

THE PRECONCENTRATION AND DETERMINATION OF Pb^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} and Zn^{2+} ELEMENTS IN WATER SAMPLES USING CITRATE FORM OF ANION-EXCHANGE RESIN

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(Received: Jan. 25th 1993 , Accepted: Jan. 23rd 1995)

ABSTRACT : *Lead, copper, cobalt, nickel, iron and zinc ions form monocationic complexes (negative charge) in citrate solution which is absorbed on the citrate form of anion- exchange resins (citrate as counter ion) by exchange of citrate ion with citrate complexes. These are subsequently recovered from the resin by 0.5M ammonium citrate eluent at pH 2.0. Under optimised conditions, quantitative recovery was achieved simultaneously for lead, cobalt, copper, nickel, iron and zinc (preconcentration factor 20). Each element could be determined by atomic absorption spectroscopy (AAS) with high precision.*

KEY WORDS : *Preconcentration, Anion- exchange, Citrate, Element in water sample.*

INTRODUCTION

Environmental pollution from toxic elements in aquatic systems are of concern to all researchers. Manganese, cobalt, iron, copper, nickel, zinc, cadmium mercury and lead ions present in natural waters and sea water are

approximately at ($\mu g/L$)[1], which usually are not detectable by major instrumental analyses, and during trace elemental analyses interference effects give rise to incorrect analytical results. Therefore, in order to obtain high sensitivity in

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1021-9986/95/1/10 6 / \$ / 2.60

trace elemental analyses, it is necessary to increase the concentration of trace elements in the sample and simultaneously reduce the interferences.

Several different techniques have been used for preconcentration of trace elements in fresh and industrial waters, including solvent extraction [1-4] and ion-exchange [5-7]. Ion-exchange method is simple and could be applied to large volumes of sample solution (liters), hence it is suitable for preconcentration of trace elements in water samples. Recently, ion-exchange resins containing chelate groups are used for separation and preconcentration at trace elemental analyses. This type of resins have greater selectivity compared with the conventional type of ion-exchange resins [8-10]. They could be divided in two major groups. First those in which the chelating groups were fixed on the surface of the resin and form complex with elements. *Chelex-100* (copolymer styrene divinyl benzene with iminodiacetic acid as active group) is one of the well used in trace element analyses. Selectivity of *Chelex-100* for cations such as copper, zinc, cadmium, nickel, lead, calcium and iron are much higher than for sodium, potassium and magnesium. Therefore it has been used for preconcentration of these elements in sea water samples.

The second group consists of resins that contain chelating groups like citrate and EDTA as their counter-ion [11-12], and are successfully used for separation and preconcentration. In these resins, elemental form ions complex with chelating group and are exchanged with the chelating counter-ion. Anion-exchange resin containing citrate ion are used for separation and preconcentration of calcium and magnesium in water samples [12]. Since citrate ion forms stable complexes with most of transition elements (Table 1), the use of anion-exchange resins with citrate ions as counter-ion was investigated for several cations. Under optimized conditions, quantitative recovery was found for preconcentration of lead, copper, nickel, cobalt, iron and zinc ions by absorbing

the citrate form of these elements on an anion-exchange column and eluting it with ammonium citrate solution.

Table 1: Uptake and recovery of various elements by citrate form resin.

| Ions | Uptake (%) | Recovery (%) | Log(K ₁)(II) [13] |
|------------------|------------|--------------|-------------------------------|
| Pb ²⁺ | 100±2 | 100±2 | 6.50 |
| Cu ²⁺ | 100±2 | 96±1 | 14.21 |
| Ni ²⁺ | 100±2 | 100±2 | 5.11 |
| Co ²⁺ | 100±1 | 98±2 | — |
| Zn ²⁺ | 96±2 | 100±1 | — |
| Fe ²⁺ | 98±1 | 100±3 | 3.08 |

EXPERIMENTAL

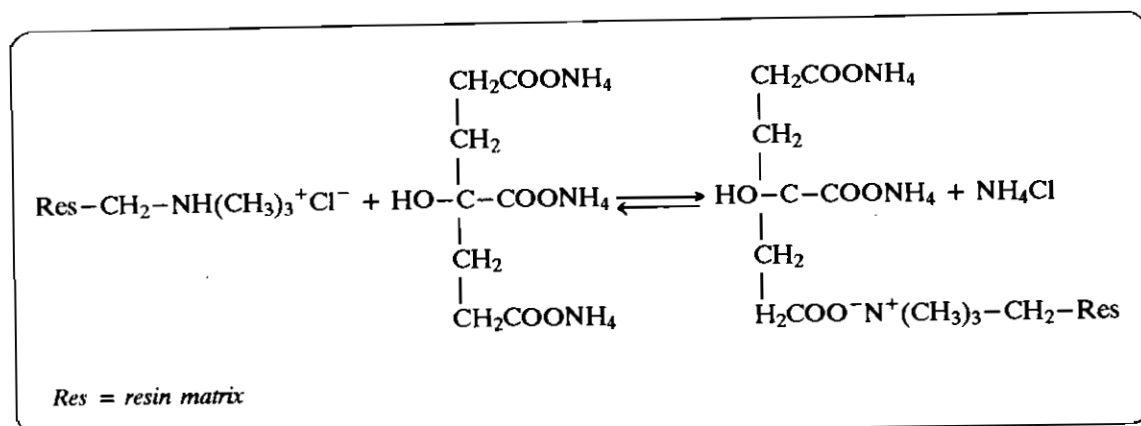
Reagents and instruments :

All reagents were of analytical reagent grade. Glassware were soaked for 24 hours in 10% (V/V) nitric acid, rinsed with distilled water and dried. Stock solution (1000mg/L) Co²⁺, Fe²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ were prepared from iron sulfate and nitrate salts of cobalt, nickel, lead, copper and zinc. Ammonium citrate solution (0.5M) was prepared by mixing of citric acid (1M) and ammonia solution (1M) in ratio of (1:3).

Determination of each elements was performed with a *Shimadzu* atomic absorption spectrometer (AAS), model 670 (air-acetylene flame).

Preparation of citrate form resin :

Chloride form *Dowex 1*, 100-300mesh (polystyrene divinyl benzene quaternary amine resin) was used for preparation of citrate form of the resin. The resin was washed with distilled water before being packed in a 20mL buret. Ammonium citrate solution (0.5M) was passed through the buret until the eluted solution gave negative result with silver nitrate solution (Scheme 1). The resin was then washed with 100mL of distilled water to remove excess ammonium citrate. This citrate form of resin was used in all subsequent experiments.



(Scheme 1)

RESULTS AND DISCUSSION

Absorption of lead citrate on citrate form resin :

A lead citrate solution (100mL, 1 μ g/mL at pH 7.0) was passed through the column (1cm \times 40cm) containing 2cm³ citrate form resin at a flow rate 0.5mL/min and the eluted solution was analyzed for its lead content by AAS. This was repeated five times and approximately 100% absorption was found for lead citrate on the resin.

In order to study the effect of resin quantity on absorption of the lead citrate, similar experiment was performed by passing lead citrate solutions through a series of columns (1cm \times 40cm) containing various volume of the resin (1,2,3,4 and 5cm³). The results are shown in a Fig.1. The absorption of lead citrate increases with the increase in resin volume up to 2cm³ and after that it remains constant.

The effect of flow rate on lead citrate absorption :

In order to test the effect of flow rate, a lead citrate solution (100mL, 1 μ g/mL at pH 7.0) was passed at various flow rate (0.5-2mL/min) through identical columns containing 2cm³ resin and the emerged solution was analyzed by AAS. The results are presented in Fig.1. Maximum absorption was found over the range of 0.5-1.5mL/min.

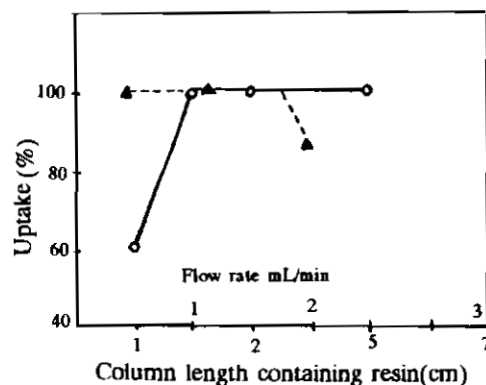


Fig.1: Percentage of lead citrate uptake from solution as a function of: (○) amounts of resin, and (▲) flow rate.

The effect of column diameter on lead citrate absorption was investigated by passing lead citrate solution (100mL, 1 μ g/mL at pH 7.0) through a series of columns with different diameters (0.3, 0.5, 1cm) containing same amount of resin (2cm³). For all columns the uptake of lead citrate was the same and hence, in the rest of experiments a column with 1cm inner diameter was used.

Recovery of absorbed lead citrate from resin:

Lead forms a monocitrate complex (negatively charge) in citrate solution and hence could be absorbed by citrate form of anion-exchange resin and then recovered from resin by exchange of lead citrate by ammonium citrate. To study the effect of factors influencing the elution

power of ammonium citrate, 100mL of lead solution (10g/mL) was passed through a column (1cm × 40cm) containing 3cm³ of citrate form resin. The column was washed by distilled water and then eluted with ammonium citrate solution, the eluate was analyzed by AAS. Results are shown in Fig. 2. It is seen that with the increase in ammonium citrate concentration up to 0.5M, recovery of lead citrate increased, there after it decreased.

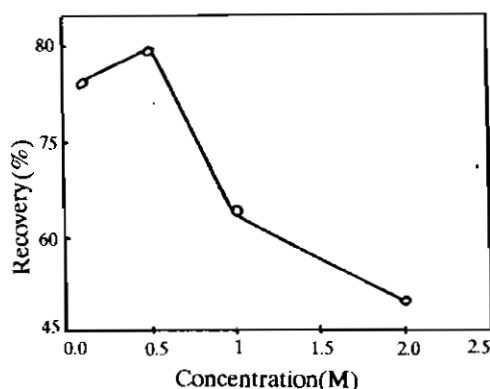


Fig. 2: Recovery of lead citrate as function of ammonium citrate concentration.

Similar experiments were carried out with 0.5M ammonium citrate solution (3:1) at various pH (2-8). Maximum recovery was found in the pH range of 2-3 (Fig.3). The effect of column diameter on lead citrate recovery also was studied (Fig.4), for columns with inner diameters between 0.2 to 0.5cm. As can be seen the amount of ammonium citrate used was less than

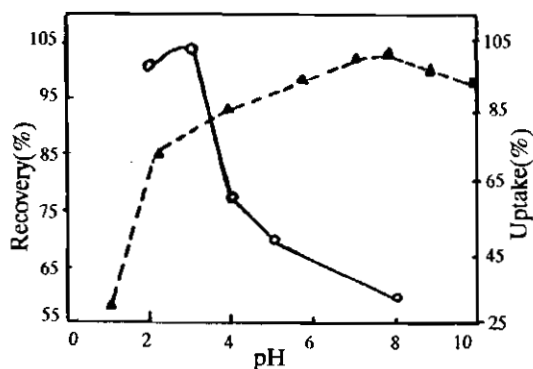


Fig. 3: (○) Recovery of lead as function of pH of ammonium citrate solution (0.5M); (▲) uptake of lead as function of tap water pH.

in the previous case with the same recovery.

Optimized conditions, for absorption of lead acetate was: column diameter 1cm, volume of resin 2- 5cm³ and for lead citrate from resin: ammonium citrate solution (0.5M, pH 2-3) with flow rate of 1-5mL/min respectively.

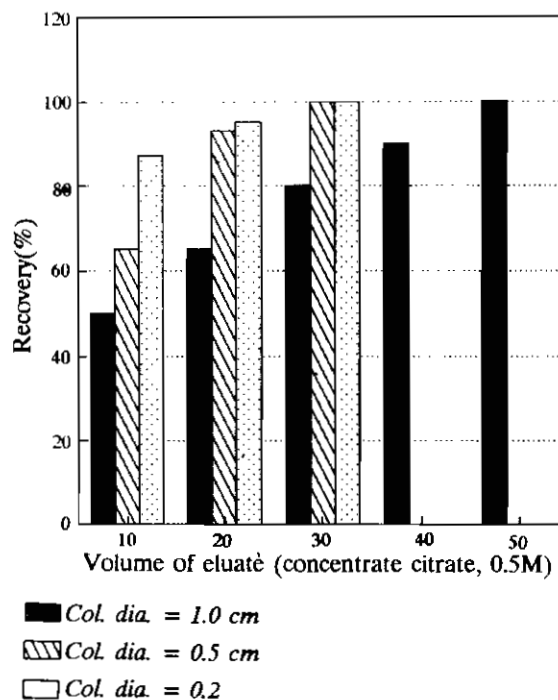


Fig. 4: Effect of column diameter and eluant volume (cm³) on recovery of lead from resin.

Recovery of absorbed citrate complexes of copper, cobalt nickel, iron and zinc from citrate form anion- exchange resin :

Other elements have tendency to give complexes with citrate anion (Table 1). Optimised conditions were used to study absorption and recovery of 100mL solution containing 1g/mL of copper, cobalt, nickel, iron and zinc citrates. Results obtained are presented on Table 1. Citrate complexes of these elements were quantitatively up taken by the resin and recovered by ammonium citrate solution (0.5M, pH 2-3).

Preconcentration of trace amounts of lead, copper, cobalt, iron, nickel and zinc from distilled and tap water :

Optimised conditions were used to study

preconcentration of 1 liter (distilled and tap water) solution containing 100 μ g of lead, copper, cobalt, iron, nickel, zinc and 5mmoles of citrate ion. Experiment was repeated for distilled water and tap water as blank. In distilled water, quantitative recovery was found for all cations with a preconcentration factor of 20 (Table 1 and 2), but in tap water 100% absorption was found for all cations except lead (60% absorption) which could be due to presents of sodium ion in tap water (Table 3). Interference effect of sodium ion, Table 4 shows that with the increase in sodium ion (sodium chloride) concentration, the lead uptake by resin is decreased. To overcome the interference due to sodium ion, the effect of pH of the tap water on uptake of lead citrate by resin was studied (Fig. 3). Interference could be overcome at pH 5-6. Therefore pH of the tap water was adjusted to 6 before preconcentration and recoveries of 99 \pm 1, 96 \pm 1, 97 \pm 1, 103 \pm 2, 98 \pm 2 and 96 \pm 1 were found for cobalt, nickel, copper zinc, lead and iron(II) respectively. Other elements (Table 3) present in tap water do not interfere.

Table 2: Uptake and recovery of various elements in tap water by citrate form resin.

| Element as citrate form | Uptake (%) | Recovery (%) |
|-------------------------|-------------|--------------|
| Pb | 60 \pm 1 | 100 \pm 1 |
| Cu | 99 \pm 2 | 96 \pm 1 |
| Ni | 98 \pm 1 | 100 \pm 1 |
| Co | 98 \pm 1 | 98 \pm 2 |
| Zn | 96 \pm 1 | 100 \pm 1 |
| Fe(II) | 100 \pm 1 | 100 \pm 1 |

CONCLUSIONS

By converting anion- exchange resin to citrate form, it is possible to preconcentrate (by a factor of 20) six elements (Pb, Cu, Fe, Co, Ni and Zn) present in tap water. Results show that only sodium ion interferes with the absorption of lead on resin, and this may be overcome by adjusting the pH of water to 6.5-7. This method

is simple and could be used for simultaneous preconcentration of the six elements. Ammonium citrate was used as eluant. Column may be regenerated and made ready to use for the next sample. This procedure was used for preconcentration of trace elements in 5 sample solutions without any decrease in column efficiency.

Table 3: Concentration of elements in sea and fresh waters [1].

| Element | Sea water (μ g/L) | Fresh water (μ g/L) |
|---------|-------------------------------|--------------------------|
| Na | 1.08 \times 10 ⁷ | 6300 |
| Mg | 1.29 \times 10 ⁶ | 4100 |
| K | 3.92 \times 10 ⁵ | 2300 |
| Ca | 4.11 \times 10 ⁵ | 1500 |
| Cr | 0.2 | 1 |
| Mn | 1.9 | 7 |
| Fe | 3.4 | 670 |
| Co | 0.05 | 0.1 |
| Ni | 2 | 0.3 |
| Cu | 2 | 7 |
| Zn | 2 | 20 |
| Pb | 0.02 | 3 |
| Cd | 0.11 | - |

Table 4: Sodium chloride interference on absorption of lead by citrate form resin.

| Concentration of NaCl in lead citrate solution(M) | Absorption (%) |
|---------------------------------------------------|----------------|
| 0 | 100 \pm 2 |
| 0.1 | 93 \pm 2 |
| 0.5 | 96 \pm 1 |
| 1 | 82 \pm 3 |
| 2 | 70 \pm 2 |

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