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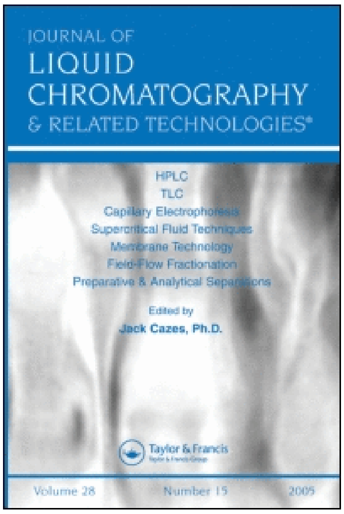

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SEPARATION OF SELECTED TRANSITION METAL IONS AND DIVALENT METAL IONS BY HPLC USING UV-VIS DETECTION

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ABSTRACT

The use of ethylenediaminetetraacetic acid, disodium salt, (pH 3-5) has been investigated as an eluant for the separation and detection of nanogram levels of selected divalent and trivalent metal ions. The effect of pH and eluant concentration upon the retention times and resolution of the system are given and the ability to alter the eluant characteristics to optimize the chromatographic results in different situations will be discussed. The method is less complicated than the method frequently used for transition metal ion determinations which uses a post-column derivitization reagent. This method is applicable to a wider range of metal ions and provides detection limits which are generally within two orders of magnitude of the post-column derivitization method.

INTRODUCTION

Ion chromatography has become a widely used technique for the analysis of inorganic ions. A recent

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emphasis has been placed on the determination of transition metal ions using ion chromatography as an alternative to atomic spectroscopy (1). In general, the separation of the transition metal ions is affected by using a complexing agent as eluant (2,3,4) followed by either conductometric (3,4,5) or UV-VIS detection (4,6,7,8,9,10). The UV-VIS detection mode frequently uses a complexing agent such as PAR and post-column derivitization to complex the already separated metal ions prior to the detection of the complex by visible spectroscopy at 520 nm. The PAR based system provides extremely low detection limits but is encumbered with the necessity of having a post-column reactor module and by the sensitivity of PAR to oxidation. The method reported here is a simplified method for the separation and detection of transition metal ions. The method does not use a post-column reactor or derivitization procedure but relies on the absorbance changes in the complexing eluant as a function of the extent of complexation. The detection limits reported here are not as good as those obtained for the PAR based system, but the system is applicable to a wider range of metal ions and provides detection limits which frequently are in the 10-50 ng range.

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EXPERIMENTAL

Equipment

The HPLC used for this work was a Kratos system. The eluant flow path is in the order of the equipment as listed here: Kratos Spectroflow 400 Pump, Kratos Spectroflow 480 injection valve (80 µL injection loop), Vydac 302IC4.6 anion exchange column, Kratos Spectroflow 783 variable wavelength detector, and a Spectra-Physics 4290 integrator. The eluant used in this research was prepared by dissolving ethylenediaminetetraacetic acid (disodium salt), referred to hereafter as EDTA, to a concentration of 0.01 M. This stock solution was then diluted to various concentrations and the pH was adjusted using acetic acid or sodium hydroxide as needed. The most common eluant was 0.0010 M EDTA at a pH Of 3.7. The flow rate was 2.0 mL/min. The detector settings were, for the majority of the work, range = 0.08 AUFS, wavelength = 220 nm, and attenuator = 2. Any deviations from these values are specified as needed.

Reagents

Stock solutions of 500 ppm Cr(III) and Fe (III) and 1000 ppm for the other metal ions were prepared from iron (III) chloride, chromium (III) sulfate pentadecahydrate, nickel sulfate hexahydrate, cobalt

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(II) chloride hexahydrate, copper (II) acetate monohydrate, zinc nitrate hexahydrate, manganese sulfate monohydrate, cadmium acetate dihydrate, calcium chloride dihydrate, and lead (II) nitrate. The stock solutions were diluted by using 0.01 M EDTA (disodium salt). The pH of the diluent was 5.7 which corresponded to the pH obtained when the EDTA was dissolved in laboratory distilled-deionized water. The diluted solutions of the metal ions varied from sub-ppm concentrations up to 100 ppm.

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Procedure

The various solutions of individual or mixtures of the transition metals, along with the additional divalent metal ions, were injected into the HPLC system. The pH and concentration of the eluant were varied in order to determine the optimum conditions for resolution and sensitivity. The optimum wavelength for detection was also determined experimentally.

The detection limits were defined as that signal which provided a signal three times as large as the baseline noise and was determined by diluting the various solutions until the 3:1 ratio was observed experimentally.

RESULTS AND DISCUSSION

Detection

The UV-VIS detection mode was selected in order to investigate further the mode of interaction of EDTA based eluant systems with this type of detection. The initial work was an undergraduate research project which has since grown to a more detailed investigation of the phenomenon. Figure 1 shows a graph of wavelength as a function of peak height (detector response) for five different species. Notice that all of the species have remarkably increased sensitivity below 300 nm and also show the potential for absorbance at around 410-430 nm. Further closer investigation showed that the maximum sensitivity was obtained at around 220 nm. This wavelength was used in all of the work performed here unless specified otherwise. The explanation for the detector response can be attributed to a change in the wavelength of maximum absorption of the EDTA eluant as a function of complexation-noncomplexation. So, in effect, the method is an indirect method since a property of the eluant is being measured, but is a direct measurement since the complexed eluant ions are the species being measured. We did detect slight variations (less than 10 nm) in the absorption maximum for different metal

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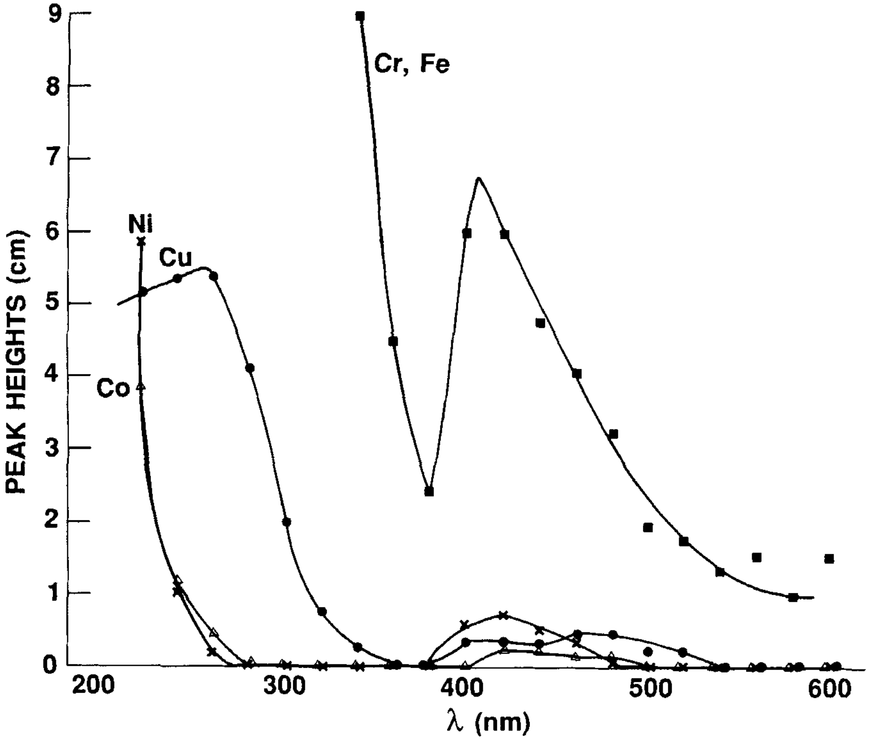

Figure 1: Absorption of light as a function of wavelength for selected metal ions. The conditions were 0.001 M EDTA at a pH of 3.7 and flow rate of 2.5 mL/min. The concentration of the metal ions was 10 ppm each.

complexes. This might be of use with a photodiode array type detector where the multiple wavelengths could be monitored to better assure peak purity. An additional example of this variation as a function of wavelength can be seen in Figure 2. In this example,

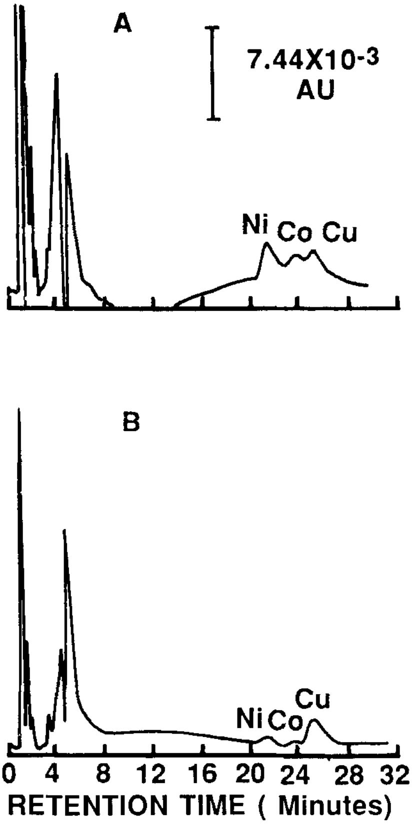

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Figure 2: Figure 2A represents the chromatogram obtained at 220 nm while Figure 2B represents the chromatogram obtained at 240 nm. The other conditions are the same and are 0.001 M EDTA eluant at pH of 3.7 with a flow rate of 2.5 mL/min.

Figure 2A represents detection of a nickel, copper, cobalt mixture at 220 nm while 2B represents the same solution at 240 nm. The nickel and cobalt peaks are slightly larger at 220 nm but the copper peak seems to have lost some relative intensity. Also, note the change in the non-labeled peaks at around 4 minutes.

Eluant pH

The pH of the eluant has an effect on the resolution and sensitivity of this method due to changes in the extent of complexation which arise as a function of pH. The macroscopic acid dissociation constants ($pK_1 = 2.0$, $pK_2 = 2.67$, $pK_3 = 6.16$, and $pK_4 = 10.26$) are of the size that will cause significant changes in the proportions of the species with reasonably small pH changes in the pH range used in this work. A detailed discussion of the mathematics of this change will not be included here, but a good discussion has been presented elsewhere (4). The overall importance of the pH and acid dissociation constant values has to do with the conditional formation constant. The conditional formation constant is the actual numerical value of the formation constant taking into account the actual concentration of the complexing form of the EDTA. Table 1 lists the value of these conditional formation constants at a pH of 3.7. There is a no definite correlation between the numerical value of the metal-EDTA formation constant (or the conditional formation constant) and the retention time. The mechanism at work here, then, must be a complex mechanism involving complexation by

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TABLE I

FORMATION CONSTANTS FOR METAL-EDTA COMPLEXES

ELUTION ORDER	METAL ION	FORMATION CONSTANT	CONDITIONAL FORMATION CONSTANT, pH 3.7
1	Cr(III)	log K = 23	log K' = 13.9
2	Fe(III)	log K = 25.1	log K' = 16.0
3	Ca(II)	log K = 10.7	log K' = 1.6
4	Cd(II)	log K = 16.5	log K' = 7.4
5	Ni(II)	log K = 18.6	log K' = 9.5
6	Zn(II)	log K = 16.5	log K' = 7.4
7	Mn(II)	log K = 14.0	log K' = 4.9
8	Co(II)	log K = 16.3	log K' = 7.2
9	Pb(II)	log K = 18.0	log K' = 8.9
10	Cu(II)	log K = 18.8	log K' = 9.7

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several different EDTA forms as well as possible ionic interaction between the resin and ions.

The trivalent metal ions, such as iron (III) and chromium (III), will form univalent complexes with the tetravalent EDTA species. The divalent metal ions will form a divalent complex with the EDTA. This is the reason for the elution of the trivalent metal species ahead of the divalent metal species.

TABLE II

VARIATION IN RETENTION TIMES OF FIVE 1 PPM METAL IONS AS A FUNCTION OF ELUANT pH

	pH			
ION	3.80	3.75	3.65	3.56
Fe(III)	5.2 min	4.8 min	4.4 min	4.2 min
Cr(III)	5.2 min	4.8 min	4.4 min	4.2 min
Ni(II)	20.8 min	20.9 min	20.7 min	20.4 min
Co(II)	23.1 min	23.1 min	22.9 min	22.8 min
Cu(II)	24.4 min	24.6 min	24.5 min	24.1 min

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Table II provides an example of the variation in the retention times which would be observed with changes in the eluant pH. This variation is much more significant for the early eluting trivalent metal ions (univalent metal-EDTA complexes) than for the divalent metal ions. This opens up the avenue of pH variations to assist in the development of methods for which a given separation can be optimized based upon the pH of the eluant. The changes in the chromatograms which would result from the change in eluant pH are exemplified in Figure 3. Here the triple mixture of

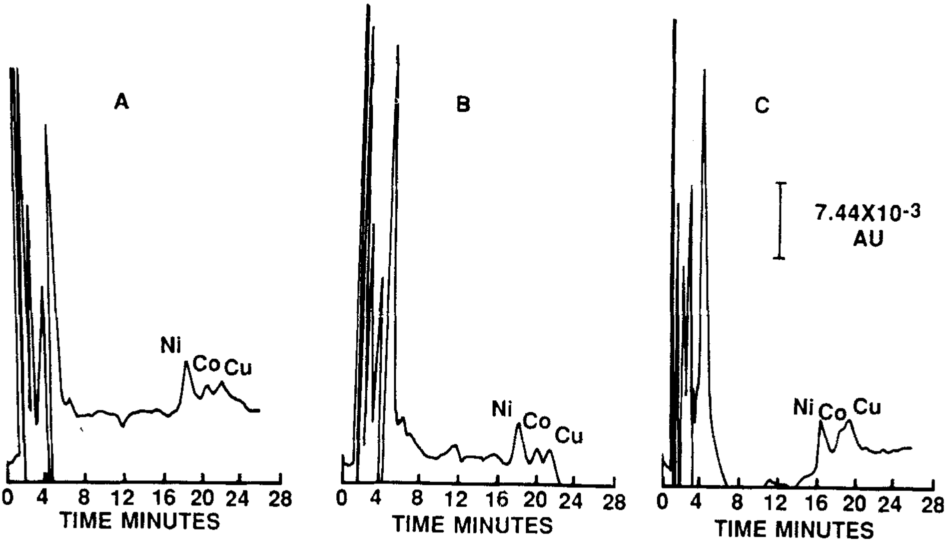

Figure 3: Figure 3A represents an eluant of pH 3.75, Figure 3B represents an eluant of pH 3.47, and Figure 3C represents an eluant of 3.27. The remaining conditions were constant and were 0.0015 M EDTA at a flow rate of 2.0 mL/min at 220 nm detection wavelength. The three metal ions are all present at the 1 ppm level.

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nickel, cobalt, and copper will be best resolved at a pH of around 3.47 with changes of 0.2 pH units in either direction resulting in decreased resolution. This provides for greater flexibility in the chromatographic method but also provides for the greater chance for error should a solution be prepared with only moderate precision.

TABLE III

RETENTION TIMES AND DETECTION LIMITS FOR SELECTED METAL IONS

ION	RETENTION TIME[1]	DETECTION LIMIT[2]
Cr(III)	4.1 min	8 ng
Fe(III)	6.5 min	5.6 ng
Ca(II)	10.5 min	320 ng
Cd(II)	15.2 min	2400 ng
Ni(II)	15.4 min	16 ng
Zn(II)	15.5 min	800 ng
Mn(II)	16.0 min	60 ng
Co(II)	16.9 min	24 ng
Pb(II)	17.5 min	60 ng
Cu(II)	17.6 min	8 ng

[1] Using 0.0015 M eluant at a flow rate of 2.5 mL/min and a pH of 3.7.

[2] signal to baseline noise ratio of 3:1

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Detection Limits and Retention Times

Representative retention times and detection limits for this procedure are given in Table III. The detection limits for the method reported here are generally one to two orders of magnitude higher than

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those for the PAR based system. Also, note that the applicability of the EDTA based system is wider since EDTA forms acceptably stable complexes with more metal ions than does PAR. EDTA can complex up to 62 different metals (11) as compared to approximately 30 for PAR (1). A crude analogy would be that the EDTA system tends to be more of a general detection system while the PAR system is more of a specific system. EDTA is capable of complexing a much larger number of ions and would thus be more amenable to a wide range of applications, especially where unexpected, and unsuspected, metals may be present.

The retention times given in Table III indicate that there is the potential for significant peak overlap, at least under the conditions used for this particular Table. It should be remembered, however, that the retention times can be altered by changing the pH of the eluant along with the eluant concentration. The conditions used for this table were those that provided reasonably good resolution for the early eluting species such as chromium and iron and also provided good resolution for the later eluting species such as cobalt and copper. Better operating performance could be obtained by optimizing the eluant and pH for a given set of metals. Also, the fact that the metal-EDTA complexes absorb at slightly different wavelengths would provide the opportunity to use detector selection to assist in quantitation and to minimize the impact of peak overlap.

The linear dynamic range for this EDTA based system was determined for the chromium (III)-EDTA complex. The linear range was from 0.1 ppm to 200 ppm chromium (III). This is a reasonably large linear operating range and would provide for the analysis of many different solutions. The linear operating range for other metal ions will of course vary, but the overall 2-3 orders of magnitude should remain fairly constant.

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Use of EDTA Matrix

The use of an EDTA based sample matrix provided an increased sample sensitivity. The reason for this is most likely based upon the shift in the equilibrium which results due to the relatively low conditional formation constants for the metal-EDTA complexes in acid solution. The presence of an excess amount of EDTA will shift the equilibrium back toward the metal complex thus providing additional stability for the species to be detected. Figure 4 illustrates the effect of the EDTA concentration in the matrix upon the relative peak height of the chromium (III) complex.

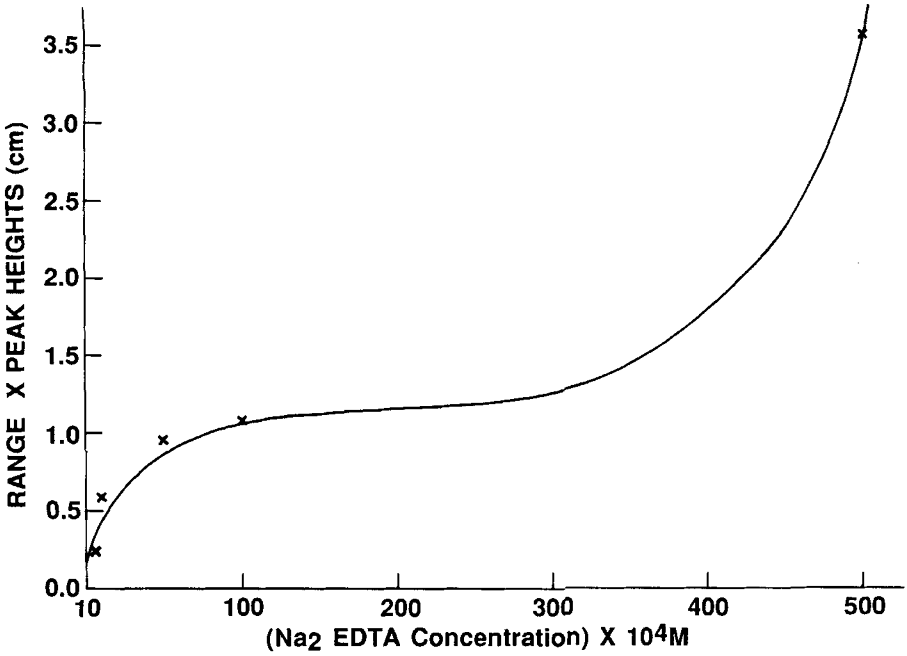

Figure 4: Effect of concentration of EDTA in the sample matrix upon the relative peak height of chromium (III)-EDTA complex. Eluant is 0.0015 M EDTA at a pH of 4.3 at a flow rate of 2.0 mL/min.

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There is an apparently level plateau from around 0.010 M to 0.03 M EDTA which provides for easy quantitation without undue matrix effects. Although higher sensitivities could be obtained at even higher EDTA matrix concentrations, the sensitivity would change significantly for only a very small change in EDTA matrix concentration. For this reason, we performed much of our analytical work with between 0.01 M and

0.02 M EDTA as the diluent for all of our samples. This apparent gain in sensitivity provides for better detection limits and better sensitivity over other techniques using EDTA based eluants. Again, there is flexibility in this method. By varying the EDTA concentration in the matrix, the species to be most effected would be those with a small conditional formation constant (see Table I). This provides a mechanism whereby different metal-EDTA complexes can be selectively optimized within certain ranges.

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Example Chromatograms

Several chromatograms are given here to illustrate the type of results which may be expected from this type of system. In these chromatograms the important aspects are the resolution, retention times, and the concentration of the ions used. In all cases, the chromatograms illustrate that the method would provide sensitive, low level detection of divalent metal ions and selected transition metal ions in a reasonably short period of time with a simple operating system.

Figure 5 illustrates a separation of five different transition metal ions. Also visible in Figure 5 are the chloride and sulfate peaks. Since the chromatography is being performed on an anion column, the inorganic anions will also undergo separation and

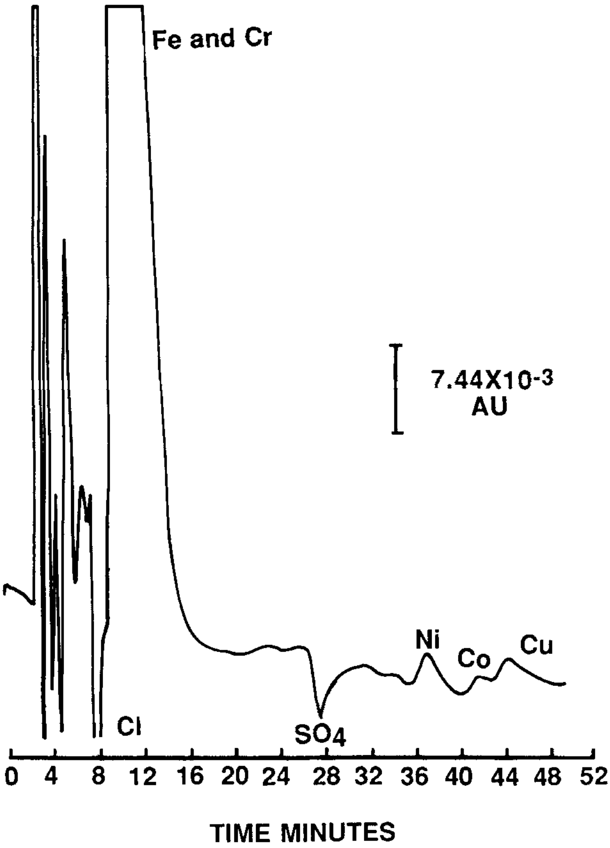

Figure 5: The separation of 10 ppm Fe(III), 10 ppm Cr(III), 1 ppm Ni(II), 1 ppm Co(II) and 1 ppm Cu(II) along with the eluting counterions. Analytical conditions are 0.0015 M EDTA eluant at a pH of 3.37 with a flow rate of 1 mL/min and a detection wavelength of 220 nm.

detection. In general, the inorganic ions will elute as negative peaks since the absorbance of the inorganic ions at 220 nm is much less than the absorbance of the EDTA. This chromatogram was essentially prepared while

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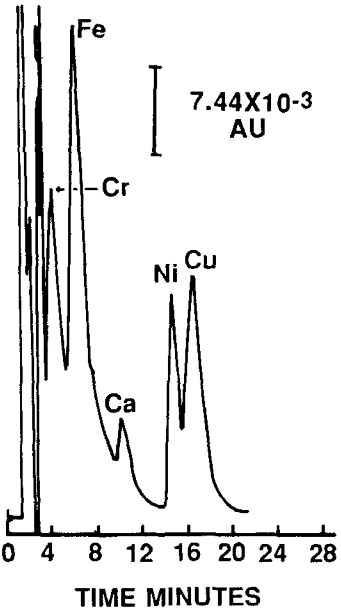

Figure 6: The separation and detection of Fe(III), Cr(III),Ni(II), Co(II), and Cu(II) each at 4 ppm concentration and 20 ppm Ca(II) using 0.0015 M EDTA eluant at a pH of 4.3 and a flow rate of 2.0 mL/min.

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studying the nickel, cobalt, copper mixture and no attempt was made to separate the chromium and iron which eluted early in the chromatogram.

Figure 6 illustrates the separation of the iron and chromium peaks along with several divalent metal ions. In this case, the iron and chromium elute as a shoulder on a broad system peak. The quantitation is still quite easy and dependable. Again, note the concentrations used in the work and the relatively

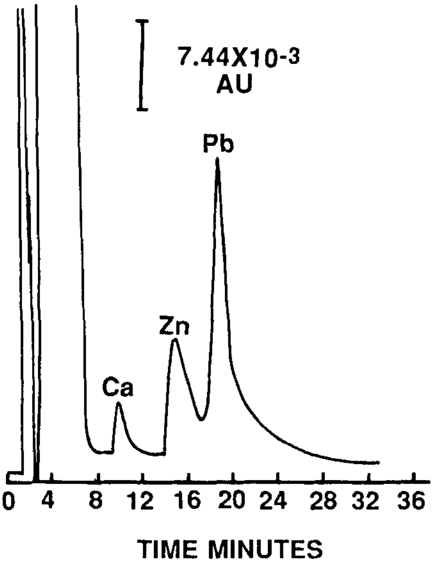

Figure 7: The separation and detection of 20 ppm Ca(II), 20 ppm Pb(II) and 100 ppm Zn(II) using 0.0015 M EDTA at a pH of 4.3 and a flow rate of 2.0 mL/min. The detection wavelength is 220 nm.

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short elution time. Calcium is also present in this chromatogram which emphasizes the advantages of using an EDTA system over a PAR system.

Figure 7 illustrates the separation and detection of a calcium, lead and zinc mixture. These species are not as sensitive as some of the others in the other chromatograms and hence the concentrations are higher. Again, the separation is nice and the EDTA is able to assist in the detection of species which might be missed by other techniques.

CONCLUSION

The method reported here for the separation and detection of transition metal ions (along with other divalent metal ions) is a readily applied method for routine analysis. The detection limits are in the low nanogram range for many metal ions which are sufficiently low for many analytical situations. The retention times are also quite short, less than 25 minutes for most species, thus providing for a rapid analysis of the sample. The absence of a post-column derivitization procedure greatly simplifies the overall method while providing better stability. The use of the strongly complexing EDTA solutions has not been a problem with regard to corrosion of any of the metallic components in the HPLC with which it comes in contact. We have used the system described in this work for approximately nine months and have seen no discernible degradation of either the system operating performance or the analytical column performance. The use of the EDTA sample matrix provides for better results and, in addition, will act as a stabilizer for transition metal solutions which might otherwise undergo some unwanted side reaction (such as precipitation). The system is extremely flexible as concentration, pH, and detector

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wavelength can all be adjusted to optimize the conditions for a given situation.

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