 3-mL rinses with nitric acid, ammonium acetate, nitric acid, and finally ammonium acetate, again, each at a rate of 3 mL/min.

Mass spectra are obtained using the "Multiple Elements" program of the Perkin-Elmer ELAN ICP-MS. The measurement routine allows the observation of each peak every 0.67 seconds, and a temporal resolution of 2 seconds. The spectrum is converted to an ASCII file and automatically sent via the Kermit communications protocol to an 80386-based microcomputer for processing. The spectrum is placed in a commercial spreadsheet by a macro that automatically finds the analyte peaks and integrates each over the optimal detection period.

Results and Discussion

Peak areas were used for quantitation. Peak widths, and therefore peak heights, sometimes varied considerably during the day. Peak areas, conversely, were very reproducible. Calibration curves were determined for each of the analytes from 0.3 $\mu g/L$ to 30 $\mu g/L$ using a 2.5-mL sample loop, and from 0.3 to 10 $\mu g/L$ using a 10-mL sample loop (the iron calibration curves were determined using ten times these concentrations). All

isotopic calibrations were linear, with the correlation coefficients ranging from 0.998 to 0.9999. Generally, the long-term precision of the method was good, but the sensitivity for lead tended to drift during the day. Lead calibrations and analyses used the internal standard intensity of bismuth to correct for this drift.

Only in the cases of copper, cadmium and lead, as well as ^{49}Ti , would more rigorous reagent purification and stringent clean-room conditions significantly improve detection limits over those obtained in this study. Conversely, the detection limits of the other isotopes would definitely improve with larger sample sizes. Even in the cases of copper, cadmium, and lead, some improvement with increased sample size is still expected.

The efficiency of the pre-concentration system was studied by comparing total integrated signals for 10- $\mu g/L$ solutions of each of the analytes, directly aspirated into the ICP-MS, with the integrated signals after pre-concentration. Ammonium nitrate, which was present in the elution front, apparently caused a pronounced enhancement of signal that gave higher sensitivities than would be expected by pre-concentration alone.

The on-line buffering technique adequately buffered standard solutions, ranging from 0.8% to 1.4% (v:v) nitric acid, to a pH of 5.4 ± 0.2 . Analyte recoveries from these solutions ranged from 90% to 103% relative to the recoveries from a standard solution in 1% nitric acid. The on-line mixing of samples and buffer caused only a 20% dilution of the samples, and eliminated hydrolysis problems which can be caused by prolonged exposure of analytes to non-acidic conditions.

In early work, some analytes exhibited elevated apparent concentrations in the first blank after a high concentration standard. It is not clear why vanadium, and to a lesser extent, titanium, cobalt and copper exhibited memory. It was later determined that alternating the resin between the hydronium and ammonium forms three times between runs of the pre-concentration program reduced the effect. This cycling of ionic forms was therefore added to the prescribed procedure.

The degree of residual interferences from molecular ions of alkali and alkaline earth metals, as well as chloride, was examined as a function of pre-elution wash-out time. At a concentration of 2000 mg/L, only calcium produced residual

spectral interferences when the wash times were at least two minutes. The spectral interferences remaining from synthetic sea-water matrix after a two minute wash-out were relatively small residual $^{48}Ca^+$ and $CaOH^+$ peaks. Minimum spike recoveries for high concentration salt matrices fell between 85% and 115%.

A major drawback to pre-concentration methodologies is the low recovery obtained in the presence of certain organic chelators. Titanium, copper, cadmium and lead showed very poor recoveries in the raw waste water included in this study. A simple microwave digestion procedure, however, was sufficient to liberate the bound metals and restore full recoveries.

Conclusions and Recommendations

On-line pre-concentration with iminodiacetate resin minimizes severe spectral and physico-chemical interferences in ICP-MS. Interferences from sodium, potassium, and magnesium are largely eliminated, and that for calcium is greatly attenuated. Anions which can cause severe spectral interferences, such as chloride, are removed. Native organic chelating agents, which might reduce pre-concentration recoveries, are eliminated from samples by a nitric acid digestion.

The efficiency and cost-effectiveness of this method could be improved with expansion to an automated, multiple column system, wherein many samples would be in various stages of analysis at a given time. Unfortunately, the current status of ICP-MS software makes complete automation of the pre-concentration techniques problematic. Not only is satisfactory support for transient signals lacking, but so is the hardware and software which would make interfacing a less daunting task.

Work on the pre-concentration method should continue, especially to extend its application to ICP-AES. Further effort should be expended to reduce the memory exhibited by some analytes. Alternate chemistries which might make possible the pre-concentration of arsenic and selenium should be investigated. Finally, a multi-laboratory evaluation should be conducted to assess the routine performance of the pre-concentration method coupled with both ICP-MS and ICP-AES.

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The complete report, entitled "Pre-Concentration Method for Inductively Coupled Plasma-Mass Spectrometry," (Order No. PB 90-181348 ;Cost: \$17.00 subject to change) will be available only from:

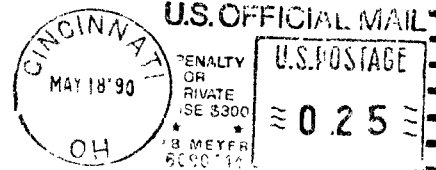
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