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EFFECT OF COMPLEXING AGENTS ON THE CHROMATOGRAPHIC SEPARATION OF POLYVALENT CATIONS

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SUMMARY

The selectivity of ion chromatography for determining chosen metal ions in mixtures can be improved by adding a complexing reagent to the sample and by using a weakly complexing eluent, such as ethylenediammonium tartrate. At pH 3.0, nitrilotriacetic acid masks a large excess of several metal ions while permitting the separation and determination of manganese(II), magnesium(II) and the alkaline earths. At pH 4.5, sulfosalicylic acid added to the sample permits the chromatographic determination of zinc(II) and several other metal ions. An ion chromatographic method is given for the selective determination of iron as iron(II) and for the speciation of iron(II) and iron(III) in mixtures.

INTRODUCTION

The speed and convenience of modern ion chromatography has created a renewed interest in the separation and analysis of metal ions by this technique. Spectrophotometry, after a post-column derivatization[1,2], and conductivity[3] are the leading detection principles used in the ion chromatography of metal cations. Sevenich and Fritz[4] extended the scope of ion chromatography with conductivity detection to a number of polyvalent metal ions. A complexing eluent, such as ethylenediammonium tartrate, was used to improve the selectivity and the quality of the separations. These authors also showed that addition of EDTA to the sample at a controlled pH would mask many metal ions and permit the chromatographic separation of ions such as magnesium(II), calcium(II) and strontium(II).

In the present work it is shown that addition of nitrilotriacetic acid (NTA) or sulfosalicylic acid (SSA) to a sample before injection into the ion chromatograph will selectively complex a number of metal cations while permitting the chromatographic separation of others. A new method is also described for the chromatographic determination of iron(II) in the presence of larger amounts of iron(III) and several other metal ions. Total dissolved iron can also be determined by reduction with ascorbic acid and measuring the iron(II) chromatographically.

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EXPERIMENTAL

Apparatus

The instrument used in this work was constructed in a modular fashion from individual components. The pump ws a Model 396 Milton Roy Singlex pump (Riviera Beach, FL, U.S.A.). The flow-rate for all work was 0.85 ml/min unless otherwise specified. The injector was a Rheodyne Model 7010 injector (Rainin, Woburn, MA, U.S.A.) with interchangeable sample loops (100, 50, and 20 μl). A pressure gauge (0–5000 p.s.i.g.) and coil-type pulse dampener (LiChroma Damp, Norristown, PA, U.S.A.) were placed off-line in a parallel configuration between the pump and injector. The detector was a Model 213 conductivity detector from Wescan (Santa Clara, CA, U.S.A.) with a 2-μl flow-through detector cell. All fittings in contact with the eluent were either glass, PTFE, Kel-F, or 316 stainless steel.

Chromatographic columns were constructed of thick-walled glass and measured 25 cm or 35 cm $\times$ 2 mm I.D. (Rainin). The ion-exchange resin was a surface-sulfonated poly(styrene-divinylbenzene) copolymer based gel-type resin having a bulk cation-cxchange capacity of 0.059 mequiv. per dry gram. The average bead size of the resin was 20 μm, with a range of particle sizes from about 5 to 30 μm. The cation-exchange material was obtained by special order from Benson (Reno, NV, U.S.A.).

The separator columns were packed by a stirred slurry, upward packing method. The resin was packed in an aqueous solution of ethylene glycol (45%, v/v) at about 2000 p.s.i.g. After packing, the column was rinsed by pumping distilled, deionized water through the column. Additional resin was added to the top of the column as necessary. At least 1 h of equilibration time with the eluent was allowed before use. The chromatographic column, detector electronics, flow cell, and eluent were all located in styrofoam lined enclosures to minimize temperature effects. All chromatograms were obtained at room temperature (*ca.* 23°C).

Reagents and solutions

Reagent-grade ethylenediamine was distilled and stored under nitrogen. Reagent grade complexing regents and metal salts were used. A small amount of perchloric acid was added to metal ion solutions to prevent hydrolysis.

The eluent was 1.5 m*M* in ethylenediamine and 2.0 m*M* in tartaric acid, giving a pH of 4.2. For experiments with added complexing regents, the eluent pH was adjusted by adding acid or base. In the iron determination the eluent was boiled to remove dissolved oxygen and was stored in an inert atmosphere whenever possible. The eluent was filtered through a 0.2-μm membrane filter and degassed before use.

Distilled, deionized water was used throughout.

RESULTS AND DISCUSSION

Addition of nitrilotriacetic acid

The choice of NTA as a masking agent for ion chromatography was based on previous success with EDTA[4]. NTA is essentially one-half of an EDTA molecule and forms somewhat weaker complexes than EDTA. Calculations of α_M, the ratio of free metal ion to all forms of the metal in solution, showed that manganese(II), mangesium(II) and the alkaline earths are not complexed significantly by NTA below

a pH of about 3.0. Iron(II) is not complexed at pH 2.0 or below, although some oxidation to iron(III)–NTA was found to occur. Many other metal ions form neutral anionic complexes with NTA at pH 3.0 and pass rapidly through the chromatographic column.

The ion chromatographic determination of manganese(II) with NTA masking of other metal ions looked particularly promising. (An earlier method[4] is selective for magnesium and the alkaline earths.) Addition of a constant excess of NTA to the sample and varying the pH showed an essentially constant peak height for manganese(II) between pH 2.0 and 3.0 (Fig. 1). For subsequent experiments, excess NTA was added to the sample and the pH was adjusted to 3.0.

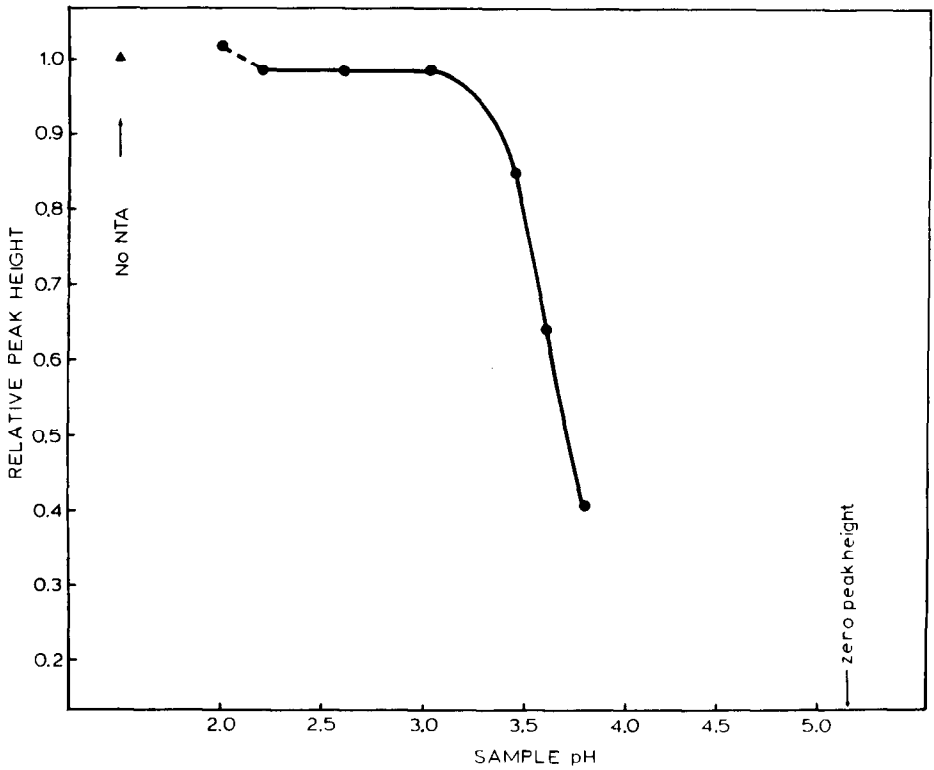

Fig. 1. Relative peak height of manganese(II) with added NTA as a function of sample pH. Each sample contains 1.00 mM manganese(II) and 10 mM NTA. Peak height was measured relative to a sample containing no NTA (pH 2.0).

Samples containing 50 μM each of magnesium(II), manganese(II) and calcium(II) plus an excess of another metal ion were treated with NTA and analyzed by ion chromatography using an ethylenediammonium tartrate eluent. No change in peak height was observed when a 10-fold or a 100-fold molar excess of iron(III), aluminum(III), copper(II) or thorium(IV) was added. A 10-fold excess of nickel(II) was also without effect, but a 100-fold excess did cause some change. Cobalt(II) and yttrium(III) are partly masked by the NTA. Lead(II), uranium(VI), cadmium(II) and

zinc(II) are not masked. However, lead(II) elutes later than manganese, magnesium and calcium and does not interfere.

The effect of NTA masking is shown clearly in Fig. 2. The large excess of copper(II) interferes badly in the first chromatogram, but causes no difficulty in the second chromatogram in which NTA was added to the sample.

Both peak heights and retention times are reproducible with excess NTA in the sample; the calibration curves are also linear. For example, a calibration curve for manganese(II) with a constant excess of aluminum(III) (5.0 m*M*) masked by 10 m*M* NTA was linear over a range of 0.020 to 0.50 m*M* manganese with a correlation coefficient of 0.999.

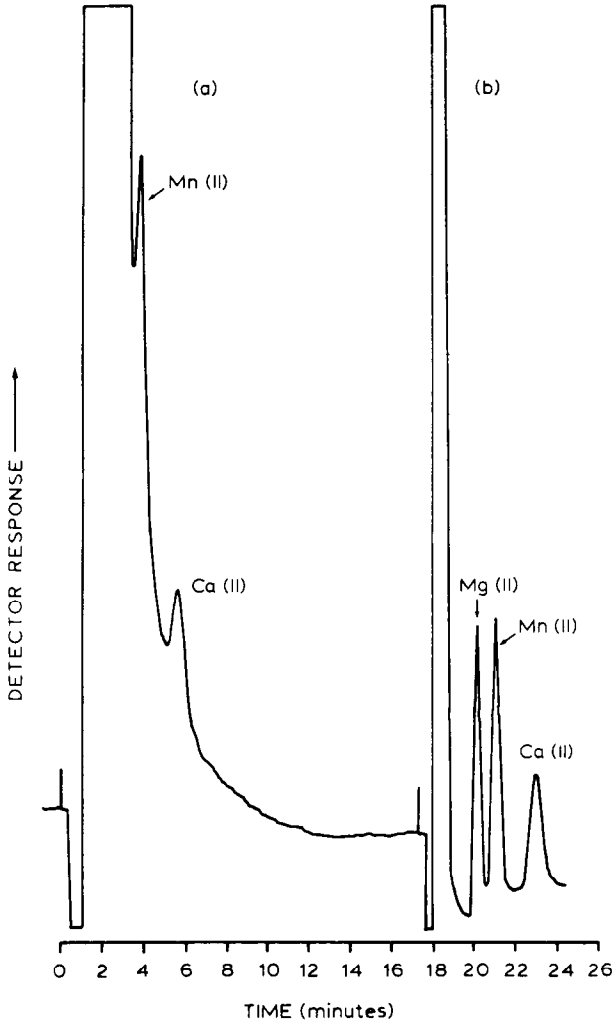

Fig. 2. Comparative chromatograms of samples containing 0.050 m*M* each of magnesium(II), manganese(II) and calcium(II), and 5.0 m*M* copper(II): (a) at pH 2.99 with no NTA; (b) at pH 2.99 with 10 m*M* NTA added.

Addition of sulfosalicylic acid

The successful application of 5-sulfosalicylic acid in ion-exchange separations was demonstrated by Fritz and Palmer[5]. At an appropriate pH, they found that aluminum(III), iron(III), uranium(VI) and vanadium(IV) are complexed and pass quickly through a cation-exchange column. A number of other cations, including the rare earths, are not complexed and are retained on the column. Their application was simply a group separation, and no chromatographic separation of individual metal ions was involved.

In the present work, zinc(II) (50 μM) was chosen as a model compound because it is not strongly complexed by SSA and it is eluted fairly early by the ethylenediammonium tartrate eluent. Calculation of α_M for zinc(II) indicated that less than 1% of the zinc(II) is complexed by SSA below pH 5.5. Experimental determination of relative peak height *versus* sample pH showed no significant complexation by SSA below pH 4.6. At sample pH values above pH 4.6 a baseline "dip" appeared just after the matrix peak (complexed metal ions) and caused some difficulty in measuring the zinc(II) peak height.

The peak height of 50 μM zinc(II) was unaffected by a 20- or 50-fold molar excess of aluminum(III), a 20-fold excess of thorium(IV), a 20-fold excess of vanadium(IV), a 20-fold excess of uranium(VI), or a 100-fold excess of iron(III) when SSA was added and the sample pH adjusted to approximately 4.5. In addition to zinc(II), rare earths, yttrium(III), nickel(II), lead(II), cadmium(II) and cobalt(II) can be chromatographed at pH 4.5 without interference from SSA. Copper(II) is partially complexed and gives a broad matrix peak that completely obscures the zinc(II) peak.

Analysis of rare earths using SSA to mask large excesses of aluminum(III) proved quite successful. Calibration curves are linear (correlation coefficient 0.9991) over at least 0.05 to 0.50 mM rare earth with 2.0 mM aluminum(III) and 10 mM SSA at pH 4.5.

Fig. 3 shows the chromatogram for the determination of 0.1% nickel in a simulated steel sample. The nickel concentration in the prepared sample solution is only 53 ppb* (0.90 μM). The iron(II) peak is an artifact of any sample containing a large excess of iron(III). In this case the iron(II) peak was reduced in size by adding hydrogen peroxide and boiling.

Preconcentration studies

Preliminary studies have shown that sample masking can be used in a preconcentration mode where the unmasked cations are taken up on a concentrator column and the masked cations pass straight through the column. The concentrator column is a short cation-exchange column put in place of the sample loop. An NTA masked sample solution containing 11 ppb (0.20 μM) manganese(II) and 1.0 mM iron(III) was passed through a concentrator column that replaced the sample loop in the injector. Essentially all of the manganese(II) was taken up from the sample solution that was passed through the concentrator column, while no iron(III) was present except that in the dead volume of the injector. Loading of the concentrator column corresponded directly to the amount of sample passed through and was independent

* Throughout the article the American billion (10^9) is meant.

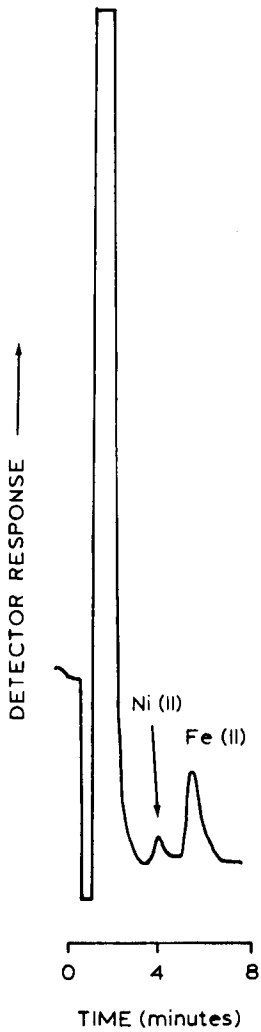

Fig. 3. Chromatogram of a simulated steel sample containing 0.1% nickel. (The diluted nickel concentration is 53 ppb.) The iron(III) was masked by SSA (0.010 *M*) at pH 3.50.

of flow-rate. Significant blanks were obtained with preconcentration. The lack of high quality water precluded further work.

Determination of iron by ion chromatography

Iron is one of our cheapest and most abundant elements. Methods for the quantitative determination of iron are also abundant in the scientific literature. However, methods that will determine iron(II) without interference from iron(III) are much less common. One approach is to measure the distinctive red color of the iron(II)–1,10-phenanthroline complex[6,7]. Care must be taken to prevent reduction during the color-forming reaction and also to ensure that other metal ions that form colored complexes with 1,10-phenanthroline are properly masked.

A method of iron speciation is presented here which incorporates the speed, convenience and simplicity of ion chromatography. Minimal sample preparation is required. Iron(II) is determined by direction of the sample onto a cation column and elution with an ethylenediammonium tartate solution. Any iron(III) is complexed by the tartrate and elutes with the initial or "pseudo" peak. Then total iron is determined chromatographically on another aliquot of the sample after reducing all of the iron to iron(II) with an appropriate reagent. The iron(III) in the original sample is the difference of the total iron and the iron(II) determinations.

Several reagents were tried for the reduction of iron(III) to iron(II). Sodium hydrosulfite gave immediate reduction of the iron(III) but the solution soon developed a cloudy white precipitate. Reduction of iron(III) with hydroxylamine hydrochloride is a common classical procedure, but the kinetics appear to be slow in dilute solutions. A plot of chromatographic peak height of iron(II) against reduction time was still rising after 1 h.

Ascorbic acid was found to be an excellent reagent for the reduction of iron(III). The reduction is almost instantaneous with mixing and neither the excess ascorbic acid nor the oxidized ascorbic acid causes any perturbations in the chromatograms. The peak height of the iron(II) is constant from the theoretical amount of added ascorbic acid [0.5 mole of ascorbic acid for 1.0 mole of iron(III)] to a 95-fold molar excess.

A linear calibration curve (with a correlation coefficient 0.999) from standards ranging from 0.10 m*M* to 4.00 m*M* iron(III) after reduction with a 7-fold excess of ascorbic acid. Essentially identical calibration curves were obtained from standards of freshly prepared iron(II), the same with ascorbic acid added, and iron(III) reduced with ascorbic acid. Freshly prepared iron(III) solutions gave no noticeable iron(II) peaks, but "week old" iron(III) standards gave small iron(II) peaks, apparently resulting from photochemical reduction.

Recoveries of iron(II) and iron(III) from solutions containing both species were examined. Each sample solution was made up in duplicate and contained different quantities of iron(II) and iron(III). One solution was diluted and injected di-

TABLE I

RECOVERIES OF IRON(II), IRON(III), AND TOTAL IRON FROM PREPARED SOLUTIONS USING CATION CHROMATOGRAPHY AND REDUCTION WITH ASCORBIC ACID

Values in parentheses are for identical samples using 1,10-phenanthroline.

Amount taken (μmoles)			*Amount found (μmoles)*			*Difference*		
Iron(II)	*Iron(III)*	*Total*	*Iron(II)*	*Iron(III)*	*Total*	*Iron(II)*	*Iron(III)*	*Total*
12.7	30.1	42.8	12.4 (12.4)	30.2 (30.2)	42.6 (42.6)	−0.3 (−0.3)	+0.1 (+0.1)	−0.1 (−0.1)
22.3	20.1	42.4	22.5 (22.6)	20.3 (20.2)	42.8 (42.8)	+0.2 (+0.3)	+0.2 (+0.1)	+0.4 (+0.4)
33.5	10.0	43.5	33.4 (33.1)	10.3 (10.6)	43.7 (43.7)	−0.4 (−0.4)	+0.3 (+0.6)	+0.2 (+0.2)
5.5	15.0	20.5	5.0	15.1	20.1	−0.5	+0.1	−0.4

rectly into the ion chromatograph, while the other had an excess of L-ascorbic acid added to it before dilution and injection. Total iron(II) present was determined from the first sample, while iron(III) was determined by the difference in iron(II) peak height between the two samples. Excellent agreement was obtained with the 1,10-phenanthroline method (Table I). All samples were run immediately to minimize equilibrium changes. With appropriate care taken in preparation, the samples showed no significant change in composition over a period of about one day. The presence of excess ascorbic acid should provide sample stability for a significantly longer period of time; however, this was not examined.

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