

## Methods for concentrating metal ions prior to analysis by ion chromatography or capillary electrophoresis

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### Abstract

In ion chromatography and particularly in capillary electrophoresis, it is often necessary to preconcentrate metal ions to be determined and to remove larger amounts of matrix ions such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ . Several general techniques for concentration of selected metal ions are reviewed and illustrated by specific examples. These techniques include the use of chelating resins and the formation of soluble complexes in solution with subsequent retention by ordinary solid-phase extraction (SPE) columns.

Many of the chelating resins used in the past for preconcentration of metal cations have been relatively inefficient. More effective resins can be created by careful attention to the particle size and physical structure of the resin, its chelating capacity, and the selectivity and kinetics of the chelating groups present in the resin. Likewise, carefully designed soluble complexing reagents can be used effectively in conjunction with modern SPE techniques. These principles are illustrated by new types of chelating resins and reagents that we have prepared and tested.

*Keywords:* Sample preparation; Metal ions

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### 1. Introduction

In capillary electrophoresis (CE), and to a somewhat lesser extent in ion chromatography (IC), a high concentration of a sample ion may form a broad zone on the capillary or column that will overlap with those of much lower concentrations of other sample ions. This problem was illustrated in a recent paper in which the determination of 1 ppm each of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  was attempted by CE in the presence of 75 ppm of  $\text{Na}^+$ . The broad  $\text{Na}^+$  peak covered up all of the divalent ion peaks except for  $\text{Mg}^{2+}$  [1].

Pretreatment/preconcentration methods are needed that will separate ions of interest from much larger

amounts of sample matrix ions. Such methods are needed particularly when CE is to be the final analytical method because a high concentration of a sample ion tends to form a broad zone within the capillary. To be practical, sample preconcentration methods need to be both convenient and fast. Several promising approaches will be discussed in this paper.

### 2. Experimental

The solid-phase extraction apparatus consisted of a 5 mm I.D. mini-column packed with the desired resin. The resin bed was held in place by 20- $\mu\text{m}$  frits above and below the bed. A circle of 0.2- $\mu\text{m}$  filter paper was placed next to the lower frit to prevent resin leakage. Resin bed depth was generally 4–6

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mm. Once the column is packed with resin, it is attached to a pressure source and 20 p.s.i. (ca.  $1.4 \cdot 10^5$  Pa) of pressure was applied to elute solutions from the column. The eluates were analysed by absorption spectrophotometry.

Iminodiacetic acid (IDA) resins with metal ion capacities of approximately 0.5 and 2.5 meq/g were obtained from Sarasep (Sarasep, Santa Clara, CA, USA).

Two different resins were used in the preparation of the dithiocarbamate resin. The first was a 10- $\mu$ m macroporous chloromethylstyrene–divinylbenzene co-polymer, and the second was an 8- $\mu$ m macroporous polystyrene–divinylbenzene resin (Sarasep). The latter was chloromethylated by reaction with paraformaldehyde and hydrochloric acid, as described by Barron and Fritz [2,3]. A 1-g amount of each of the chloromethylated resins was reacted with 15 ml of 1-amino-2-propanol at 100°C for 24 h. Each resin was filtered through a glass frit and rinsed with deionized water, 2-propanol, and methanol. After drying, each resin was mixed with 5 ml 2-propanol, 5 ml 20% potassium hydroxide in methanol, and 5 ml carbon disulfide. These mixtures were stirred at room temperature and allowed to react for 48 h. The reaction mixtures were filtered and rinsed as previously described.

### 3. Ion-exchange preconcentration

A small ion-exchange precolumn is often used in conjunction with ion chromatography. A valve arrangement allows the analyte ions to be concentrated on the precolumn while the rather large sample volume passes out to waste. Systems of this type are used extensively to concentrate ultra trace amounts of cations or anions from condensed steam and other water samples [4–7].

Preconcentration and separation of analyte ions from a higher concentration of other ions may also be possible if there is a sufficient selectivity for the analyte ions. For example, 2+ ions and particularly 3+ ions are more strongly retained by a cation exchanger than 1+ ions such as  $\text{Na}^+$ . But even if this favorable situation exists, the cation-exchange capacity not used by the analyte ions will be occupied by the  $\text{Na}^+$ . Also, some kind of cation will

be needed to elute the analyte ions (and  $\text{Na}^+$ ) from the column. Thus, only a partial separation of analyte ions from matrix ions is likely.

It may be possible to design the chemical structure of the ion exchanger to obtain better selectivity for a sample ion. For example, in analyzing sea water by IC the huge  $\text{Cl}^-$  peak may obscure the smaller, later-eluting  $\text{I}^-$  peak. This situation can be improved by using an ion exchanger with a benzyltributylammonium or benzyltriethylammonium function instead of the usual benzyltrimethylammonium group. Use of resins with the larger alkyl groups increases the retention time ratio of  $\text{I}^-:\text{Cl}^-$  by two to four times the ratio with a conventional anion exchanger [2]. By increasing the ionic concentration of the mobile phase, the large chloride peak will pass through the column more quickly and the iodide peak will appear in a reasonably short time.

### 4. IDA chelating resins

In many instances a chelating resin or chelating reagent will be needed to provide the necessary selectivity for concentrating the analyte ions. For example, resins containing an IDA functional group are often used. The IDA chelates a considerable number of metal cations and provides good selectivity over metal ions that are not complexed. However, some problems can still occur.

A high concentration of IDA groups on the chelating resin results in more complete complexation of metal ions from solution. A high concentration of complexing groups may also cause the resin to retain metal ions from a more acidic sample. However, stronger complexation of metal ions means that a more concentrated acid solution must be used to break up the complex and thereby desorb metal ions from the resin. The presence of excess acid may complicate the determination of sample ions by ion-chromatography or capillary electrophoresis.

An additional complication is that two kinds of metal ion uptake can occur with IDA resins. The desired kind of uptake involves chelation of metal ions with the nitrogen and carboxyl groups of the IDA as ligands. The other type is simple ion exchange of cations that are electrostatically attracted to the negatively charged carboxylate groups. This

simple ion exchange can take up a significant amount of  $\text{Na}^+$  or other unwanted cations, particularly if the resin contains a high concentration of IDA groups.

On balance, the best choice of an IDA resin might be one with a moderately low capacity (ca. 0.5 meq/g, for example) for retaining metal ions by chelation. A resin particle size of ca. 10  $\mu\text{m}$ , instead of the 40–50  $\mu\text{m}$  size generally used in solid-phase extraction (SPE) cartridges, permits effective concentration of metal ions with a resin bed of only a few millimeters.

## 5. DTC chelating resins

A resin with a dithiocarbamate (DTC) functional group is more selective than IDA resins.

Resins can be prepared by reacting a chloromethylated polystyrene–divinylbenzene resin with a primary amine and then with carbon disulfide to give: resin- $\text{CH}_2\text{-NR-C=S(S}^-)$ . This resin should complex the following metal ions:  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mo(VI)}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{VO}^{2+}$ , and  $\text{Zn}^{2+}$  and perhaps others. Such resins have essentially no affinity for metal ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ . Additional selectivity is possible by control of pH and use of certain masking reagents.

Of the two resins described in the experimental section, the resin prepared from the chloromethylstyrene–divinylbenzene co-polymer failed to complex metal ions such as copper(II). However, the resin that was chloromethylated after polymerization formed a dark yellow-brown complex with copper(II) and had a copper(II) capacity of ca. 0.2 mmol/g. It is believed that the chloromethyl groups in this resin are mostly close to the surface and therefore are readily available for reaction.

A mini-column packed with a bed of DTC resin approximately 4 mm in length retained  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc. in a very compact colored band near the top of the resin bed. These bands were formed using 1–2 ml of 100 ppm metal solutions at pH 4. No breakthrough of these metal ions was observed. The problem was in finding a method for rapid and complete removal of the metal ions which form very

stable complexes with DTC. Hydrochloric acid, 1–2 *M*, either in water or in an organic solvent failed to break up the metal ion complexes completely. However, warm (70–80°C) 8 *M* nitric acid did elute copper quantitatively provided it was allowed to stand in contact with the resin for 1–2 min before being eluted from the column. The acidic and oxidative properties of the nitric acid combine to destroy the complex and leave free, uncomplexed metal ions in solution for analysis by capillary electrophoresis, ion chromatography, or other means. A solution of dilute bromine in 90–100% acetic acid was also found to be effective for eluting complexed metal ions from the resin. These acids destroyed the functionality of the resin and therefore, its chelating properties. Evaporation and/or dilution were used to lower the acid concentration in the samples before analyses were performed.

## 6. Complexation in solution and solid-phase extraction

Another way to use the excellent selectivity of DTC complexes for metal ion preconcentration is to add a soluble DTC reagent to the aqueous sample. The metal ion complexes are then collected on a SPE resin column. Salts of diethyldithiocarbamate or pyrrolidinedithiocarbamate have been used extensively for complexation of metal ions, but their metal complexes tend to be sparingly soluble in water. King and Fritz [8] concentrated metal ions by complexation with sodium bis(2-hydroxyethyl)dithiocarbamate (NaHEDC) and sorption on a Rohm and Haas XAD-4 resin column. This DTC reagent forms complexes with good water solubility by virtue of the two hydroxyl groups in the molecule. However, the metal complexes which generally have a DTC:metal ion ratio of 2:1 are sufficiently bulky and organic in nature to be extracted well by the resin. After the SPE step, metal ion complexes are easily eluted by a small volume of a dilute solution of nitric acid in ethanol.

We have been able to make significant improvements over the earlier technique. King and Fritz [8] used ground-up sieved resins of 74–105  $\mu\text{m}$  particle size. These were packed in a 175×9 mm glass column. We now use a 5 mm I.D. mini-column

packed with 10- $\mu$ m polystyrene–divinylbenzene resin to a height of only 3 mm. These columns are constructed as previously detailed in the experimental section. Such a column requires a compressed-air pressure of ca. 30 p.s.i. ( $2.1 \cdot 10^5$  Pa) to pass the sample through at a flow-rate of 1–2 ml/min. A 10-ml sample volume containing 0.3 ppm of the metal at pH 4 was passed through the column. Subsequent desorption of the metal complexes was readily obtained by 1 ml of 1 M nitric acid in ethanol.

Solid NaHEDC requires rather careful preparation, purification, and storage to prevent oxidation. In the current work, these problems have been virtually eliminated by preparing the reagent in solution by a procedure similar to that originally proposed by Fritz and Sutton [9].

Diethanolamine (1.0 ml) and carbon disulfide (30  $\mu$ l) are added to 5–10 ml of methanol. The container is stoppered and allowed to stand for a few minutes to allow the reaction to be completed. The solution is then diluted to 25 ml with methanol. This solution shows almost no change in DTC concentration for at least 16 days and remains clear and usable for at least 2 months.

Contamination of complexing reagents by metal ions is often a problem. Most organic chemicals and solvents contain significant amounts of various inorganic impurities. Metal ions that may be adsorbed on the container walls may enter the solution by the complexing action of the reagent. The reagent blank can be reduced to very low levels simply by passing the DTC solution through a resin column to remove the complexed impurities. Typical values of the reagent blank (ng/ml) are: Cd(II) < 0.02; Cu(II), 0.6; Fe(III), 1.0; Hg < 0.02; Pb(II) < 0.2; Zn, 0.6 [8].

## 7. Conditions for metal ion preconcentration

The theoretical combining ratio of the HEDC reagent to a divalent metal ion is 2:1. Studies have shown that at least a 50% excess of reagent is needed for complete complexation and sorption of the metal ions. The reagent is known to decompose rapidly in acidic solution [10]. However, metal ions complex rapidly with HEDC and the complexes are much more stable towards acid. Nevertheless, in acidic

solutions it is best to use an excess of reagent and to perform the SPE step without undue delay.

Even at or near neutral pH values, solutions of metal–DTC complexes that are allowed to stand for some time often become turbid from oxidation of DTC by dissolved oxygen. This can be prevented by addition of 2.0 g/l of sodium sulfite to the test solution [8].

It is necessary to buffer the sample solution within a certain pH range in order to obtain quantitative adsorption and recovery. Use of an acidic pH will cause a smaller group of metal ions to be complexed and retained on the SPE column. The pH values at which 95–100% recovery of metal ions can be obtained are given in Table 1 [8].

In addition to pH control, selectivity can be increased through the use of an auxiliary complexing reagent as a “masking agent”. For example, bismuth(III), copper(II), mercury(II), and silver(I) are quantitatively adsorbed by a resin column from solutions of pH 5–9 containing HEDC plus 0.01 M EDTA. At pH 9, cadmium(II), cobalt(II), iron(III), nickel(II), lead(II), and zinc(II) are completely complexed by EDTA, giving 0% recovery by SPE. At pH 9.0, 0.01 M cyanide masks cobalt(II), copper(II), nickel(II) and zinc(II) while allowing 100% recovery of bismuth(III), cadmium(II) and lead(II) [11].

The ability of the HEDC solid-phase extraction method to isolate trace elements from high concentrations of sodium, calcium, and magnesium is

Table 1  
pH range for 95–100% recovery of metal ions

| Ion            | pH range |
|----------------|----------|
| Bismuth(III)   | 1–10     |
| Cobalt(II)     | 1–10     |
| Copper(II)     | 1–10     |
| Lead(II)       | 1–10     |
| Mercury(II)    | 1–10     |
| Thallium(I)    | 1–10     |
| Tin(II)        | 1–10     |
| Silver(I)      | 3–10     |
| Cadmium(II)    | 4–10     |
| Nickel(II)     | 4–10     |
| Zinc(II)       | 5–10     |
| Iron(III)      | 5– 8     |
| Molybdenum(VI) | 1– 4     |
| Vanadium(V)    | 1– 7     |
| Uranium(VI)    | 6– 7     |

illustrated by the analysis of sea water [11]. Sea water was spiked with each of eight metal ions in concentrations ranging from 2 to 60  $\mu\text{g/l}$ : Cd(II), Co(II), Cu(II), Fe(III), Hg(II), Ni(II), Pb(II), and Zn(II). Recoveries ranged from 97% to 105%, with an average standard deviation of  $\pm 5\%$ .

Plantz et al. [11] used another water-soluble DTC reagent, bis(carboxymethyl)dithiocarbamate, to complex and concentrate trace metal ions from samples of high salt content. This reagent is easily prepared by reacting iminodiacetic acid with carbon disulfide in ethanol containing some ammonium hydroxide. Metal ions having an affinity for sulfur form complexes preferentially with the dithiocarbamate part of the molecules; for example:  $\text{Cu}[\text{SSCN}(\text{CH}_2\text{CO}_2\text{H})_2]_2$ .

At a pH of 3.5 (formate buffer) metal ion complexes have no apparent charge and are retained on a polystyrene–divinylbenzene solid-phase extraction column. Elution with an aqueous buffer containing ammonium hydroxide desorbs the metal complexes from the column rapidly and quantitatively. The basic eluent ionizes the carboxyl groups, causing the metal complex to be eluted from the resin. In the results reported, complexes of V, Cr, Ni, Co, Cu, Mo, Pt, Hg and Bi were concentrated effectively from seawater and urine [11].

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