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Ion chromatographic separation of transition metals on a polybutadiene maleic acid-coated stationary phase

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Abstract

Transition metals are traditionally analyzed by cation-exchange or ion-pair chromatography. Divalent metal ions are separated on sulfonic acid cation stationary phase using various eluents along with conductivity detection. An alternative method is reversed-phase ion-pair chromatography coupled with conductivity detection. This method of detection is not very sensitive for transition metals. For better separation and sensitivity, UV–Vis detection along with pre- or post-column derivatization with an absorbing ligand is the most common method applied. This method is messy and complicated.

This paper describes the separation of transition metals on a polybutadiene maleic acid stationary phase. This cation-exchange stationary phase has been successfully applied for the simultaneous separation of mono- and divalent cations. Several cations including group I and group II cations along with transition metals can be analyzed using complexing acid eluents. Detection limits and the effect of different eluent concentrations are discussed.

1. Introduction

Traditional ion chromatography techniques for the determination of transition metals are based on ion-pair chromatography, cation-exchange chromatography or coordination chromatography. Reversed-phase ion interaction chromatography or ion-pair chromatography is the most common method used for the determination of transition metals [1]. The transition metals are separated on a reversed-phase stationary phase using an eluent containing an ion-pairing reagent and detected by conductivity or post-column derivatization and UV–Vis detection. Conductivity detection provides detection sensitivity for transition metals in the ppm (mg/l) range. Post-column derivatization along with UV–Vis detection is free of interferences and is more sensitive. A light-absorbing chelating reagent such as pyridilazoresorcinol (PAR) is used to complex the metal ions which are then detected at 520 nm. However this method requires messy reagents and complicated instrumentation.

Cation-exchange chromatography along with conductivity detection is another method used for the determination of transition metals. Divalent metal ions including heavy metal ions are separated on conventional sulfonic acid columns and detected by conductivity detection. For effective elution of divalent metal ions, an eluent containing a divalent cation is required. For example an eluent containing ethylenediammonium tartrate is used to separate several divalent metal ions on the conventional sulfonic acid columns [2]. Usage of such a complexing eluent along with the addition of a complexing reagent to the sample has also been reported [2]. For example, ethylenediamine tetraacetic acid

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(EDTA) and nitrotriacetic acid (NTA) are added to the sample to improve the separation [2]. Cation exchange separation along with post-column UV detection is another common method used to determine transition metals [3]. Even though this method improves the sensitivity of metal ions as mentioned earlier, requirement of stringent instrumentation and messy post column reagents makes it less desirable.

A convenient and frequently used method for the determination of metal ions is by coordination chromatography. Metal ions are separated on a stationary phase made of resin or silica material in which a suitable ligand is immobilized. One of the most common chelating stationary phase is a silica-based imminodiacetic acid (IDA) stationary phase, which exhibits different complexing abilities towards different transition metals [4]. A weak carboxylic acid is the functional group on this stationary phase. The retention of cations are controlled by the concentration of the complexing agent and the pH of the eluent. Weak complexing acids such as citric acid, tartaric acid or strong complexing acids such as pyridine-2,6-dicarboxylic acid or nitrilotriacetic acid are used for the separation.

This paper describes the application of an alternative stationary phase made of polybutadiene maleic acid (PBDMA) coated on silica material for the determination of transition metals. The column has been successfully used for the simultaneous separation of mono and divalent cations. This report focuses on the separation of several transition metal ions on this stationary phase using a mixture of two different complexing acids. By changing the eluent concentrations, different metal ions can be separated along with mono and divalent cations.

2. Experimental

The Alltech modular ion chromatography system (Alltech Associates, Deerfield, IL, USA) which includes Model 325 HPLC pump, Model 320 conductivity detector, Model 330 column heater and Model 9125 injection valve was used for all applications. The temperature of the column and the detector cell were maintained at 35°C. All data were recorded by a Model SP 4400 chromjet integrator (Spectra-Physics, Santa Clara, CA, USA). A column packed with PBDMA coated on silica material (Alltech Universal Cation Column, 100 mm × 4.6 mm) was used for the separation of metal ions.

All eluents and standards were prepared from reagent grade chemicals (Aldrich, Milwaukee, WI, USA) and deionized (18 MΩ) water. Stock solutions of 100 m*M* tartaric and oxalic acids were prepared and these solutions were diluted to prepare mixtures of tartaric and oxalic acid eluents.

2.1. Sample preparation

The fermentation broth and cooling tower water samples were diluted with deionized water before injection. To prepare the plant material for ion chromatographic analysis, 1 g of bean leaves was ashed at 600°C for 6 h and 0.1 g of this sample was dissolved in 100 ml of deionized water containing 0.2 ml of 12 *M* hydrochloric acid. This sample was then diluted five times and injected on the ion chromatograph. The brass ferrule was dissolved in concentrated nitric acid and 0.5 ml of this sample was diluted in 50 ml of deionized water before injection.

3. Results and discussion

Separation of mono- and divalent cations on the PBDMA stationary phase using various eluents and electrical conductivity detection has been reported by several authors. Some of these eluents are organic complexing acids such as citric acid, tartaric acid, phthalic acid, salicyclic acid and pyridine- 2,6-dicarboxylic acid and mineral acid eluents such as hydrochloric acid [5]. Mineral acid eluents are not suitable for transition metal analysis because many transition metals do not form complexes with chloride or nitrate and will not be eluted from the stationary phase. Organic acid eluents such as citric, tartaric or phthalic acid eluents can separate a few

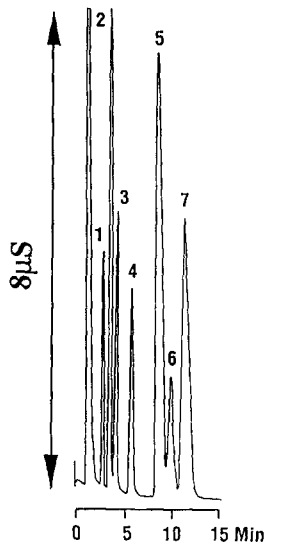

Fig. 1. Citric acid eluent on PBDMA stationary phase. Peaks: 1 = lithium (0.2 mg/l); 2 = sodium (1.5 mg/l); 3 = ammonium (1.5 mg/l); 4 = potassium (2.5 mg/l); 5 = magnesium (2 mg/l); 6 = iron(II) (5 mg/l); 7 = calcium (2 mg/l). Column: Universal Cation (100 mm × 4.6 mm); eluent: 7 m*M* citric acid; flow-rate: 1 ml/min; detector: conductivity; injection volume: 100 µl.

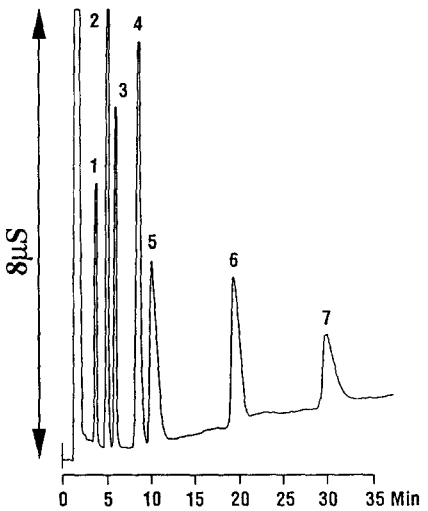

Fig. 2. Oxalic acid eluent on PBDMA stationary phase. Peaks: 1 = lithium (0.2 ppm); 2 = sodium (1.5 mg/l); 3 = ammonium (1.5 mg/l); 4 = zinc, nickel, cobalt; 5 = potassium (2.5 mg/l); 6 = magnesium (2 mg/l); 7 = calcium (2 mg/l). Column: Universal Cation (100 mm × 4.6 mm); eluent: 2 m*M* oxalic acid; flow-rate: 1 ml/min; detector: conductivity; injection volume: 100 µl.

transition metals on the PBDMA stationary phase.

Fig. 1 shows the separation of iron(II) on the PBDMA stationary phase using 7 m*M* citric acid. With this eluent, iron(II) is eluted between magnesium and calcium. If other transition metals such as zinc, manganese, cobalt or nickel were present in the sample they all will be eluted at the same retention time as iron(II). The same results were obtained with tartaric, phthalic or salicyclic acid eluents. These organic acids exhibit similar properties hence changing the eluents from citric to tartaric, phthalic or salicylic acids did not affect the retention time of the metal ions [6].

Oxalic acid was also investigated as an eluent for the separation of transition metals on the PBDMA stationary phase. Fig. 2 shows the separation of transition metals along with mono-/divalent cations using oxalic acid eluent on the PBDMA stationary phase. Under these conditions the transition metals eluted before the divalent cations and some are co-eluting with the monovalent cations. The metal complexes of oxalic acid are more stable than those of divalent cations and hence they elute first [7]. Another drawback with this eluent is that the retention time of divalent cations is too long.

A mixture of tartaric and oxalic acids was investigated as a possible eluent for the separation. Fig. 3a shows the separation of transition metals on the PBDMA stationary phase using a combination of 2 m*M* tartaric acid and 1 m*M* oxalic acid. Fig. 3b shows the separation of mono- and divalent cations using the same conditions. If the above sample had manganese or cadmium they will co-elute with magnesium and calcium, respectively. However, the separation of lithium, sodium, ammonium, potassium, nickel, zinc, cobalt, magnesium and calcium is very good.

To solve the co-elution problem of manganese and cadmium with divalent cations a different type of eluent was developed. By adding pyridine-2,6-dicarboxylic acid (PDCA) to tartaric acid, a change in selectivity for the divalent cations was found as shown in Fig. 4. Under

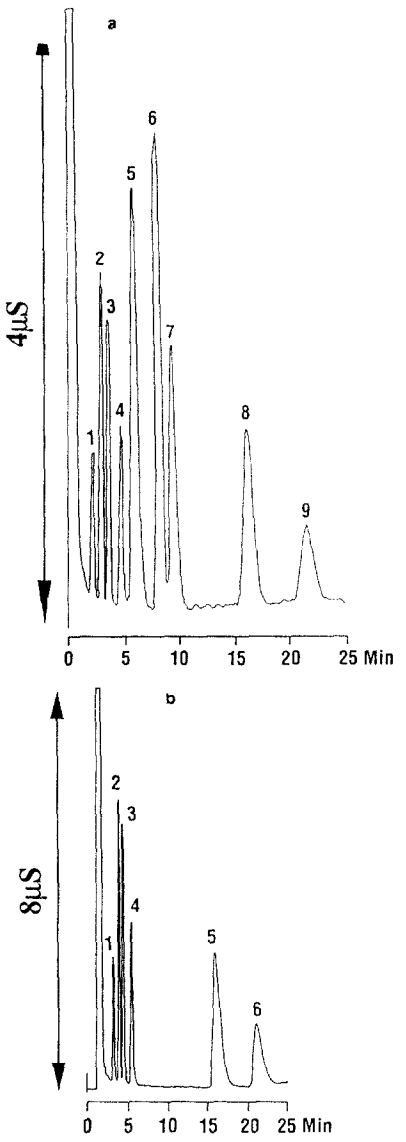

Fig. 3. (a) Separation of transition metals using a mixture of tartaric and oxalic acid eluent. Peaks: 1 = lithium (0.1 ppm); 2 = sodium (0.75 mg/l); 3 = ammonium (0.75 mg/l); 4 = potassium (1.3 mg/l); 5 = nickel (5 mg/l); 6 = zinc (5 mg/l); 7 = cobalt (5 ppm); 8 = manganese (5 mg/l); 9 = cadmium (5 mg/l). Column: Universal Cation (100 mm × 4.6 mm); eluent: 2 m*M* tartaric acid–1 m*M* oxalic acid; flow-rate: 1 ml/min; detector: conductivity; injection volume: 100 μl. (b) Mono- and divalent cation analysis using a mixture of tartaric and oxalic acid eluent. Peaks: 1 = lithium (0.2 ppm); 2 = sodium (1.5 mg/l); 3 = ammonium (1.5 mg/l); 4 = potassium (2.5 mg/l); 5 = magnesium (2 ppm); 6 = calcium (2 ppm). Column: Universal Cation (100 mm × 4.6 mm); eluent: 2 m*M* tartaric acid–1 m*M* oxalic acid; flow-rate: 1 ml/min; detector: conductivity; injection volume: 100 μl.

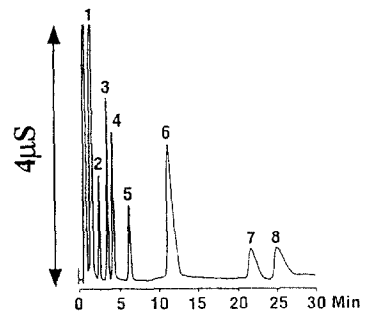

Fig. 4. Separation of cadmium and manganese on PBDMA stationary phase peaks: 1 = cadmium (10 mg/l); 2 = lithium (0.2 ppm); 3 = sodium (1.5 mg/l); 4 = ammonium (1.5 mg/l); 5 = potassium (2.5 mg/l); 6 = manganese (10 mg/l); 7 = calcium (2 mg/l); 8 = magnesium (2 ppm). Column: Universal Cation (100 mm × 4.6 mm); eluent: 3m*M* tartaric acid–0.5 m*M* PDCA; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 μl.

these conditions, calcium eluted before magnesium. This is due to the formation of strong complexes of Ca–PDCA which is much more stable than Mg–PDCA [8]. Magnesium and manganese can be separated by this eluent. The same eluent is useful for the separation of cadmium which elutes before lithium as shown in Fig. 4. If the sample contain other transition metals they may co-elute with cadmium.

By changing the concentrations of tartaric and oxalic acids different transition metals can be separated on the PBDMA column. For example, Fig. 5 shows the separation of copper, sodium, ammonium, potassium, zinc, cobalt, magnesium, calcium and lead with an eluent containing 1.5 m*M* tartaric and 1 m*M* oxalic acids. Under these conditions retention time for lead is excessive. A combination of 3 m*M* tartaric–2 m*M* oxalic acid eluent was found suitable for the determination of lead. Fig. 6 shows the separation of copper, sodium, ammonium, potassium, zinc, magnesium, calcium and lead. Under these conditions retention time for lead is reduced to 25 min.

The separation and retention of metal ions on the PBDMA stationary phase is greatly influenced by various eluent concentrations. The elution ability of the organic acids in the eluent dependent upon their dissociation and complex-

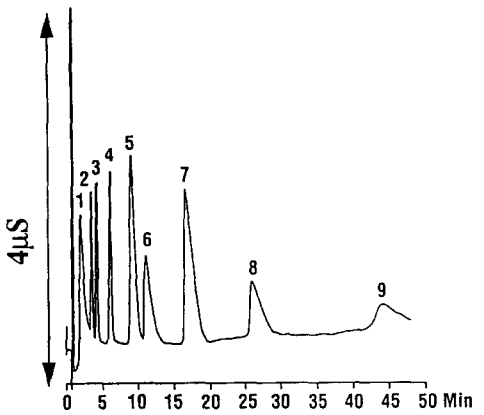

Fig. 5. Separation of transition metals using tartaric and oxalic acid eluent. Peaks: 1 = copper (10 mg/l); 2 = sodium (0.75 mg/l); 3 = ammonium (0.75 mg/l); 4 = potassium (1.3 mg/l); 5 = zinc (10 mg/l); 6 = cobalt (10 mg/l); 7 = magnesium (2 mg/l); 8 = calcium (2 mg/l); 9 = lead (10 mg/l). Column: Universal Cation (100 mm × 4.6 mm); eluent: 1.5 m*M* tartaric acid–1 m*M* oxalic acid; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 µl.

ing stability constants as well as the concentrations used. The eluent pH also affect the retention of metal ions on the PBDMA stationary phase. An increase in pH dramatically decreases the retention time for transition metals and other cations. When the eluent pH was increased from 2.4 (eluent pH unadjusted) to 3.4, all transition metal ions and other cations were co-eluted with each other. This may be due to the strong complex formation of metal ions at a higher pH which causes the metal ions to move rapidly through the column. For complete separation of metal ions, the eluent pH should be kept low so the complexation is only partial [8].

The detection limits (calculated as a signal-to-noise ratio of 3) obtained for transition metals using tartaric acid–oxalic acid eluent, based on a 100 µl injection are shown in Table 1. The detection limits vary from 45 to 410 µg/l. Even though post-column derivatization is more sensitive for the determination of transition metals, the simplicity of the methods described here are much more desirable. The plots of peak area *vs.* concentrations of zinc and cadmium gave linear calibration curves over two orders of magnitude. Correlation coefficients (*r*) for peak area response against ionic concentrations for zinc and cadmium ions were 0.999 and 0.998, respectively.

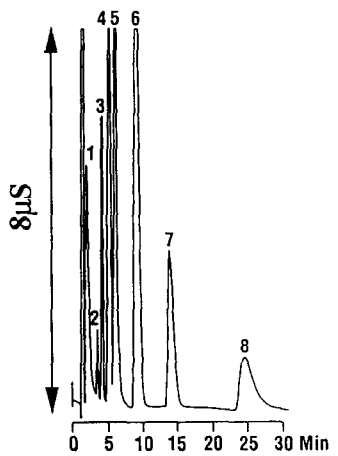

Fig. 6. Effect of higher eluent concentration on PBDMA column: Peaks: 1 = copper (10 mg/l); 2 = sodium (0.75 mg/l); 3 = ammonium (0.75 mg/l); 4 = potassium (1.3 mg/l); 5 = zinc (10 mg/l); 6 = magnesium (2 mg/l); 7 = calcium (2 mg/l); 8 = lead (10 mg/l). Column: Universal Cation (100 mm × 4.6 mm); eluent: 3 m*M* tartaric acid–2 m*M* oxalic acid; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 µl.

3.1. Applications

Many samples contain transition metals and mono-/divalent cations and by choosing optimum conditions, PBDMA stationary phase can

Table 1
Method detection limits for transition metals

Transition metals	Method detection limit[a] (mg/l)
Zinc	0.045
Cobalt	0.120
Manganese	0.040
Copper	0.150
Cadmium	0.035
Lead	0.410
Nickel	0.150
Iron(II)	0.060

[a] Injection volume 100 µl; calculated as 3 × signal-to-noise ratio.

separate these species simultaneously. Some examples of applications are given here. Fig. 7a shows the ion chromatographic separation of sodium, potassium, zinc, magnesium and calcium in cooling tower water. Separation of copper and zinc in brass ferrule is shown in Fig. 7b. Figs. 7c and d show chromatograms of plant extract and fermentation broth, respectively.

4. Conclusions

PBDMA stationary phase provides a simple ion chromatographic method for the separation of transition metals. By using a mixture of two complexing acids, tartaric and oxalic acids, various metal ions can be separated along with mono- and divalent cations. The method is

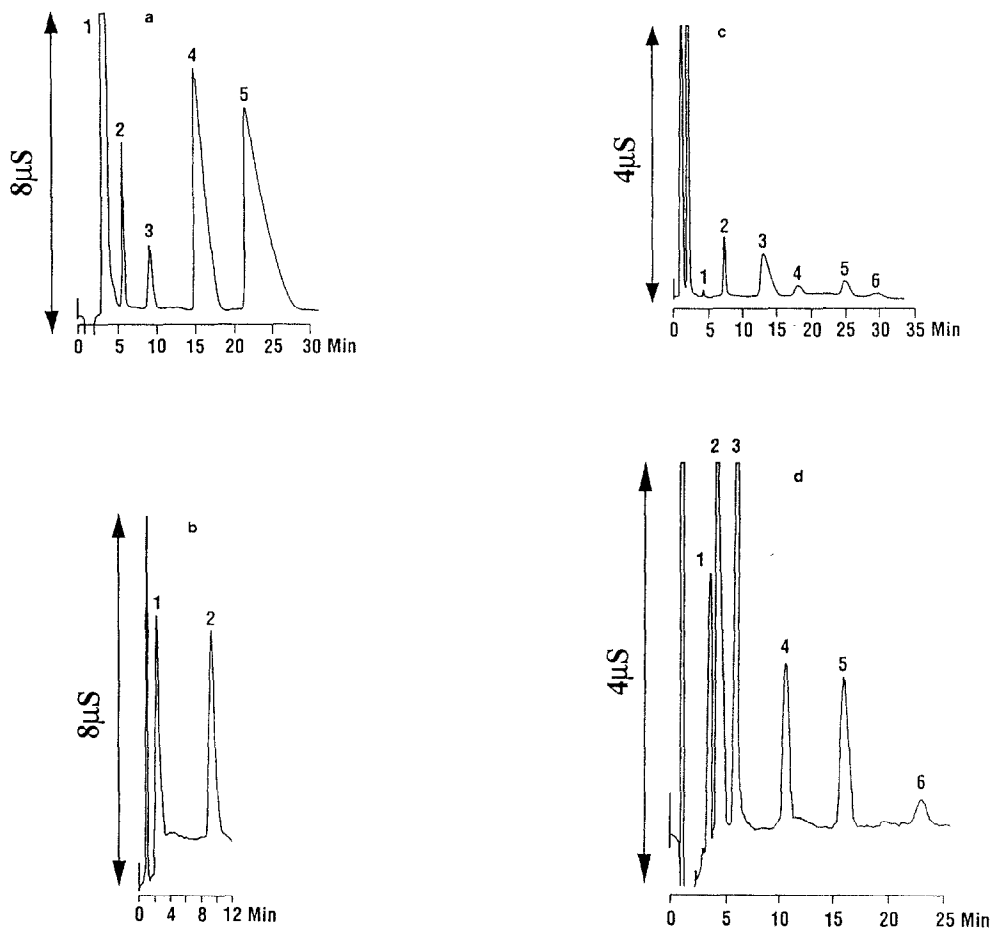

Fig. 7. (a) Cooling tower water. Peaks: 1 = sodium; 2 = potassium; 3 = zinc; 4 = magnesium; 5 = calcium. Column: Universal Cation (100 mm × 4.6 mm); eluent: 1.5 m*M* tartaric acid–1 m*M* oxalic acid; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 µl. (b) Brass ferrule. Peaks: 1 = copper; 2 = zinc. Column: Universal Cation (100 mm × 4.6 mm); eluent: 3 m*M* tartaric acid–2 m*M* oxalic acid; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 µl. (c) Manganese in soybean leaves. Peaks: 1 = sodium; 2 = potassium; 3 = manganese; 4 = unknown; 5 = calcium; 6 = magnesium. Column: Universal Cation (100 mm × 4.6 mm); eluent: 3 m*M* tartaric acid–0.5 m*M* PDCA; flow-rate: 1 ml/min; detector: conductivity; injection volume: 100 µl. (d) Fermentation broth. Peaks: 1 = sodium; 2 = ammonium; 3 = potassium; 4 = magnesium; 5 = calcium; 6 = lead. Column: Universal Cation (100 × mm × 4.6 mm); eluent: 3 m*M* tartaric acid–2 m*M* oxalic acid; flow-rate: 1.5 ml/min; detector: conductivity; injection volume: 100 µl.

simple and less complicated compared to many existing methods. The detection limits for transition metals are in the μg/l range. The ability of PBDMA stationary phase to separate transition metals from mono-/divalent cations is useful for routine analysis of many samples.

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