

# A FIELD SYSTEM FOR RAPID PRECONCENTRATION OF TRACE METALS IN NATURAL WATERS



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**A FIELD SYSTEM FOR RAPID PRECONCENTRATION  
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## ABSTRACT

A rapid preconcentration-preservation sampling system for the routine monitoring of trace metals in natural waters has been designed for use in conjunction with the inductively coupled argon plasma (ICAP) for cost effective analysis. Consisting of a hand-operated pump, a cartridge-type filter unit, and an ion exchange column, the system is lightweight, rugged, simple to operate, and otherwise well-suited to field application. The fast-sampling flow rates (up to 500 mL/minute) allow samples to be preconcentrated 200-fold in just 10 minutes. Once preconcentrated the trace metals do not require any further preservation, simplifying sample transport and storage.

Trace metal preconcentration is accomplished on a 15 mL resin bed of the chelating ion exchange resin CHELEX 100. Column loading and elution parameters were optimized with respect to maximum analyte recovery from solution under conditions typical of natural waters. Cadmium, copper, lead, manganese, and nickel were efficiently collected over the pH range of 3-8 and a temperature range of 1-40°C. The pH-dependent recovery of aluminum was attributed to incomplete uptake of the dissolved mononuclear and polynuclear hydroxo-complexes present in solution.

Normal sample alkalinity, hardness, and conductivity did not interfere with analyte recovery, however, both fulvic and humic acid inhibited quantitative analyte uptake when present in the sample at sufficient concentrations. To eliminate spectral interferences, a modified procedure for removal of the alkali and alkaline earth elements prior to column elution was necessary. Comparison studies conducted on natural water samples have shown good correlation of results with preconcentration by evaporation.

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## INTRODUCTION

### Analysis of Trace Metals in Natural Waters

Trace metals enter the water courses managed by the National Park Service (NPS) from a variety of sources, both natural and anthropogenic. The weathering of rocks and soils directly exposed to surface waters are among the largest natural sources (1). For the most part, these natural sources are relatively small in comparison to the many anthropogenic inputs (2). The last few decades have witnessed a significant increase in industrial development and production, automotive traffic, high technology, resource exploration and excavation, and the combustion of fossil fuels. These anthropogenic sources have placed considerable stress on the environment in the form of acidic precipitation and trace metals, which threaten the quality of the water systems in our parks.

To insure the continued safety and productivity of these water systems, extensive water quality monitoring programs must be implemented. However, comprehensive, routine water monitoring for trace metals can be very expensive with the analysis techniques available. To reduce costs, emphasis has been towards the development of simultaneous multi-element analysis methods (such as Inductively-Coupled Argon Plasma [ICAP] atomic emission spectrometry) to replace more commonly used methods (such as atomic absorption spectrometry [AAS]) that are more amenable to measuring only one metal at a time. Unfortunately, the determination limits of the ICAP are not sufficient for the adequate analysis of many trace metals in natural waters (3,4,5) and the method often requires isolation of the trace metals from other constituents in the water sample (5). However, with

appropriate sample preconcentration, the ICAP can provide economical analysis for trace metals in natural waters.

### **Preconcentration of Trace Metals**

While most sample preconcentration methods are appropriate for natural water analysis, consideration must be given both to the requirements of the ICAP and to collection of the sample being concentrated. With the ICAP in mind, an appropriate preconcentration method must:

1. bring the metals of interest into an appropriate concentration range for analysis by the ICAP;
2. provide adequate isolation of the trace metals from interfering species present in the sample; and
3. preserve the integrity of the sample during storage prior to analysis.

Collection of the sample is another problem. Usually, sample enrichment procedures are conducted in the laboratory, but this requires that relatively large quantities of sample be adequately preserved and transported back to the analysis facility. Unfortunately, collecting and handling large samples often is not practical in wildland areas. Access to stream sampling points may be limited or even difficult. Where access by motor vehicle is not feasible, samples may need to be backpacked. Therefore, field implementation of sample preconcentration is preferred but requires that the equipment involved be 1) rugged, waterproof, lightweight, and otherwise suited to field application; 2) relatively simple to operate even under adverse conditions; and 3) nonpolluting.

While sample enrichment by evaporation (3), precipitation (5), and liquid extraction (5) are widely used, it is clear that these

approaches are not appropriate for field implementation. The use of ion exchange or chelating resin methods clearly are the methods of choice in the field (6).

### **Experimental Objectives**

The goal of this research was the development, characterization, and evaluation of a rapid field-preconcentration/preservation sampling system for the routine monitoring of trace metals in natural waters. Specifically, it was designed to do the following:

1. determine the optimum ion exchange resin, column design, and sampling system for the rapid preconcentration of trace metals;
2. optimize the resin elution conditions with respect to the most efficient eluant and eluant concentration, temperature and flow rate;
3. characterize trace metal uptake by the resin with respect to sample pH, temperature, and concentrations;
4. investigate common constituents of natural waters as potential interferents to trace metal uptake and to eliminate, minimize, or characterize their influence; and
5. compare sample preconcentration by the resin sampling system with a commonly used sample preconcentration method.

## EQUIPMENT AND PROCEDURES

### Equipment

Resin column. Development of a system capable of concentrating elements from relatively large volumes of waters (3-5 L) in a reasonable period of time was an important experimental requirement. Lightweight, rugged, and inexpensive polyethylene columns, equipped with 35  $\mu\text{m}$  polypropylene frits and compression-fit end caps to contain the resins, were investigated for this purpose (calcium chloride drying tubes, Cole-Parmer Instrument Company, Chicago, Illinois). Experiments with packed columns of varying diameters and lengths up to 12 cm indicated that a column diameter of 1.6 cm internal diameter (i.d.) and a packed length of 10 cm or less was necessary to attain the desired flow rate of at least 500 mL/minute when the solution was forced through the column by a hand-operated pump.

Final selection of the column length was based on measuring transition metal retentions for various packed lengths when sample was delivered at flow rates of 100-500 mL/minute. Complete retention was attained at flow rates up to 600 mL/minute with a 1.6 cm i.d. x 7.5 cm column having a wet resin volume of 15 mL and a dry mass of 1.9 grams.

Field equipment. Field sampling was performed using the equipment shown in Figure 1. Selection of the hand-operated pump and filter unit was based on performance and compatibility with the resin column. The pressure developed by the pump had to be sufficiently large and the back-pressure developed by the filter unit sufficiently small to provide a continuous flow rate of 400-600 mL/minute through the pump/ filter/resin-column system. A siphon/lift pump (model 6437-00, Cole-Parmer Instrument Company; approximately \$16.00) and a

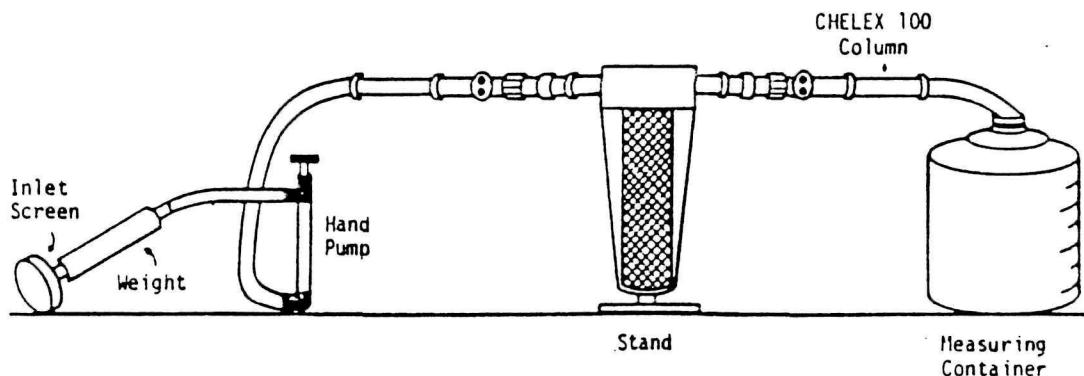


Figure 1. The field pre-concentration-preservation system.

cartridge-type filter unit (Cuno AMF, General Filter Products Division, Meriden, Connecticut; approximately \$22.00) that uses polypropylene wound filter cartridges (Micro-Wynd II, Cuno AMF; approximately \$6.00 apiece) were chosen. A 3 molar (M) nitric acid wash followed by a distilled deionized water rinse was found necessary to reduce contamination from the filter cartridges. The system includes a detachable nylon inlet screen, polypropylene tubing and connectors, and a 20 L collapsible polyethylene container calibrated to allow measurement of the water volume sampled. Once collapsed, the entire system, including several columns, is less the size of four loaves of bread and weighs approximately 7 pounds.

Sampling was accomplished by placing the inlet screen into the water and using the hand pump to force water through the filter, the column, and into the measuring container. A continuous, steady pumping action is required during the entire sampling period.

Laboratory equipment. Sample loading and column elution were performed in the laboratory using the two systems shown in Figure 2. The sample-loading system consisted of three 4 L polyethylene wide-mouth bottles used as sample reservoirs and a peristaltic pump with

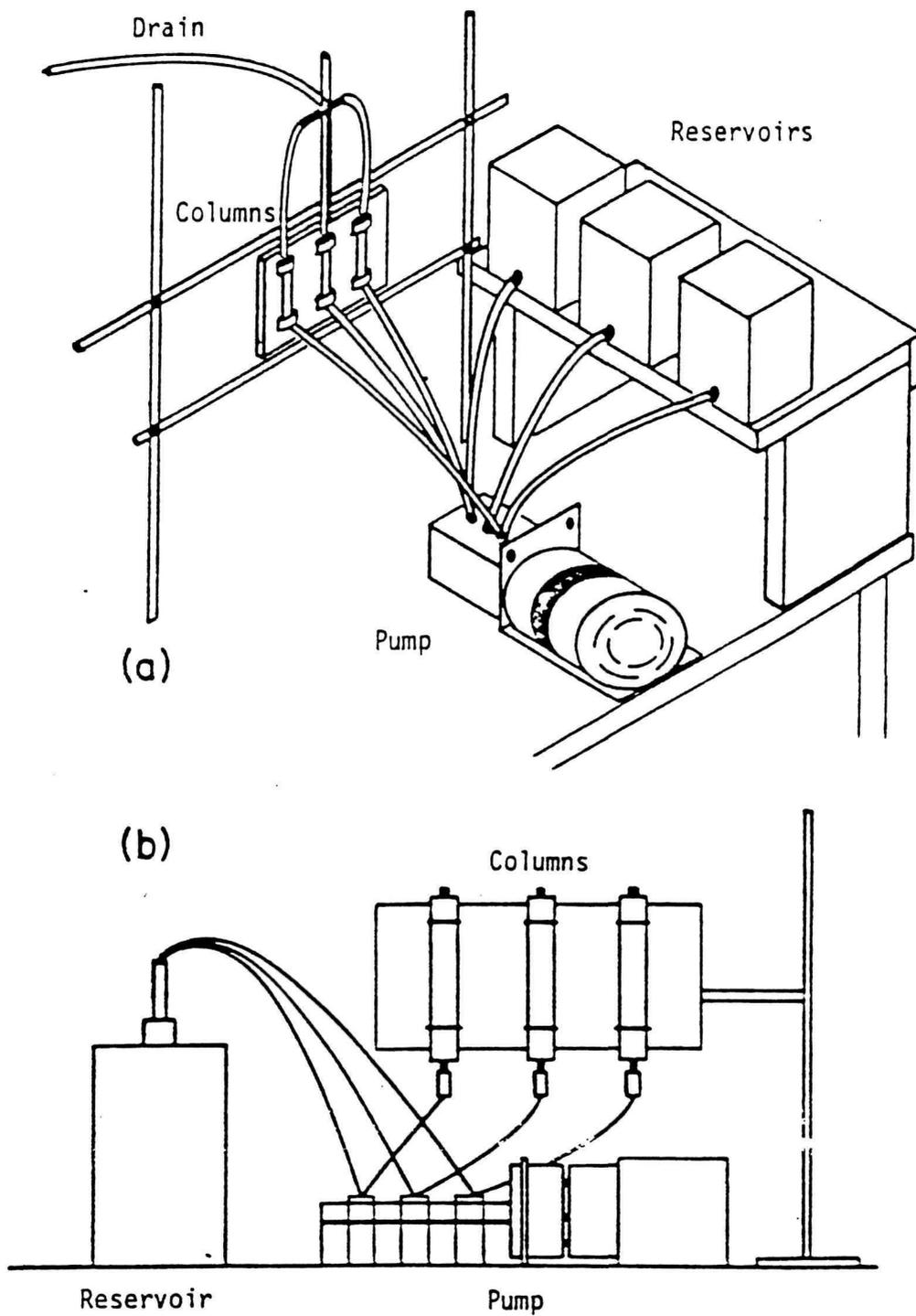


Figure 2. Apparatus used to (a) load and (b) elute the CHELEX 100 columns.

three pump heads (Masterflex, 7015 model pump heads, Cole-Parmer Instrument Company). Three columns could be loaded simultaneously with a sample solution at a flow rate of 100-500 mL/minute with this system. The column elution system employed a 2 L polypropylene bottle as an eluant reservoir and a peristaltic pump with three pump heads (Masterflex, 7013 model pump heads, Cole-Parmer Instrument Company). This system could elute three columns simultaneously at 1-6 mL/minute into 50 mL polypropylene screw-cap vials. Both systems used silicon tubing throughout, which allowed simple compression-fit connections to reservoirs and resin columns. Each system was washed with 6 M nitric acid and rinsed with distilled water prior to sampling.

Instrumentation. The inductively coupled argon plasma unit used was a model HFP 2500D power source equipped with a model T1.0 torch, a model SC-2 spray chamber, and a model GN-1 concentric glass nebulizer (RF Plasma Products, Cherry Hill, New Jersey). The load coil was a 3-turn coil of 1/8 in. outside diameter (o.d.) copper tubing. Operating parameters used are given in Table 1.

Table 1. Operating conditions for the inductively coupled argon plasma.

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ICAP	Power: 1.5 kW indicated incident power (<5 W reflected)
	Plasma Argon: 15 L/min
	Auxiliary Argon: 0 L/min
	Nebulizer Argon: 0.75 L/min
Nebulizer	Sample Flow Rate: 0.75 mL/min
Spectrometer	Observation Height: 12 mm above coil Entrance Slits: 100 $\mu\text{m}$ x 50 $\mu\text{m}$ wide Exit Slits: 400 $\mu\text{m}$ x 50 $\mu\text{m}$ wide

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The spectrometer and data acquisition system employed was a Spectrametrics Spectrascan III unit. The system consisted of a 0.75 m direct-reading prism/echelle grating polychromator, 20 end-on photomultiplier tubes, and a 20-channel analyzer equipped with a Texas Instruments Silent 700 thermal printer. Sample measurements were based on three successive integrations of 10-second duration.

Reagents. Synthetic water samples were prepared by dilution of commercial standards (Banco, Anderson Laboratories Inc., Fort Worth, Texas) with distilled water. Adjustments of sample pH were made by drop-wise addition of nitric acid or ammonium hydroxide with readjustment of the pH at 3-hour intervals over a 12-hour period to assure maintenance of pH. These solutions were stored in Teflon<sup>®</sup> bottles at 4°C and were brought to room temperature just prior to use. All other reagents used were the highest purity available.

## **Procedures**

Testing of exchange resins. Six resins were selected for initial study based upon their reported element retention, pH behavior, exchange capacity, selectivity, and availability (Table 2). All resins were purchased from Bio-Rad Laboratories (Richmond, California) except Amberlite XAD-2, which came from Mallinckrodt, Inc. (Paris, Kentucky). The resins were used as received without further purification, sizing, or change of ionic form. To minimize column back-pressure, the largest resin particle size available was obtained.

Each resin investigated was slurry-packed into six 0.45 cm i.d. x 4.0 cm glass columns equipped with 35  $\mu$ m polypropylene frits on each end and rinsed with 10.0 mL of distilled deionized water. A peristaltic pump (Masterflex, 7013 model pump head) was used to force

Table 2. List of resins initially investigated.

Resin	Type	Active (O-Polymer Lattice)	Particle Size (mesh)	Wet Capacity (meq/mL)
AG 1	Strongly Basic Anion Exchanger	$O-CH_2N^+(CH_3)_3$	20-50	1.4
AG3	Weakly Basic Anion Exchanger	$O-CH_2N^+(R)_2$	20-50	1.9
AG 50W	Strongly Acidic Cation Exchanger	$O-SO_3^-$	20-50	1.7
BIO-REX 70	Weakly Acidic Cation Exchanger	$R-COO^-$	20-50	2.4
CHELEX 100	Weakly Acidic Chelating Resin	$O-CH_2N \begin{matrix} CH_2OO^- \\ CH_2OO^- \end{matrix}$	50-100	0.7
XAD-2	Nonionic Macroreticular	0	20-50	--

pH-adjusted water samples upwards through the columns at 10 mL/minute. Individual element concentrations of the six synthetic water samples varied due to precipitation and coprecipitation of insoluble products formed during pH adjustment. These insoluble products were removed by filtration prior to column loading. Table 3 lists the measured element concentrations for the synthetic water sample at each pH investigated.

Elution conditions. The columns were slurry-packed with 15 mL of CHELEX 100 (ammonium-form) and loaded with 3 L of the synthetic water sample (Table 4) at 100 mL/minute. Excess solution was removed from the columns after sample loading using a water aspirator to draw off the liquid.

Table 3. Element concentrations in the synthetic water sample after pH adjustment.

Element	Element Concentrations ( $\mu\text{g}/\text{mL}$ )					
	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8
Aluminum	2.32	2.13	1.23	.193	.187	.184
Barium	.695	.651	.569	.563	.545	.505
Beryllium	.265	.244	.190	.015	.005	.004
Boron	.559	.524	.452	.450	.433	.409
Cadmium	4.63	4.37	4.15	4.12	3.90	3.73
Calcium	4.26	3.92	3.25	3.12	3.09	3.03
Chromium	2.56	2.29	1.93	1.92	1.89	1.78
Copper	.498	.457	.404	.399	.385	.365
Lead	.693	.602	.519	.473	.471	.323
Magnesium	4.93	4.65	4.37	4.30	4.09	3.93
Manganese	.498	.469	.424	.411	.391	.390
Molybdenum	8.03	7.26	6.27	6.11	6.00	5.64
Nickel	4.96	4.55	4.15	4.07	3.93	3.70
Phosphorus	10.0	10.0	8.08	7.84	7.41	7.23
Potassium	4.31	4.16	3.44	3.33	3.67	3.08
Silicon	8.88	7.48	4.69	4.39	3.99	3.89
Strontium	4.35	3.95	3.62	3.53	3.41	3.12

Table 4. Pristine synthetic water sample.

Element	Solution Concentrations*	
	Sample ( $\mu\text{g}/\text{mL}$ )	Sample ( $\text{meq}/\text{L}$ ) $\times 10^5$
Aluminum	10.0	111.0
Cadmium	20.0	35.5
Copper	2.00	6.29
Lead	10.0	9.65
Manganese	2.00	7.28
Nickel	20.0	68.1

\*In 1.0 M nitric acid and 0.1 M hydrochloric acid matrix.

(1) Choice of eluant. Hydrochloric acid, nitric acid, and ammonium hydroxide (Fisher Scientific Company, Fair Lawn, New Jersey) were screened as eluants. Sample-loaded columns were eluted at 1 mL/minute with 2 M concentrations of each test eluant. Analyte recoveries for each eluant were determined and used to evaluate the effectiveness of individual eluants. To determine the optimum eluant concentration, solutions of 1-10 M hydrochloric acid and nitric acid were used to elute sample-loaded columns. Elution volumes of 50 mL were collected for analysis.

(2) Influence of eluant flow rate. The influence of eluant flow rate on the column of eluant required to elute the CHELEX 100 column was studied by eluting sample-loaded columns at six flow rates between 1-6 mL/minute with 2 M nitric acid. At each eluant flow rate, elution volumes of 10, 20, 30, 40, and 50 mL were collected.

(3) Influence of eluant temperature. The influence of elevated eluant temperatures on the elution volume was examined by eluting sample-loaded columns at 6 mL/minute with 2 M nitric acid heated to 20, 40, 60, and 80°C. At each eluant temperature, elution volumes of 10, 15, 20, and 25 mL were collected for analysis. Prior to elution, the sample-loaded resin columns were preheated in a drying oven to the same temperature as the eluant. The 2 M nitric acid eluant was heated by passing the eluant through a 16 cm diameter coil of 1 mm i.d. x 13m long glass tubing immersed in a constant temperature bath (LAUDA K-4R, Brinkmann Instruments, West Germany).

Sample preservation. To test the ability of the resin to preserve a sample, 72 resin-filled columns were loaded at 500 mL/minute with 3 L of the synthetic water sample adjusted to pH 7. Half of the sample-loaded columns were placed into a polyethylene bag and

stored in a cold room at 4°C. The other half of the sample-loaded columns were placed into an identical polyethylene bag and stored at room temperature. At one-month intervals, three columns at each storage temperature were eluted and the eluate analyzed. Columns stored at 4°C were allowed to come to room temperature prior to elution.

Characterization of trace metal uptake. Trace metal retention characteristics of the CHELEX 100 column were investigated using the synthetic water solution described in Table 4. All columns were eluted in the same manner according to the optimum procedures and conditions previously established.

(1) Influence of sample pH. Fifteen-liter volumes of the synthetic water sample were transferred into six 20 L polyethylene carboys and adjusted to pH 3, 4, 5, 6, 7, and 8, respectively. At each pH, 3 L volumes of the multi-element sample solution were loaded onto resin-filled columns at flow rates of 100, 200, 300, 400, and 500 mL/minute.

(2) Influence of sample temperature. Four 20 L volumes of synthetic water sample were transferred to 20 L carboys and adjusted to pH 7. After pH adjustment, 3 L volumes of the solution were transferred to 4 L polyethylene wide-mouth bottles and heated or cooled to temperatures of 1, 10, 20, 30, and 40°C. Three-liter volumes of pH-adjusted synthetic water sample at each temperature were loaded onto resin-filled columns at flow rates of 100, 200, 300, 400, and 500 mL/minute. Heating and cooling of the sample solution was affected by placing the 4 L bottles, three at a time, in a 25-gallon rubber basin half-filled with water and equipped with a constant temperature unit (Thermomix 1419, B. Braun, West Germany). The

constant temperature unit provided stable temperature control at 20, 30, and 40°C, while ice was used to attain temperatures of 1 and 10°C.

(3) Influence of sample concentration. Fifteen-liter volumes of the synthetic water sample were made up at 0.5, 1, 5, 10, 25, and 50 times normal concentration by appropriate dilution of the concentrated stock solutions. The pH of each solution was adjusted to pH 7. Three-liter volumes of the synthetic water sample at each concentration were loaded onto resin-filled columns at 100, 200, 300, 400, and 500 mL/minute.

Chemical interference studies. Common constituents of natural waters were tested as possible interferents to metal uptake by the CHELEX 100 columns.

(1) Inorganic species. Each potentially interfering species was studied individually by adding appropriate volumes of a 1000 µg/mL stock solution (Banco) of the interfering species to 3 L volumes of the synthetic water sample and loading them onto CHELEX 100 columns at 500 mL/minute. All of the potential interferents were investigated at 1, 10, 50, and 100 µg/mL concentrations. The sample solutions were adjusted to pH 7 prior to sample loading.

(2) Conductivity. Three-liter volumes of the synthetic water sample were adjusted to 100, 250, 500, 1000, 2500, 5000, 10000, and 20000 µS/cm with electrochemical-grade potassium nitrate. Solution conductivities were measured using a portable conductivity meter (Model SC 51, Yokogawa Hokushin Electric, Shenandoah, Georgia) and were corrected to 25°C. All solutions were adjusted to pH 7 prior to conductivity adjustment except those solutions adjusted to less than 500 µS/cm. These solutions could not be adjusted to pH 7 due to the contribution by ammonium hydroxide to the solution conductivity.

After adjustment to the appropriate pH and conductivity, solutions were loaded onto CHELEX 100 columns at 500 mL/minute.

(3) Hardness. Ten-liter volumes of the synthetic water sample at pH 7 were adjusted to 50, 100, 250, and 500 ppm  $\text{CaCO}_3$  hardness. Hardness adjustments were made by adding reagent-grade calcium carbonate (Fisher Scientific Company, Pittsburgh, Pennsylvania) to each sample solution until aliquots titrated with ethylenediaminetetraacetic acid (EDTA) to the Calgamite (Mallinckrodt) endpoint gave the desired hardness (7). After equilibration for 24 hours, 3 L volumes of each solution were loaded onto CHELEX 100 columns at 500 mL/minute.

(4) Alkalinity. Ten-liter volumes of the synthetic water sample at pH 7 were adjusted to 50, 100, 250, 500 ppm  $\text{CaCO}_3$  alkalinity. Alkalinity adjustments were made by adding reagent-grade calcium carbonate to each sample solution until aliquots titrated with hydrochloric acid to the methyl red endpoint gave the desired alkalinity (7). After equilibration for 24 hours, 3 L volumes of each solution were loaded onto CHELEX 100 columns at 500 mL/minute.

(5) Organics. Two organic constituents of natural waters were investigated as possible interferents.

(a) Fulvic acid. A 1.00 mg/mL fulvic acid stock solution free of trace metals was prepared by dissolving 6.000 grams of dried fulvic acid (8) in 6 liters of DDW. The solution was filtered through a 0.45  $\mu\text{m}$  membrane filter (Millipore Corporation, Bedford, Massachusetts), previously cleaned with nitric acid. Less than 10 mg of residue was collected by the filter. To remove trace metals, the 6 L solution was adjusted to pH 7 with ammonium hydroxide and stirred for 72 hours with 250 mL of CHELEX 100 (ammonium-form). The resin was

removed by vacuum filtration, and the stock solution was stored in 2 L Teflon<sup>®</sup> bottles.

Fulvic acid concentrations of  $1 \times 10^{-6}$ ,  $5 \times 10^{-6}$ ,  $1 \times 10^{-5}$ ,  $5 \times 10^{-5}$ , and  $1 \times 10^{-4}$  M were investigated in the pH range 3-8 by adding appropriate volumes of the fulvic acid stock solution to 3 L volumes of the synthetic water sample and adjusting the pH with ammonium hydroxide and/or nitric acid. Calculation of fulvic acid concentrations were based on a molecular weight of 644 g/mole as estimated by Skogerboe and Wilson (8). The 3 L solutions were equilibrated for 48 hours prior to column loading. This equilibration period was found adequate for complete formation of metal-ligand complexes in natural waters by Gorman (9). The prepared solutions were loaded onto CHELEX 100 columns at both 500 mL/minute and 2 mL/minute.

(b) Humic acid. A 600 mg/L stock solution of humic acid free from trace metals was prepared by dissolving 1.000 g of humic acid (Aldrich Chemical Company, Milwaukee, Wisconsin) in 1 L of 0.10 M ammonium hydroxide and filtering the solution through a precleaned 0.45  $\mu$ m membrane filter (Millipore). After drying, the filter contained 0.40 grams of undissolved residue. Trace metals were removed from the solution by slurring 50 mL of CHELEX 100 (ammonium-form) in the solution for 72 hours. The resin was removed by vacuum filtration, and the stock solution was stored in a 1 L Teflon<sup>®</sup> bottle.

Humic acid concentrations of 1 mg/L and 10 mg/L were investigated in the pH range 3-8 by adding appropriate volumes of the humic acid stock solution to 3 L volumes of the synthetic water sample and adjusting the pH with ammonium hydroxide and/or nitric acid. Since an accurate molecular weight was not available for the humic acid,

solution concentrations were expressed as a mass of material per volume. As with the fulvic acid solutions, humic acid solutions were equilibrated for 48 hours before they were loaded onto CHELEX 100 columns at 500 mL/minute and at 2 mL/minute.

(6) Natural waters. Analyte recovery from two sources of natural water as a function of pH was investigated. The first natural water sample was taken from the Cache la Poudre River at a site 10 yards below the Greeley Diversion Dam west of the city of Fort Collins, Colorado. The second water sample was taken from a well at the State of Colorado Division of Wildlife Laboratory located in Fort Collins. Twenty liters of each water sample were filtered (0.45  $\mu\text{m}$ ) and collected in precleaned 20 L polypropylene carboys.

Ambient metals were stripped from each natural water sample by pumping the waters through eight 1.6 cm i.d. x 20 cm (40 mL) CHELEX 100 columns in series at 2 mL/minute. Synthetic water samples were made by diluting the commercial metal standards previously used with the trace-metal-free waters. These solutions were adjusted to a pH between 3-8 with ammonium hydroxide and/or nitric acid. The pH of each solution was readjusted every six hours as necessary during the 48-hour equilibration period. After equilibrating, the solutions were loaded onto CHELEX 100 columns at 500 mL/minute.

Comparison studies. Sample concentration by the developed system was compared to evaporation.

(1) Great Smoky Mountains National Park. Five locations in the park were selected as sampling sites. At each site three CHELEX 100 columns were loaded at approximately 500 mL/minute with 5 L of water using the developed sampling system. A 1 L water sample was also collected at each site using the hand-pump and filter unit of the

system to fill acid-cleaned 1 L polyethylene bottles. The 1 L water samples were immediately acidified with 1 mL of concentrated nitric acid and sealed. Columns and sample bottles were shipped without further preservation.

Immediately upon receipt, the water samples were concentrated ten-fold by evaporation in a 110°C drying oven. Three 20 mL aliquots of each sample were taken to dryness in 25 mL polypropylene vials and the residues taken up in 2 mL of 2 M nitric acid. The sample-loaded columns were rinsed with 200 mL of 1 M ammonium acetate buffer and 50 mL of DDW, and eluted with 2 M nitric acid.

(2) Cache la Poudre River. Six locations along the Cache la Poudre River in northern Colorado were selected as sampling sites. Water temperature, conductivity, and pH were measured at each sampling site (Table 5). At each site, three CHELEX 100 columns were loaded with 3 L of river water at approximately 500 mL/minute using the developed sampling system. Again, 1 L water samples were also collected using the pump and filter unit to fill acid-cleaned 1 L polyethylene bottles. The bottles were immediately sealed, packed in ice, and transported back to the lab for preconcentration.

In the laboratory, the water samples were allowed to warm to room temperature. Aliquots of each water sample were titrated to determine sample hardness and alkalinity (Table 5). Sample evaporation and column elution were carried out in the same manner previously outlined. Concentrated sample solutions and column eluates were analyzed on the ICAP used in previous studies.

Table 5. Sample characteristics of water taken along the Cache la Poudre River, Colorado.

Location	Temperature (°C)	Conductivity ( $\mu$ S/cm)@25°C	Alkalinity (ppm CaCO <sub>3</sub> )	Hardness (ppm CaCO <sub>3</sub> )	pH
Greeley Diversion Dam	2.7	94.8	24.5	25.0	7.7
Lincoln Street Bridge	4.5	170	73.7	103.0	8.0
Prospect Street Bridge	5.2	201	94.1	129.7	8.1
I-25 Rest Area	5.8	543	129.6	358.2	8.2
Above Town of Windsor	7.7	787	152.8	395.1	8.3
Below Town of Windsor	7.8	832	170.4	408.8	8.3

## RESULTS AND DISCUSSION

### Selection of the Resin

Six resins were investigated with respect to element retention, pH behavior, exchange capacity, and element selectivity (see Table 2). These characteristics were determined using a synthetic water sample adjusted to pH 3-8 in increments and measuring both the influent and effluent element concentrations. Fractionation of the column effluents allowed determination of resin capacity and selectivity. Element retention and pH behavior for the six resins are shown in Figures 3-8. Individual points in the figures are typical results for the elements indicated. Resin performance is discussed below for each type of resin investigated.

Cation exchange resins. The two cation exchange resins, AG 50W and BIO-REX 70, behaved identically in the pH range 3-8. Elements that existed as cations in solution were completely retained whereas anionic species were not, regardless of pH. The observed decrease in the retention of aluminum with increasing pH is most likely due to the conversion of free  $Al^{3+}$  to hydrolysis species in solution (10). This strongly suggests that only free  $Al^{3+}$  and labile hydrolysis species are retained by the cation exchange resins.

Anion exchange resins. Identical behavior was again observed for the two anion exchange resins studied. Most of the elements expected to exist as cations were not retained by either resin. However, aluminum, beryllium, copper, and lead were retained, presumably due to the formation of hydroxy- and chloro-complexes on the resins, which were basic and in the chloride form. The decrease in retention of molybdenum with increasing pH is again indicative of hydrolysis and

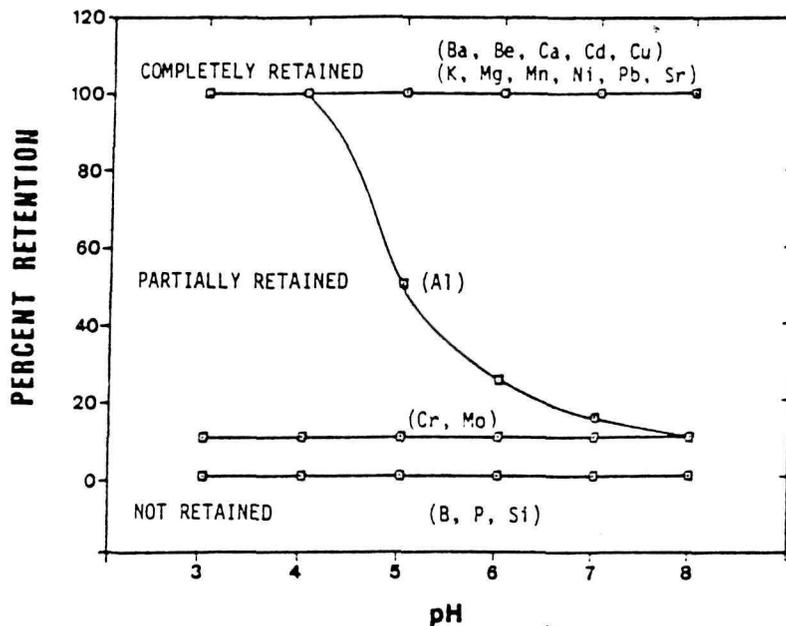


Figure 3. Element retention as a function of pH on the cation exchange resin AG 50W.

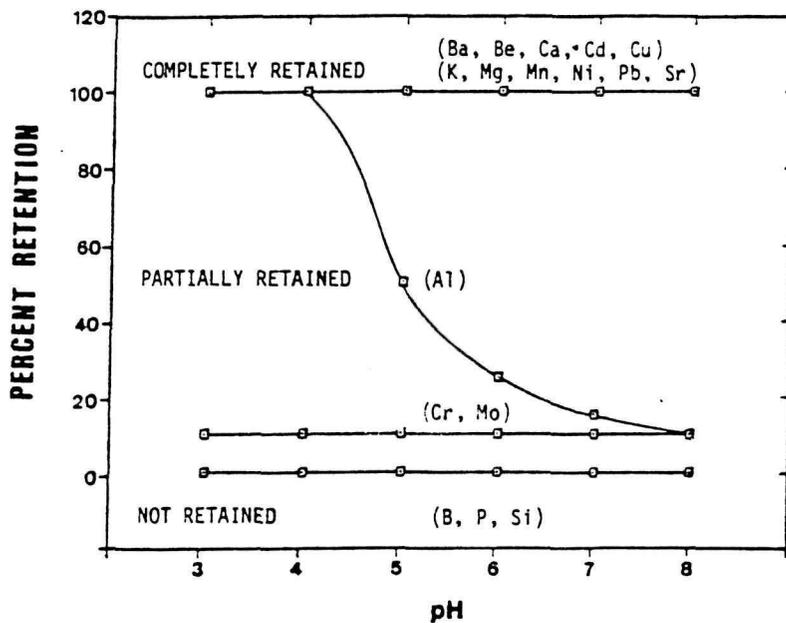


Figure 4. Element retention as a function of pH on the cation exchange resin BIO-REX 70.

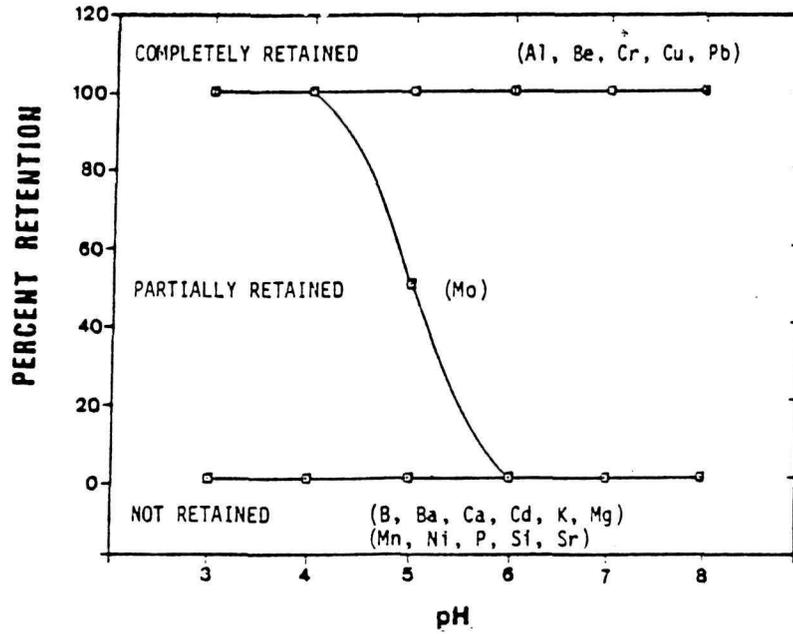


Figure 5. Element retention as a function of pH on the anion exchange resin AG 1.

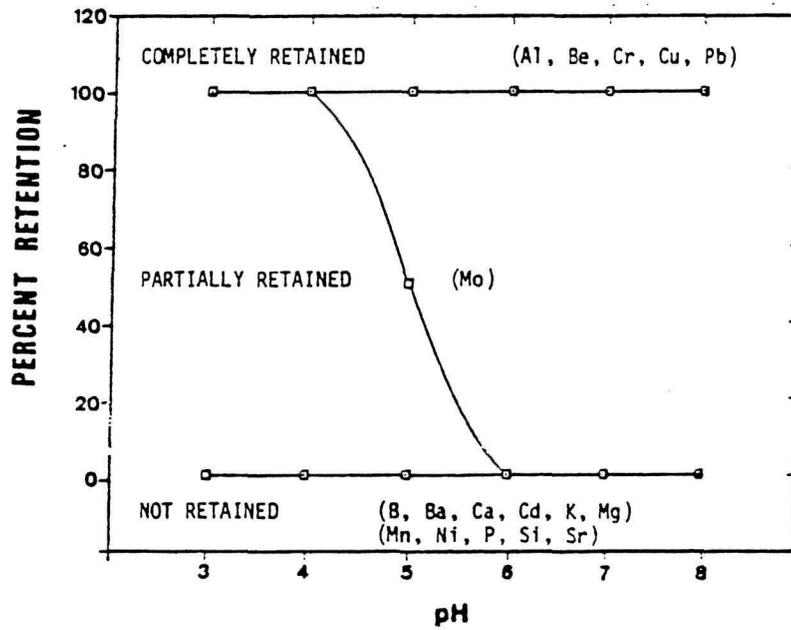


Figure 6. Element retention as a function of pH on the anion exchange resin AG 3.

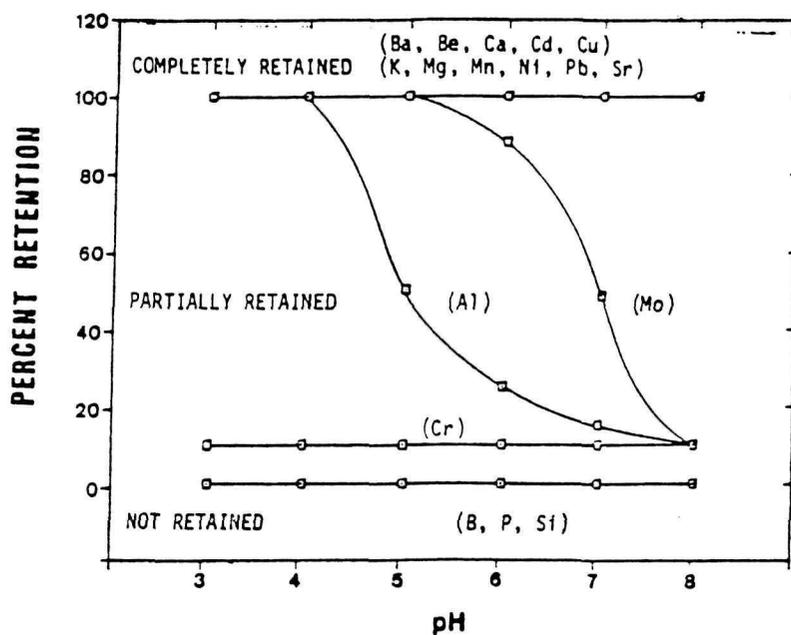


Figure 7. Element retention as a function of pH on the chelating resin CHELEX 100.

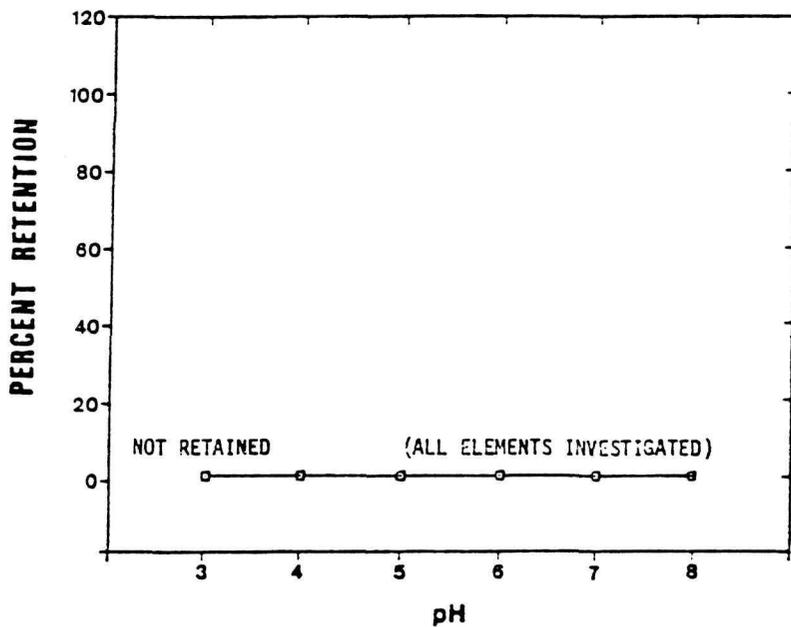


Figure 8. Element retention as a function of pH on the nonionic macroreticular resin XAD-2.

the loss of the mononuclear molybdate anion to higher order polymeric oxides (10).

Chelating resin. The chelating resin, CHELEX 100, behaved similarly to the cation exchange resins except for the retention of molybdenum. The pH-dependent retention of molybdenum more closely resembled the performance of the anion exchange resins. This suggests that CHELEX 100 can retain the molybdate anion but is not capable of complexing the polynuclear hydrolysis species present in media of higher pH (11).

Macroreticular resin. None of the elements investigated were retained by the nonionic macroreticular resin XAD-2. This result is consistent with the fact that this type of resin is primarily used in the separation of nonionic macromolecules (12). Had the elements present been complexed by large organic ligands, retention by XAD-2 may have been observed.

The breakthrough curves in Figures 9-11 demonstrate the element selectivity for the cationic and chelating resins studied. Due to the relatively poor performance of the anionic and macroreticular resins, they were dropped from further investigations. At column breakthrough, both AG 502 and BIO-REX 70 gave up the transition metals in preference to the alkali and alkaline earth elements. However, CHELEX 100 at column breakthrough released the alkali and alkaline earth elements and continued to accumulate the transition metals. This property of CHELEX 100 has been exploited by Riley and Taylor to preconcentrate transition metals from sea water (11). This point is also important to inland water sampling, since even in fresh waters calcium and magnesium concentrations typically exceed the concentration of transition metals by orders of magnitude.

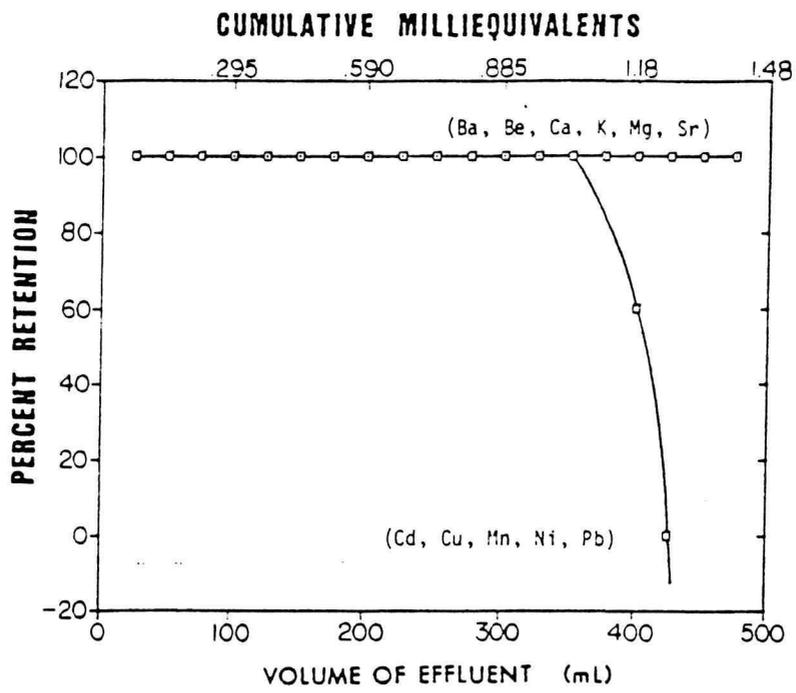


Figure 9. Exchange capacity and element selectivity of AG 50W.

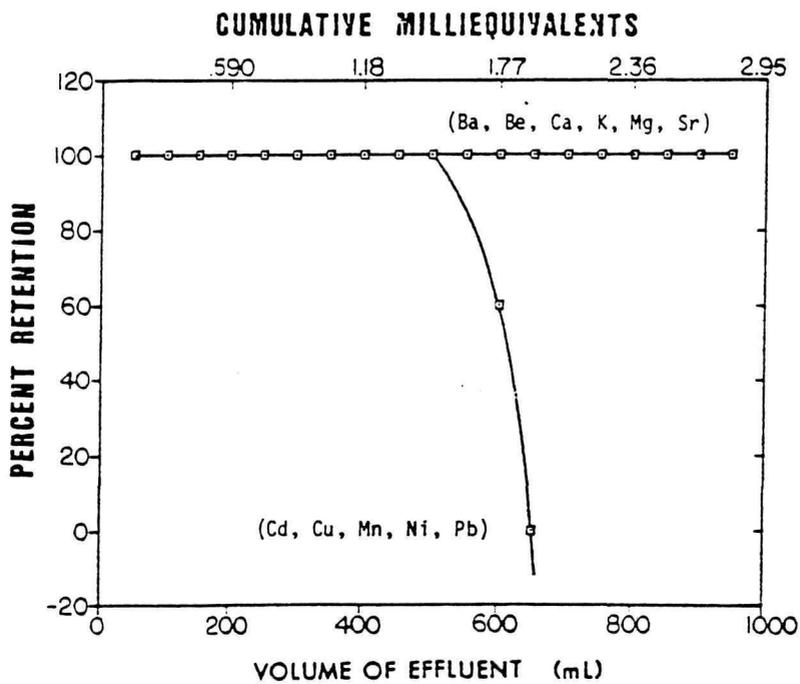


Figure 10. Exchange capacity and element selectivity of BIO-REX 70.

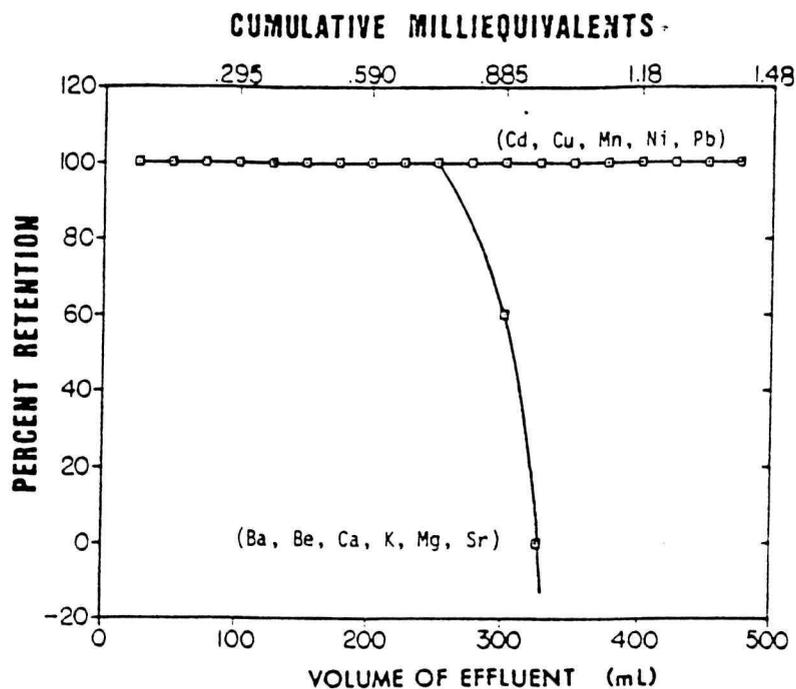


Figure 11. Exchange capacity and element selectivity of CHELEX 100.

In view of the superior performance of CHELEX 100 over the cation exchange resins with regard to element retention in the pH range investigated and its marked preference for the transition elements over the alkali and alkaline earth elements, only CHELEX 100 was considered for further study.

#### Optimization of Column Elution Conditions

Choice of eluant. An excellent table of appropriate eluants for 29 metals preconcentrated from sea water has been compiled by Riley and Taylor (11). Using their data as a guide, hydrochloric acid, nitric acid, and ammonium hydroxide were chosen as potential eluants for the present study. Retention results for all metals investigated showed consistently low recoveries (<40%) for ammonium hydroxide, intermediate recoveries (50-70%) for hydrochloric acid, and complete recoveries for nitric acid. Therefore, ammonium hydroxide was

eliminated from further study and experiments to determine the optimum eluant concentration were restricted to the two acids. In the eluant concentration range of 1-10 M, metal recoveries with hydrochloric acid were incomplete, generally in the 50-70% range, and were quite independent of eluant concentration. With nitric acid, recoveries were again complete and independent of concentration. It was observed, however, that severe resin discoloration occurred during column elution when the concentration of nitric acid exceeded 3 M. This yellow-brown discoloration was due to destructive oxidation of the resin (12). Discoloration did not occur with 2 M nitric acid and was therefore chosen as the eluant for all subsequent studies.

Influence of eluant flow rate and temperature. Eluant flow rate and temperature studies indicated that 1) metal recoveries were independent of eluant flow rate between 1 and 6 mL/minute and eluant temperature between 20 and 80°C, and 2) an eluant volume of 12.5 mL produced > 95% recovery, while 18-20 mL assured complete recovery (Table 6). To confirm these results, individual columns that were completely saturated with each metal were eluted with 25 mL volumes at 6 mL/minute. In each case, the recoveries were complete within the experimental error limits of ±5%. These experiments also indicated an average exchange capacity of 0.56 meq/mL of the wet resin, providing a total column capacity of 8.4 meq (4.4 meq/gm dry weight). The ability to concentrate elements from relatively large volumes of water without analyte breakthrough is inferred from this.

Batch elution experiments were also conducted in which varying volumes of 2 M nitric acid were equilibrated with the loaded resin for 0.5-1 hour, removed by filtration, and analyzed to determine recovery. These results indicated that a batch elution volume of 45-50 mL was

Table 6. Cumulative analyte recovery during elution.

Cumulative Elution Volume, mL	Cumulative Percent Analyte Recovery					
	Al	Cd	Cu	Mn	Ni	Pb
2.5	1.1	1.1	1.1	2.1	1.2	0.9
5.0	24.8	3.2	23.7	8.0	25.9	3.7
7.5	71.6	28.5	81.7	34.3	84.5	9.1
10.0	90.4	81.7	94.1	84.3	97.4	23.1
12.5	96.2	96.7	97.9	96.7	100	94.1
15.0	97.3	98.4	100	99.9	-	96.5
17.5	98.4	100	-	-	-	99.7
20.0	100	-	-	-	-	-

required to assure recovery in excess of 95%. Since this would result in a nominal 2-fold reduction of the preconcentration factor when compared to the column elution approach, the latter was selected for further work.

#### Characterization of Trace Metal Uptake

The goal of this investigation was to determine the maximum sampling flow rate that would still provide 100% metal retention. Since metal recovery depends on both the exchange kinetics and thermodynamic properties of CHELEX 100, the influences of sample pH, concentration, and temperature were examined.

Influence of sample pH. Analyte recovery was found to be complete and independent of pH, over the pH range of 3-8, for all elements investigated except aluminum. The decrease in percent recovery for aluminum from 100% at pH 4 to 30-40% at pH 6 has been

attributed to conversion of free  $\text{Al}^{3+}$  to aluminum-hydrolysis products not retained by CHELEX 100 (13).

Influence of sample temperature. Even at an influent flow rate of 500 mL/minute, analyte recovery was complete and independent of sample temperature from 1-40°C.

Influence of sample concentration. Analyte recovery was complete even at a total influent metal concentration of  $10^{-4}$  meq/L.

### **Sample Preservation**

An important requirement of the CHELEX 100 column is sample preservation from the time of sampling until analysis. Typically, water samples are collected in plastic bottles and acidified to pH 2 for transport to a laboratory. Upon arrival at the analysis facility, samples are usually stored at 4°C until analyzed. These procedures are costly, increase risk of sample contamination, and complicate sample transport.

The degree of sample preservation on the column was investigated by eluting and analyzing columns at one-month intervals for a year. Half of the columns were stored at 4°C and half at room temperature to evaluate the need of refrigeration. No degradation in sample quality could be detected after one year of storage (Fig. 12). Columns stored at each temperature gave equivalent results, indicating that cold storage is not required.

### **Spectral Interference Studies**

The alkali and alkaline earth elements are known to cause severe spectral interferences in the ICAP (14, 15, 16, 17, 18). This type of interference is most pronounced with calcium and magnesium, which are

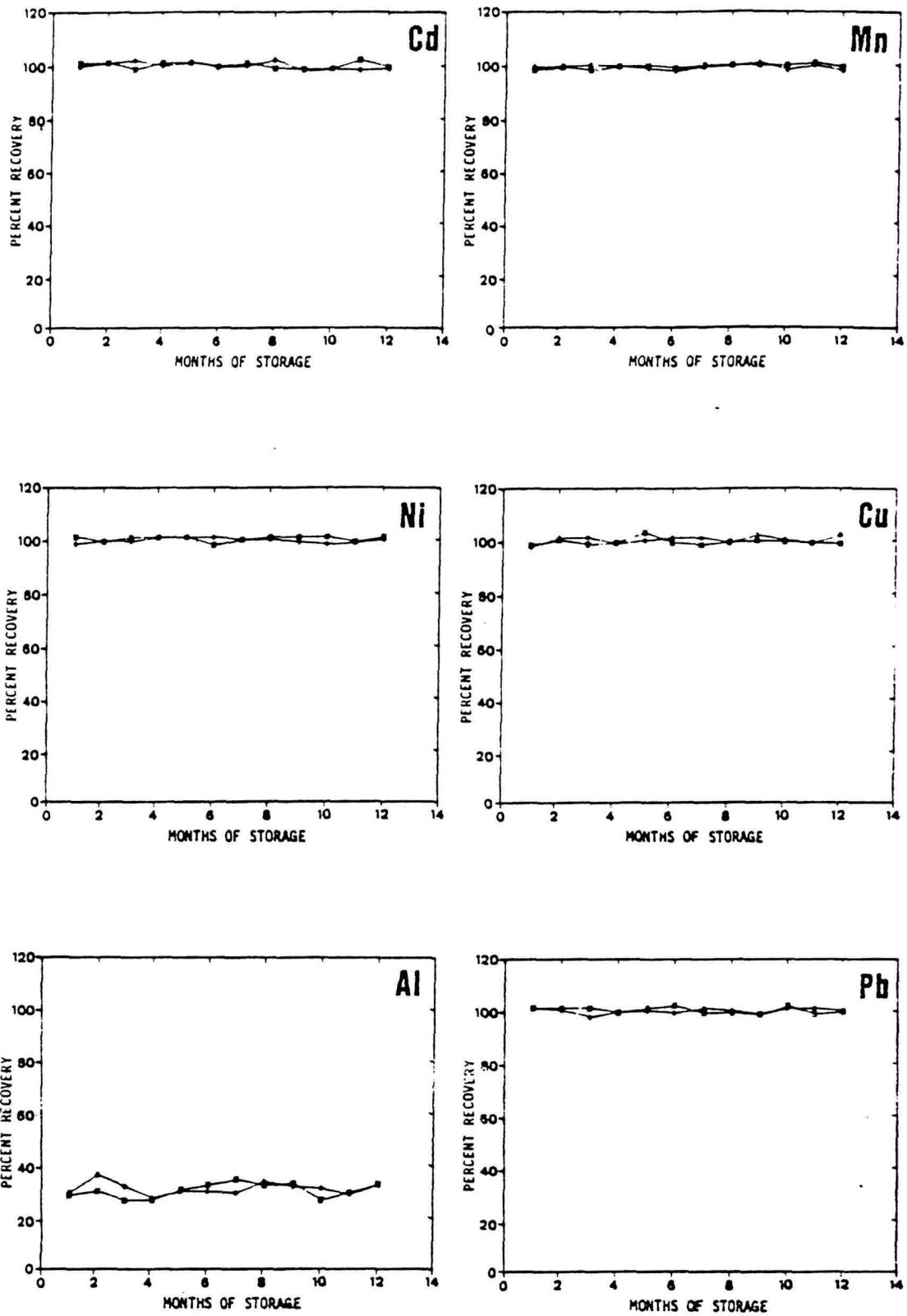


Figure 12. Analyte recovery as a function of storage time at (◇) 4°C and (□) room temperature.

common to most natural water systems and occur in much higher concentrations than most metals of interest. These interfering species are preconcentrated on the CHELEX 100 column along with the trace metals of interest and are coeluted. With preconcentration factors of 100-200, typical of the CHELEX 100 column, concentrations of calcium and magnesium in the eluate can exceed 8000  $\mu\text{g/mL}$  and 4500  $\mu\text{g/mL}$ , respectively. At these interferent concentrations, severe spectral overlap from stray light renders the analysis of many metals difficult (14). While correction for these effects is possible (19), it was considered preferable to separate the calcium and magnesium from the transition metals prior to the ICAP analysis.

To achieve this, the preferential elution of alkali and alkaline earth elements by the method of Kingston et al. (20) was explored. It was confirmed that these elements could be selectively eluted from the column with a 1 M ammonium acetate solution buffered to pH 5.2-5.3. For the present system, rinsing the column with 200 mL of this solution at 2 mL/minute prior to column elution completely removed the interfering elements without loss of analyte recovery.

#### **Chemical Interference Studies**

A number of researchers have observed that the uptake of metals by CHELEX 100 from natural waters is incomplete under conditions normally favorable for metal ion uptake (21, 22, 23). Evidently, some metals present in natural waters exist in forms that prevent them from exchanging on the resin. Such chemically inert forms would include thermodynamically stable inorganic and organic metal complexes, nonlabile metal complexes, and colloidal suspensions.

Inorganic species. Twelve common inorganic constituents of natural waters were investigated as potential interferences to analyte recovery on the CHELEX 100 column. Each potential interferent was investigated over a wider concentration range than is normally encountered in fresh waters (Table 7). Many of the typical anions found in natural waters form stable anionic complexes with metals and could conceivably compete with CHELEX 100 for the metals of interest. However, none of the four anions examined--chloride, sulfate, nitrate, and carbonate--caused any loss of analyte recovery. This is consistent with the results of Riley and Taylor (10), who did not report any chemical interference from the anion-complexes present in sea water. Evidently, these metal-anion complexes formed in solution are labile and break up on the column during sampling.

None of the four alkali and alkaline earth elements studied--sodium, potassium, calcium, and magnesium--caused any analyte recovery losses either. As previously discussed, these elements accumulate on the CHELEX 100 column along with the metals of interest during sampling and could conceivably compete for the available exchange sites. However, the more strongly binding transition metals are able to displace the more weakly bound alkali and alkaline earth elements and are completely retained.

Likewise, none of the four non-group IA and IIA metals studied--aluminum, manganese, molybdenum, and iron--interfered with analyte recovery. Presumably, these metals do not compete with the analytes for the resin because with the exception of manganese, these metals are readily hydrolyzable and thus poorly retained by CHELEX 100 (10). Manganese is retained by the resin, but is one of the more weakly held

Table 7. Common inorganic constituents of natural waters tested as potential chemical interferents.

Type	Species	Concentration Range (ug/mL)
Anions	Cl <sup>-</sup>	0 - 100
	SO <sub>4</sub> <sup>2-</sup>	0 - 100
	NO <sub>3</sub> <sup>-</sup>	0 - 100
	CO <sub>3</sub> <sup>2-</sup>	0 - 100
Alkali and Akaline	Na <sup>+</sup>	0 - 100
	K <sup>+</sup>	0 - 100
Earth Elements	Mg <sup>2+</sup>	0 - 100
	Ca <sup>2+</sup>	0 - 100
Transition Metals	MoO <sub>4</sub> <sup>-</sup>	0 - 100
	Fe <sup>3+</sup>	0 - 100
	Al <sup>3+</sup>	0 - 100
	Mn <sup>2+</sup>	0 - 100

transition metals and probably yields its exchange sites to stronger binding metals.

Conductivity. Conductivity or specific conductance is a typical measurement made during water sampling and can be related, although not easily, to ionic strength. Most inland waters of the U.S. have conductivities ranging from 5-5000 μS/cm. It has been reported, however, that approximately 95% of the waters of the U.S. supporting good fish life have conductivities of 1100 μS/cm or less (24).

Figures 13 and 14 show the influence of sample conductivity on analyte recovery by the CHELEX 100 column. Analyte recovery was

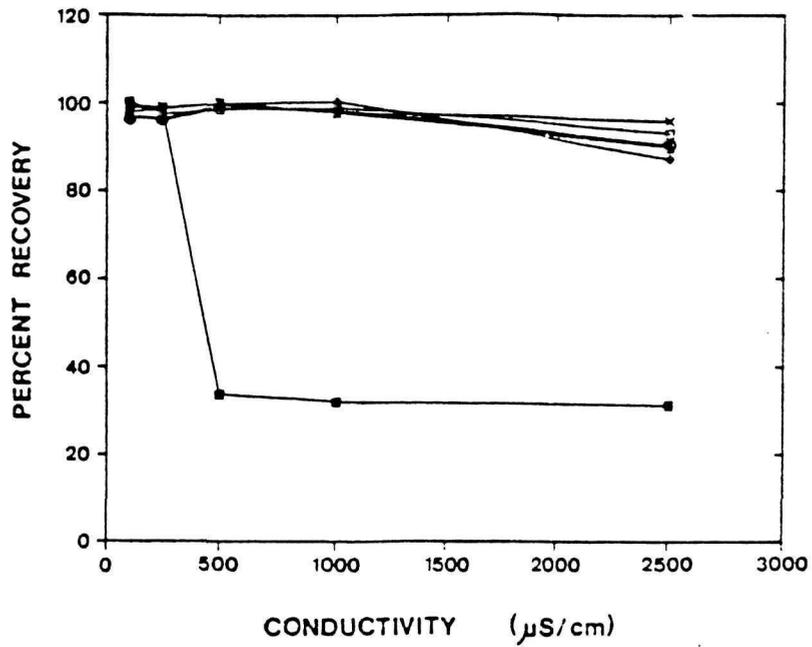


Figure 13. Analyte recovery from low to medium conductivity solutions: (■) aluminum; (□) cadmium; (x) copper; (⊗) lead; (◇) manganese; and (Δ) nickel.

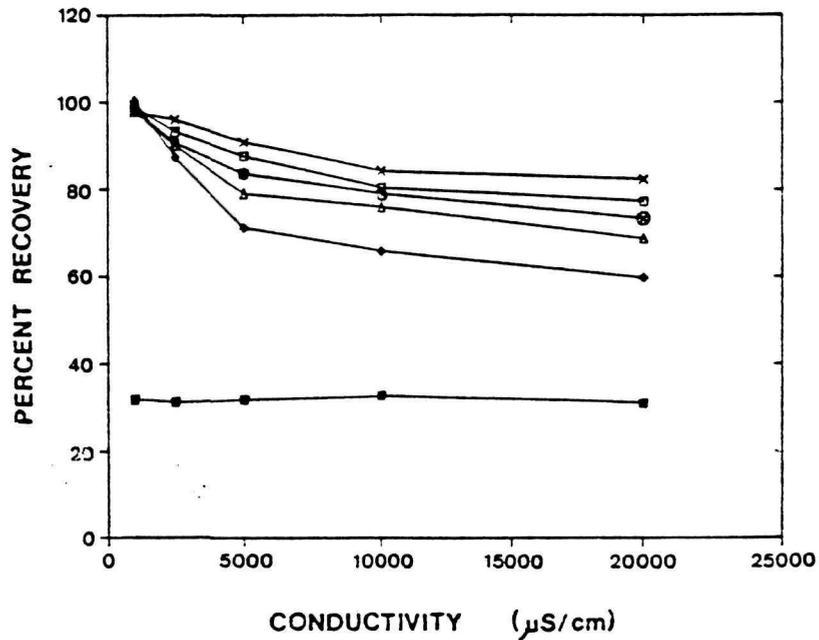


Figure 14. Analyte recovery from high conductivity solutions: (■) aluminum; (□) cadmium; (x) copper; (⊗) lead; (◇) manganese; and (Δ) nickel.

complete from solutions with conductivities typical of inland surface waters. Only at solution conductivities exceeding 2500  $\mu\text{S}/\text{cm}$  did analyte recoveries begin to decline.

Hardness. Water hardness in most natural waters is a result of calcium and magnesium concentrations and is usually reported as an equivalent concentration of calcium carbonate ( $\text{CaCO}_3$ ). Most inland waters of the U.S. have a measured carbonate hardness of less than 500 mg/L  $\text{CaCO}_3$ , with waters exceeding 150 mg/L  $\text{CaCO}_3$  hardness being considered hard waters (25). Analyte recovery was found to be complete from solutions with carbonate hardness in the range normally experienced (<500 ppm  $\text{CaCO}_3$ ).

Alkalinity. Alkalinity is defined as the sum total of components in the water that elevate the pH of the water above a value of 4.5 (25). It is usually measured by titration with an acid and is commonly expressed as an equivalent concentration of calcium carbonate ( $\text{CaCO}_3$ ). Actually, many species are responsible for alkalinity in natural waters, including carbonates, bicarbonates, phosphates, and hydroxides. Analyte recovery from solutions with alkalinity in the range normally encountered (<500 ppm  $\text{CaCO}_3$ ) were complete and not interfered with.

Organics. The influence of organic constituents common to natural waters on analyte recovery by the CHELEX 100 column was investigated using purified humic materials. These humic materials are widespread in the environment and result from the chemical and biological degradation of plant materials and from the synthetic activities of microbes (26). Christman and Minear (27) have reported that humic substances appear to be present in nearly all natural

surface waters, and according to Stumm and Morgan (28) they are present in the concentration range of 0.1-10 mg/L.

The observed chemical interferences of fulvic and humic acids as a function of sample pH and interferent concentration are shown in Figures 15-18. The graphs in these figures indicate an inhibition in metal ion uptake by the CHELEX 100 column that increases with both sample pH and interferent concentration. The degree of inhibition appears to be partially dependent on the sampling flow rate, although small differences in sampling flow rate (20-30%) would probably yield imperceptibly small differences in analyte recovery.

An observation apparent in the analyte recovery curves of both humic materials is the increased recovery of aluminum at relatively low interferent concentrations. Aluminum interactions with fulvic and humic acids in aquatic environments have been studied and are thought to be partially responsible for elevated aluminum solubility in these systems (29). Results of this research suggest that fulvic and humic acid can effectively compete with hydroxide as complexing ligands and postpone hydrolysis of aluminum to a higher pH. The increased ability of CHELEX 100 to retain organically-bound aluminum over hydrolyzed aluminum is probably due to differences in the rate of ligand exchange.

Natural waters. Metal ion interactions with constituents of natural waters are well documented (8, 30, 31, 32, 33, 34, 35). Recent investigations have shown trace metal uptake from many natural water systems by CHELEX 100 to be incomplete, presumably due to some type of relatively nonlabile complex formation (4, 11, 13, 36, 37, 38). Simulated natural water conditions in this research using fulvic and humic acids has confirmed that these humic materials can inhibit

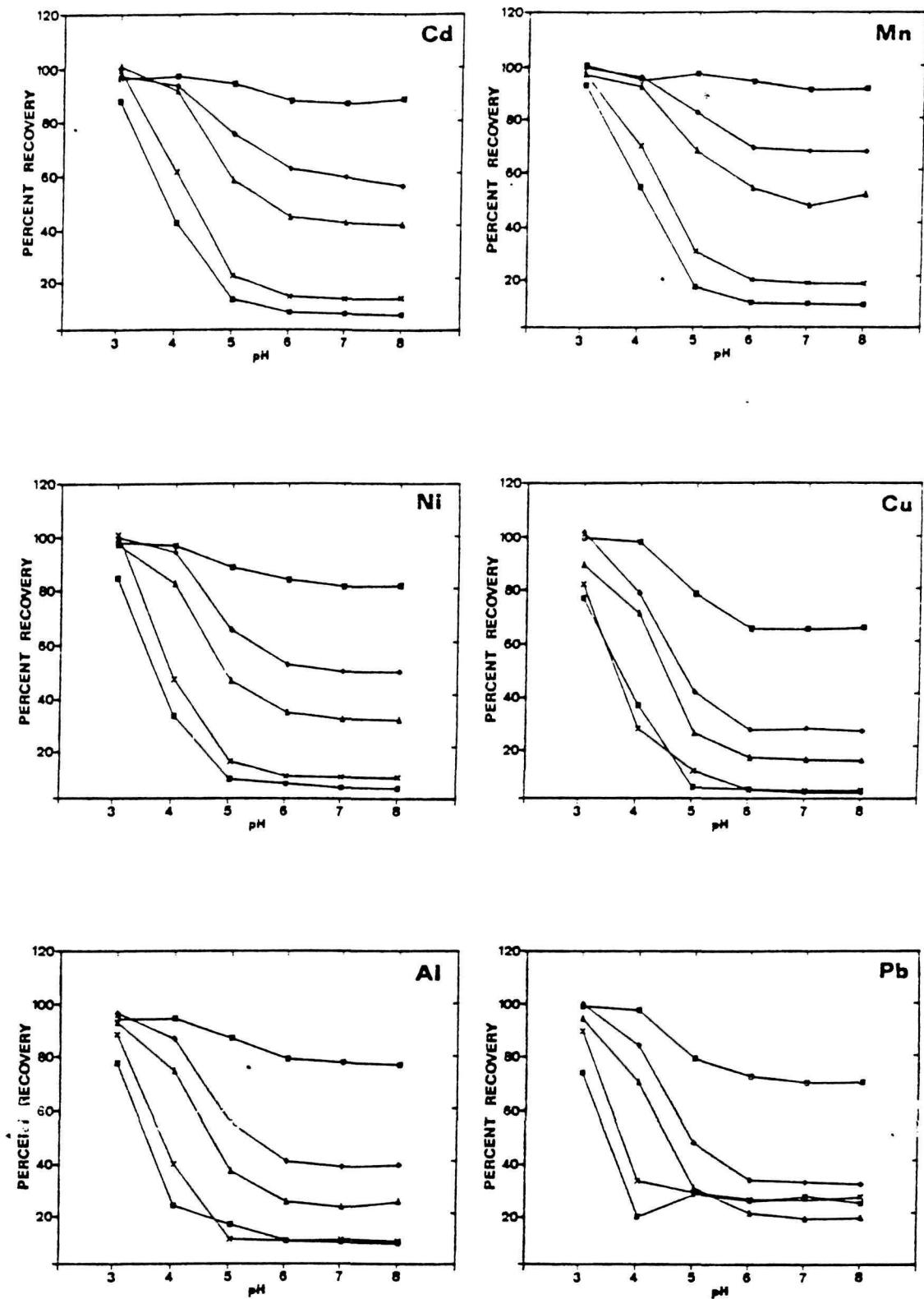


Figure 15. Interference of fulvic acid with analyte recovery at high sampling flow rates as a function of pH and fulvic acid concentration: ( $\square$ )  $1 \times 10^{-6}$  M; ( $\diamond$ )  $5 \times 10^{-6}$  M; ( $\Delta$ )  $1 \times 10^{-5}$  M; ( $\times$ )  $5 \times 10^{-5}$  M; and ( $\blacksquare$ )  $1 \times 10^{-4}$  M.

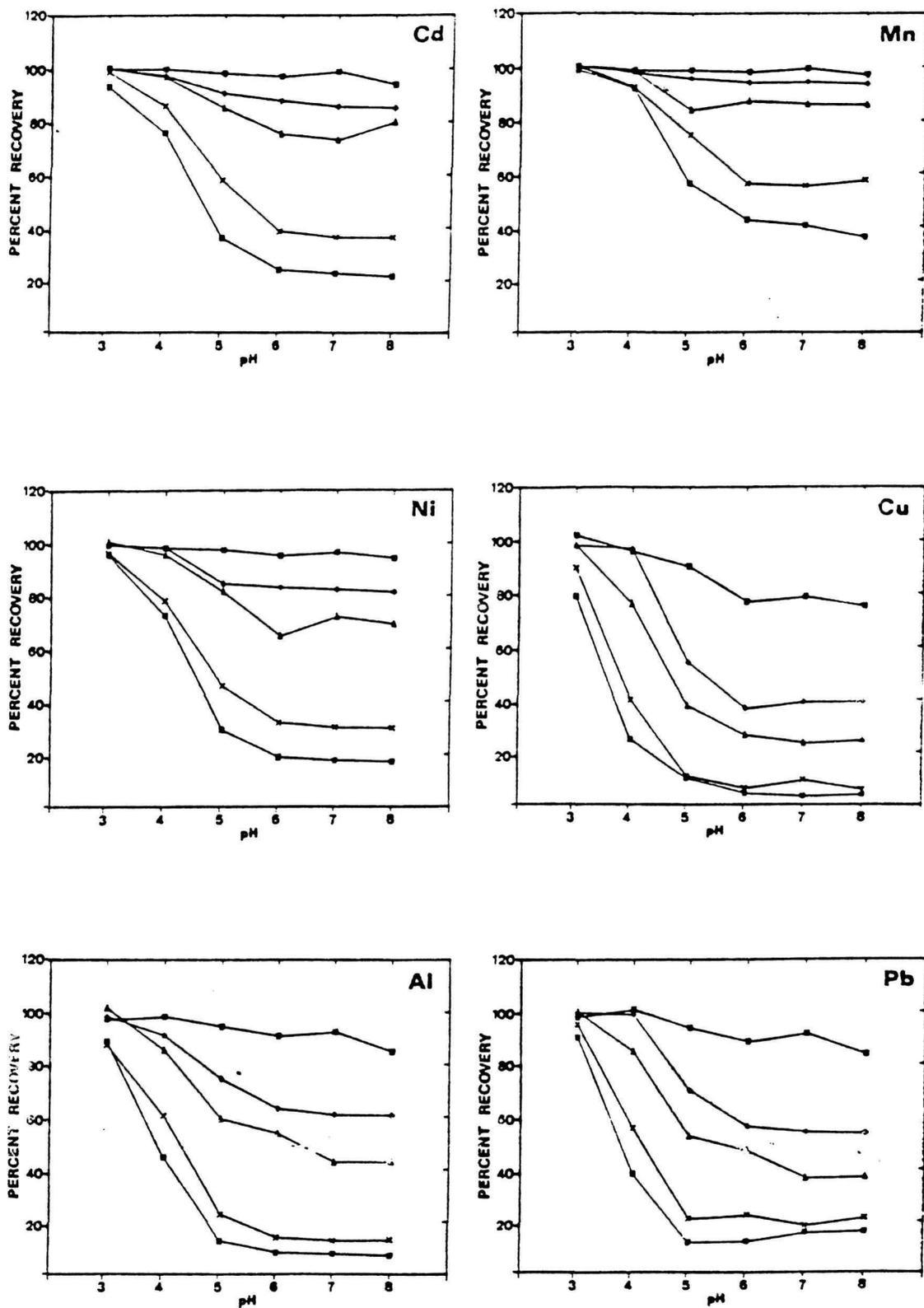


Figure 16. Interference of fulvic acid with analyte recovery at low sampling flow rates as a function of pH and fulvic acid concentration: ( $\square$ )  $1 \times 10^{-6}$  M; ( $\diamond$ )  $5 \times 10^{-6}$  M; ( $\Delta$ )  $1 \times 10^{-5}$  M; ( $\times$ )  $5 \times 10^{-5}$  M; and ( $\blacksquare$ )  $1 \times 10^{-4}$  M.

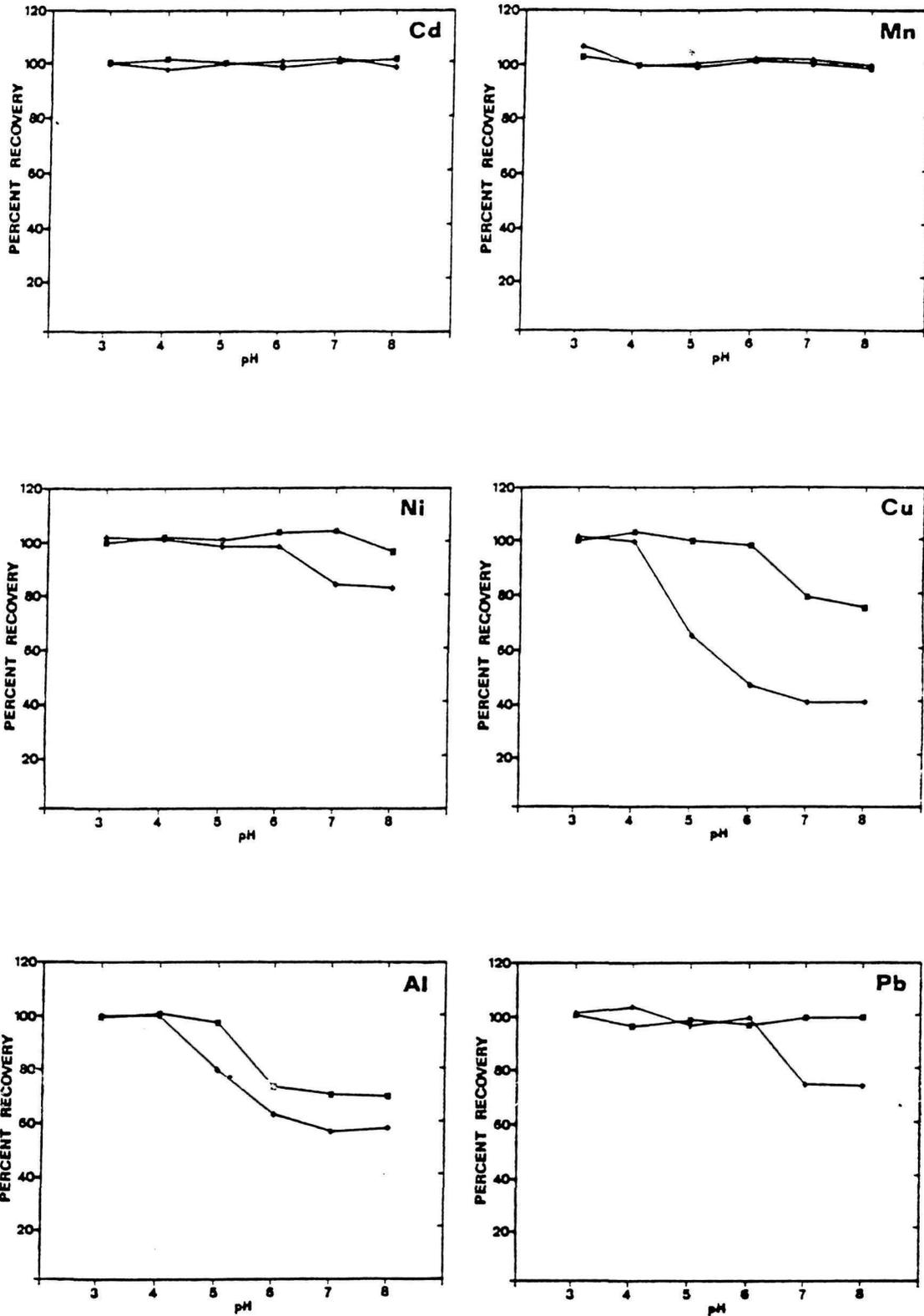


Figure 17. Interference of humic acid with analyte recovery at high sampling flow rates as a function of pH and humic acid concentration: ( $\square$ ) 1 mg/L; ( $\diamond$ ) 10 mg/L.

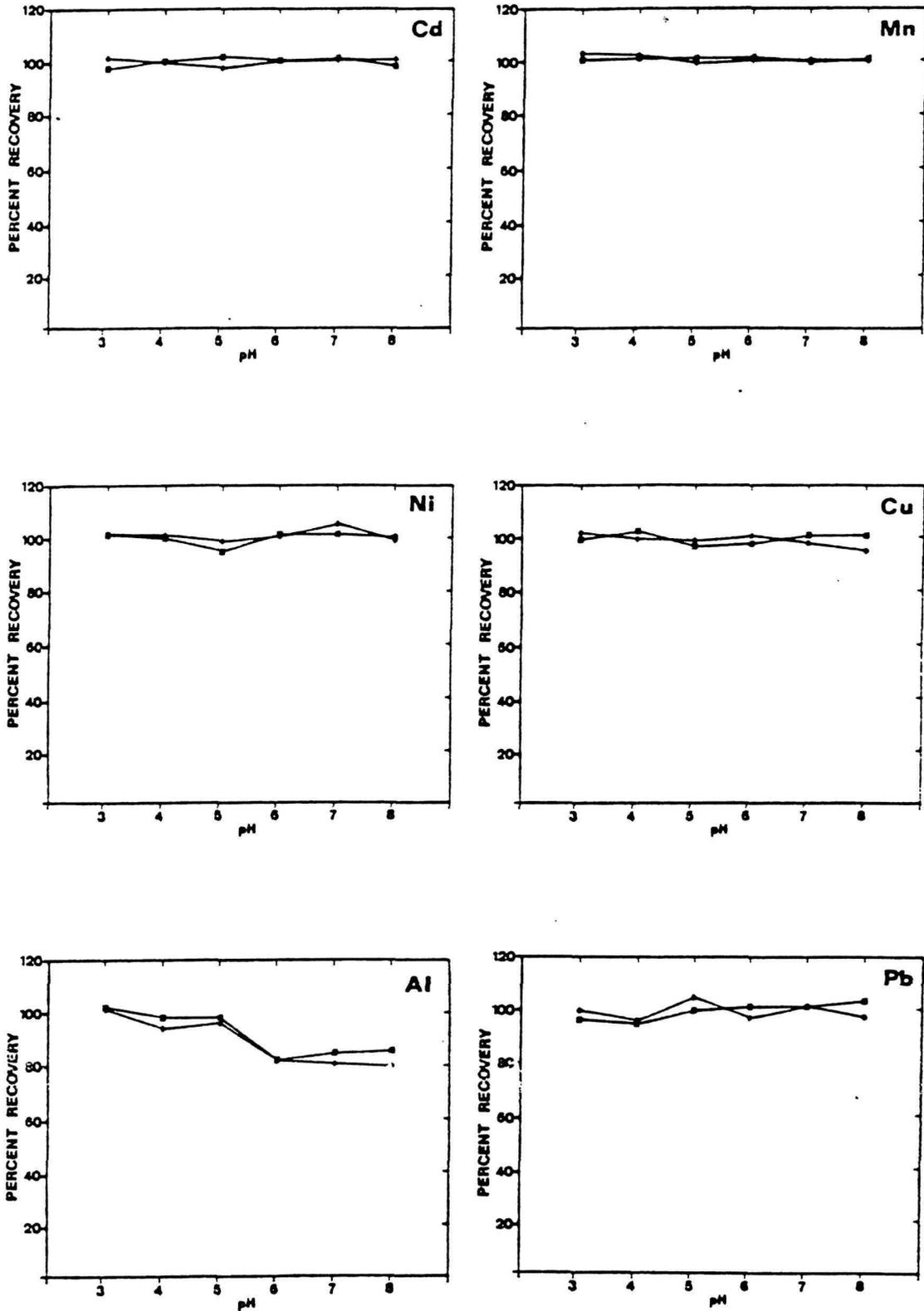


Figure 18. Interference of humic acid with analyte recovery at low sampling flow rates as a function of pH and humic acid concentration: (□) 1 mg/L; (◇) 10 mg/L.

metal ion uptake if present in sufficient concentration and if appropriate pH conditions exist. However, a more realistic idea of the degree of inhibition was obtained by observing the analyte recovery from trace-metal-free natural waters spiked with known quantities of analyte. Trace-metal-free natural waters do not, of course, occur naturally, and instead, ambient metals were stripped from natural water samples with CHELEX 100. It should be noted that this treatment undoubtedly modifies the water samples investigated. Since the alkali and alkaline earth metals are known to be complexed by humic materials (33) and are present in much higher concentrations than the trace metals of interest, removal of these species by the CHELEX 100 probably shifts the equilibrium for the spiked metals and results in lower analyte recoveries than would otherwise occur.

The results of this investigation are shown in Figures 19 and 20 for a river water sample and a well water sample, respectively. The graph for the river water sample clearly shows the pH-dependent interference typical of the humic materials previously studied. The well water sample did not show any significant (95% confidence level) interference even in the pH region of 6-8, suggesting the absence or very low concentrations of fulvic and humic acids. No reference to differences in humic material content of surface and subsurface waters was found in the literature.

### **Comparison Studies**

Two comparison studies were conducted to evaluate the performance of the CHELEX 100 column system against an accepted method for sample preconcentration. Comparison of the two preconcentration techniques was accomplished by graphing the results obtained by the CHELEX 100

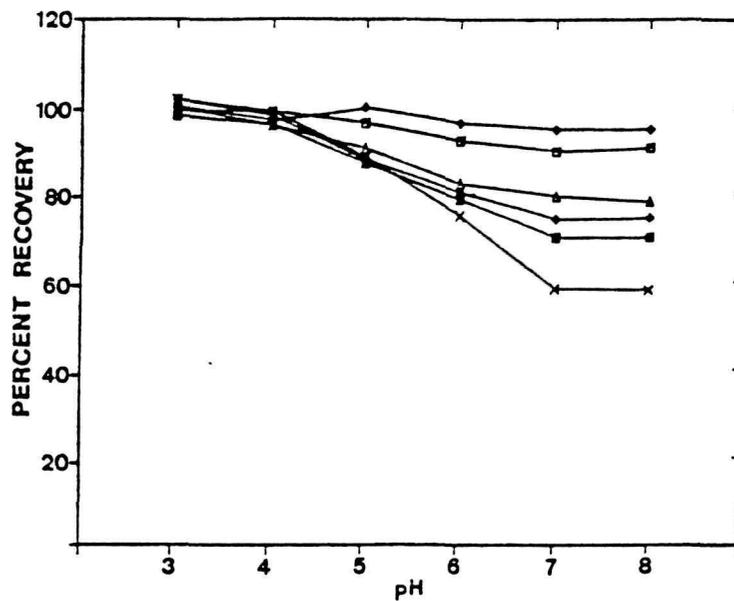


Figure 19. Interference with analyte recovery by species present in the Cache la Poudre River: (◆) aluminum; (□) cadmium; (x) copper; (■) lead; (◇) manganese; and (Δ) nickel.

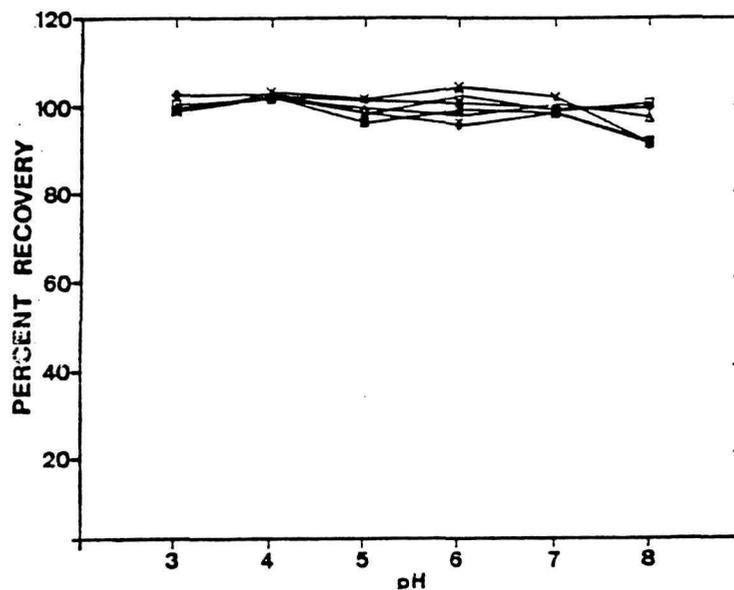


Figure 20. Interference with analyte recovery by species present in a well water sample: (◆) aluminum; (□) cadmium; (x) copper; (■) lead; (◇) manganese; and (Δ) nickel.

column system against those obtained by evaporation for each site sampled. Points lying along the diagonal indicate samples for which the two preconcentration techniques gave similar values. It should be noted that evaporation results are not affected by the presence of humic materials.

Great Smoky Mountains National Park. Six metals were found in sufficient concentration to permit comparison of the two preconcentration techniques (Fig. 21). Both preconcentration techniques gave similar values for manganese, zinc, lead, and nickel. Only two points, representing two sites, were available for comparison with lead and nickel due to the low ambient concentrations of these metals at the other sites. Aluminum and iron, however, were not appreciably retained by the CHELEX 100, as evidenced by the points lying along the X-axis. As stated earlier, these metals are easily hydrolyzable and their uptake by CHELEX 100 is low, unless the hydrolysis equilibrium is offset by complexation with organic ligands. Consequently, sampling of this water system using the CHELEX 100 column system was not inhibited due to interferences by humic materials.

Cache la Poudre River. Only three metals were found in sufficient concentration to permit comparison of the two preconcentration techniques (Fig. 22). Both preconcentration techniques have similar values for manganese and copper, but again, aluminum was incompletely recovered by the CHELEX 100 column. All of the copper results were essentially identical because of the nearly constant concentration of copper along the river. Once again, adequate sampling of this water system using the CHELEX 100 column system was not inhibited due to interferences by humic materials.

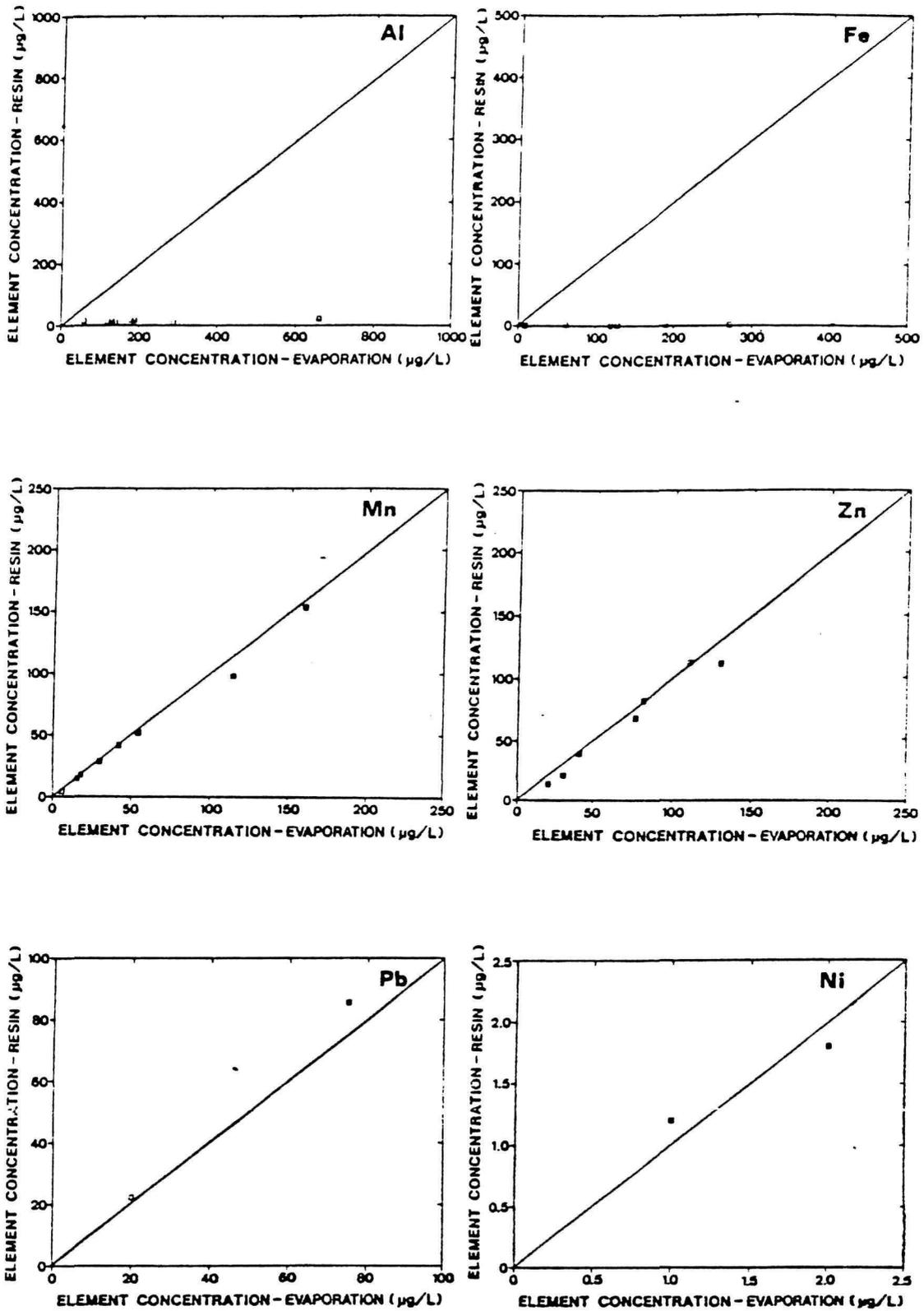


Figure 21. Concentrations of six metals found in the waters of the Great Smoky Mountains National Park, comparing sample preconcentration by the CHELEX 100 column system with conventional evaporation.

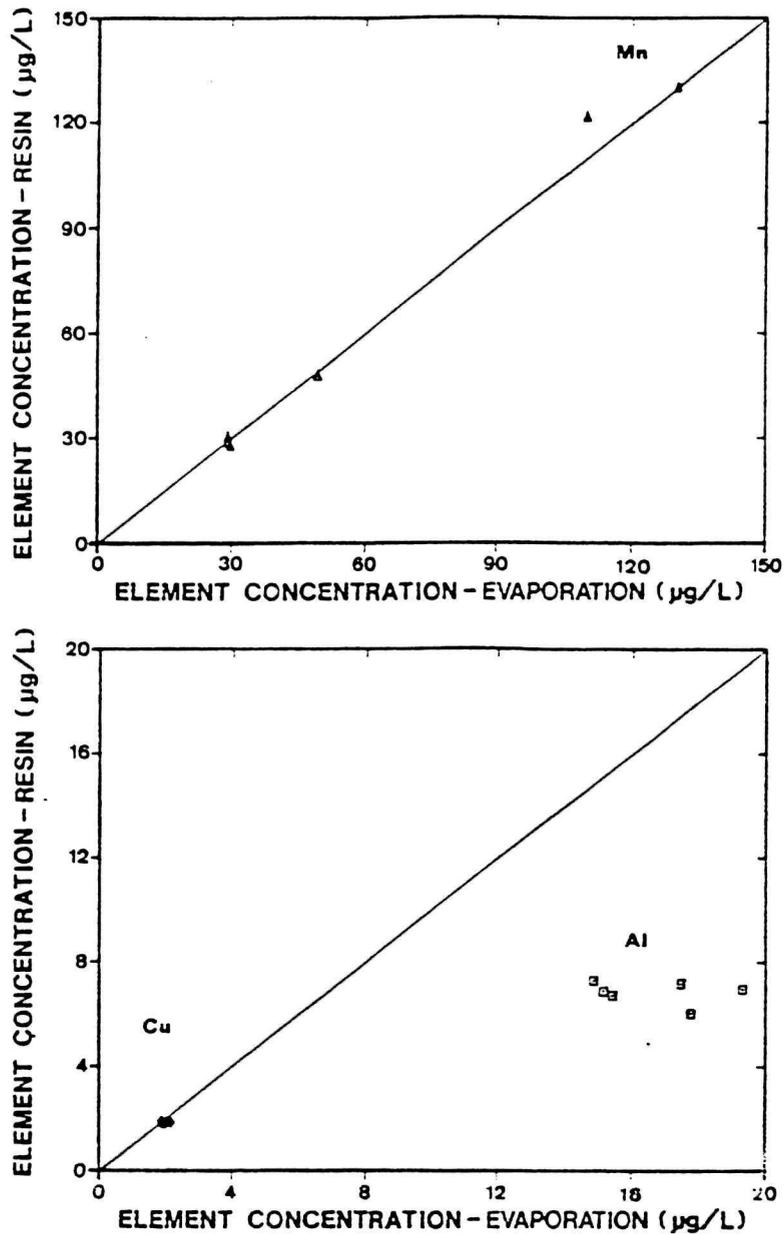


Figure 22. Concentrations of three metals found in the waters of the Cache la Poudre River, comparing sample preconcentration by the CHELEX 100 column system with conventional evaporation.

## FUTURE INVESTIGATIONS

Further testing and application of the rapid field-preconcentration/preservation system developed is warranted and encouraged. Three major areas towards which future investigations should be directed are the following:

1. evaluation of the developed system's performance in complex, polluted water systems;
2. application of the system to trace-metal speciation studies; and
3. development and testing of a complementary integrating, trickle-type sampling unit.

So far, actual testing of the field sampling system developed has been restricted to relatively clean, nonpolluted waters. However, preliminary investigations indicate that this system would be an effective approach to the identification and monitoring of pollution sources. Potential trace-metal pollution sources affecting the aquatic habits and water supplies in wildlands and parks managed by the National Park Service (NPS) include runoff from commercial mining operations and oil fields, industrial discharge, leaching from landfills, and hazardous waste dumping. Once evaluated, this system could provide NPS investigators with a simple and cost-effective field-sampling device.

Another area that in recent years has been receiving increased interest is the field of trace-metal speciation in natural waters. Numerous efforts have been made to characterize these trace-metal species and to develop a method for measuring the fraction of the total trace-metal concentration that is actually toxic to aquatic biota. The interferences with analyte uptake observed in this research due to hydrolysis products and the presence of humic

materials indicate that this system is sensitive to the chemical form of the trace metal and may be well-suited to such studies. Initial investigations should (1) evaluate the effect of filtration on trace-metal uptake and its ability to differentiate between organically bound metals and metals adsorbed to colloidal matter; (2) relate trace-metal lability, as determined by this system, with anodic-stripping voltammetry results already employed in speciation schemes (33); and (3) investigate the relationship between the measured trace-metal concentration using this system and toxicity-testing results.

Finally, the development and testing of an integrating, trickle-type sampler is strongly encouraged. Such a unit, utilizing the developed CHELEX 100 column, would be a sampling system complementary to the one developed. By monitoring trace-metal concentrations over time (integrating for days or weeks), day-to-day fluctuations in metal levels due to weather, stream flow, and the impact of weekend recreational activities could be averaged out to yield, in many instances, a more accurate analysis of trace-metal concentrations.

## SUMMARY AND CONCLUSIONS

The experimental work discussed in this report demonstrates that the sampling system developed generally satisfies the aforementioned requirements for its application to routine monitoring for trace metals in natural waters. The following summary of experimental results supports this statement and mentions the limitations of the system.

1. The development of an ion-exchange resin column for field preconcentration of trace metals prior to analysis by the inductively coupled argon plasma is feasible and warrants further testing.
2. The chelating resin, CHELEX 100, has element retention properties comparable to the more commonly used cation exchange resins for the preconcentration of trace metals over the pH range likely to be encountered in natural waters.
3. The selectivity of CHELEX 100 for the transition metals over the alkali and alkaline earth elements makes CHELEX 100 ideally suited for trace-metal preconcentration from natural waters.
4. A 1.6 cm i.d. x 7.5 cm polyethylene column with 35  $\mu\text{m}$  polypropylene frits provides an appropriate bed volume of resin and is well-suited to field use.
5. Optimum elution of the developed CHELEX 100 column is affected in the column mode using 2 M nitric acid at an eluant flow rate of 6 mL/minute.
6. Analyte retention on the column is independent of sample pH, temperature, and concentration in the ranges normally encountered in natural waters.
7. Metals retained on the column do not require additional preservation measures or refrigeration during transport or long-term storage.
8. Spectral interferences from the alkali and alkaline earth elements can be eliminated by removing the interfering species from the column with a 1 M ammonium acetate buffer at pH 5.3 prior to column elution. This provides the ICAP with a relatively simple sample matrix.
9. Common inorganic constituents of natural waters at typical concentrations do not inhibit analyte uptake by the column.

10. Extremely high sample conductivities do reduce analyte retention on the column, but samples in the normal range of 10-2000  $\mu\text{S}/\text{cm}$  do not interfere.
11. Sample hardness and alkalinity in the ranges normally encountered in field sampling do not interfere with trace-metal uptake.
12. Incomplete analyte recovery can occur when significant amounts of fulvic or humic acids are present in the sample.
13. Comparison with evaporation shows good correlation of results for preconcentration of trace metals in natural waters, except for easily hydrolyzable metals.

The above synopsis of conclusions derived from experimental results indicates the strategy used for development, characterization, and evaluation of the resin column sampling system. Major areas towards which future investigation should be directed have also been presented. These suggestions do not define the limits of application of this system, but rather identify areas of immediate need.

## REFERENCES

1. Minear, R. A.; Keith, L. H., "Water Analysis: Inorganic Species", Academic Press, New York, 1982.
2. Hall, G. S., "Trace Element Analysis of Groundwater: Comparison of Proton-Induced X-Ray Emission (PIXE) With Atomic Absorption Analysis (AA)", Center for Coastal and Environmental Studies, Rutgers, 1983.
3. Topp, N. E.; Pepper, K. W., J. Chem. Soc., 1949, 3299.
4. Smits, J.; Nelissen, J.; Van Grieken, R., Anal. Chim. Acta., 1979, 111, 215.
5. Leyden, D. E.; Wegscheider, W., Anal. Chem., 1981, 53, 1059A.
6. Samuelson, O., "Ion Exchange Separation in Analytical Chemistry", John Wiley & Sons, New York, 1963.
7. Skongstad, M. W.; et al., "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments", Open-File Report 78-679, United States Geological Survey, 1978.
8. Skogerboe, R. K.; Wilson, S. A., Anal. Chem., 1981, 53, 228.
9. Gorman, Jr., Wm. C., Ph.D. Dissertation.
10. Baes Jr., C. F.; Mesmer, R. E., "The Hydrolysis of Cations", National Science Foundation, 1974.
11. Riley, J. P.; Taylor, D., Anal. Chim. Acta., 1968, 40, 479.
12. Bio-Rad Products Catalog, 1985, pp. 3-22.
13. Campbell, P. G. C.; Bisson, R.; et al., Anal. Chem., 1983, 55, 2246.
14. Anderson, T. A.; Parsons, M. L., Appl. Spectrosc., 1984, 38, 625.
15. Anderson, T. A.; Forster, A. R.; Parsons, M. L., Appl. Spectrosc., 1982, 34, 504.
16. Barnes, R. A., Editor, "Applications of Plasma Emission Spectroscopy", Hyden and Sons, Inc., Philadelphia, 1979, pp. 46-62.
17. Berman, S. S.; McLaren, J. W.; Willie, S. N., Anal. Chem., 1980, 52, 488.
18. Parsons, M. L.; Forster, A.; Anderson, D., "An Atlas of Spectral Interferences in ICP Spectroscopy", Plenum Press, New York, 1980.
19. Matsuzura, H.; Wadachi, Bull. of Chem. Soc. of Japan, 1975, 48, 3456.

20. Kingston, H. M.; et al., Anal. Chem., 1978, 50, 2064.
21. Abdullah, M. I.; El-Rayis, O. A.; Riley, J. P., Anal. Chim. Acta., 1976, 84, 363.
22. Figura, P.; McDuffie, B., Anal. Chem., 1977, 49, 1950.
23. Florence, T. M.; Batley, G. E., Talanta, 1976, 23, 1979.
24. McKee, J. E.; Wolf, H. M., "Water Quality Criteria", State Water Resources Control Board, State of California, Publication No. 3-A, 1976 reprint.
25. U.S. Environmental Protection Agency, "Quality Criteria for Water", Washington, D.C., 1976.
26. Bohn, H.; McNeal, B.; O'Connor, G., "Soil Chemistry", John Wiley & Sons, New York, 1979.
27. Christman, R. F.; Ghassemi, M., J. Amer. Water Works Assoc., 1966, 58, 723.
28. Stumm, W.; Morgan, J. J., "Aquatic Chemistry", John Wiley & Sons, New York, 1970.
29. Burrows, W. D., CRC Crit. Rev. Environ. Control, 1977, 167.
30. Van den Berg, C. M. C.; Kramer, J. R., Anal. Chim. Acta., 1979, 106, 113.
31. Skogerboe, R. K.; Wilson, S. A.; Osteryoung, J. G., Anal. Chem., 1980, 52, 1960.
32. Florence, T. M.; Batley, G. E., CRC Critical Reviews in Analytical Chemistry, 1980, 9.
33. Florence, T. M., Anal. Chim. Acta., 1982, 141, 73.
34. Florence, T. M.; Batley, G. E., Talanta, 1977, 24, 151.
35. Batley, G. E.; Florence, T. M., Anal. Lett., 1976, 9, 379.
36. Figura, P.; McDuffie, B., Anal. Chem., 1979, 51, 120.
37. Figura, P.; McDuffie, B., Anal. Chem., 1980, 52, 1433.
38. Florence, T. M.; Batley, G. E., Talanta, 1975, 22, 201.