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Evaluation of 1,2-diaminocyclohexanetetraacetic acid as eluent in the determination of inorganic anions and cations by ion chromatography

Eduardo A. Gautier*, Raquel T. Gettar, Roberto E. Servant, Daniel A. Batistoni

Dto. Química Analítica, Div. Espectrometría de Masas, Comisión Nacional de Energía Atómica, Av. Libertador 8250, 1429 Buenos Aires, Argentina

Abstract

The chelating agent 1,2-diaminocyclohexanetetraacetic acid (DCTA) was tested as an eluent for the separation and determination of inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) and some selected metals using single-column ion chromatography with ultraviolet detection. The effects of pH and eluent concentration on retention times for the system were studied to overview the possibilities of attaining optimum separations. The metals studied included Fe(III), Cr(III), Y(III), La(III), Nd(III), Gd(III), Ba(II), Ca(II), Cd(II), Co(II), Cu(II), Hg(II), Mg(II), Ni(II), Pb(II), Sr(II), Zn(II) and Mo(VI). The detection limits were generally below 0.5 $\mu g\ ml^{-1}$. Results for the analysis of synthetic samples and drinking water are presented.

1. Introduction

The possibility of using a complexing agent in the mobile phase for the determination of metals in the form of ligand complexes has become a widely used technique in the field of ion chromatography, with metal species being separated using either cation, anion or combined anion/cation exchangers [1–15]. Highly charged, strongly complexing anions such as aminopolycarboxylic acids react with most metals producing singly or doubly charged anions, allowing the simultaneous determination of metal cations and inorganic anions.

1,2-Diaminocyclohexanetetraacetic acid (DCTA), acting as a multidentate chelating ligand, forms strong complexes with most divalent and trivalent metals. The combination ratio of DCTA with metals ions is 1:1, the chelate being negatively charged. These complexes have chemical structures similar to those formed with EDTA but have higher stability constants for most metals. EDTA complexes have been widely studied [1,3–15], but few reports about DCTA complexes have been published [1,2,7].

The purpose of this work was to investigate the ion chromatographic behaviour of some inorganic anions and of several di- and trivalent metals using DCTA as eluent. The ultimate goal of the study was to separate and determine these ionic species.

* Corresponding author.

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2. Experimental

2.1. Apparatus

A Konik (Barcelona, Spain) KNK-500A liquid chromatograph with a Rheodyne Model 7125 injector and equipped with a 100-μl sample loop and a Vydac 302 IC 4.6 silica-based anion-exchange column (25 cm × 4.6 mm I.D.) was used for all separations. A Linear (Reno, NV, USA) UVis 204 variable-wavelength UV–Vis detector was employed. Data were transferred to a personal computer via an A/D interface and processed by means of integration software (Konikrom Chromatography Data System V.5). Molecular absorptions spectra of the complexes were obtained with a Perkin-Elmer (Norwalk, CT, USA) Model 559A UV–Vis spectrophotometer.

2.2. Reagents

Water used for the preparation of all solutions and eluents was obtained by passing distilled water through a Nanopure water-purification unit (Sybron/Barnstead, Boston, MA, USA). Stock standard solutions of the different cations were prepared from analytical-reagent grade chemicals. All metal ion solutions (except chromium) were injected directly into the instrument. The metal ion complexes were formed within the chromatographic system, which was operated in the isocratic mode at 30°C. Cr(III) required the addition of the complexing agent before injection. Formation of the chromium complex was attained by heating the mixture at 80°C for 20 min.

Eluents were prepared by dissolving DCTA (Merck, Darmstadt, Germany) in water, followed by pH adjustment with 1 *M* sodium hydroxide solution. All eluents were passed through a 0.22-μm membrane filter and deaerated with helium.

3. Results and discussion

To establish the optimum conditions for chromatography, factors that affect the retention behaviour and the detection, such as pH and concentration of the eluent and UV wavelength, were studied. The solution pH and the DCTA concentration are considered to be the most important factors in the chelation reaction.

Trivalent metal ions such as Fe(III), Cr(III), Y(III), La(III), Nd(III) and Gd(III) form monovalent complexes with DCTA, while the divalent metal ions form divalent complexes. For that reason, the trivalent metal ions are eluted earlier than the divalent species Ca(II), Cd(II), Co(II), Cu(II), Hg(II), Mg(II), Ni(II), Pb(II), Sr(II) and Zn(II)).

An exception was Ba(II), which showed a short retention time. This behaviour could arise from the lower formation constant ($\log K = 7.99$) [16] of the Ba–DCTA complex when compared with other divalent ion constants and the larger ionic radius of the metal ion.

3.1. Effect of eluent concentration

The retention times of metals were studied at four different eluent concentrations, 0.75, 1.2, 1.5 and 2 m*M*, at pH 5.8. The variation of the logarithm of the capacity factors ($\log k'$) as a function of the logarithm of DCTA concentration is shown in Fig. 1. In each instance a peak from an unretained compound was employed as reference for t_0 estimation.

The retention time decreases for high concentrations of the eluent because once the complex is formed, an increase in DCTA concentration will increase the concentration of the non-complexed anions of DCTA which compete with the metal complex ions for the ion-exchange sites.

Straight lines were obtained. The negative slope of the lines is considered to be equal to x/y, where x is the charge of the complexed metal anion and y the charge of the eluent anion [1,17].

Experimental values of the slope ranged from −0.48 to −0.56 for trivalent cations and from −0.57 to −0.62 for divalent cations. These results agree with an effective charge of about −2 and −3.3, respectively, for the eluent. However, equilibrium calculations for the distribution

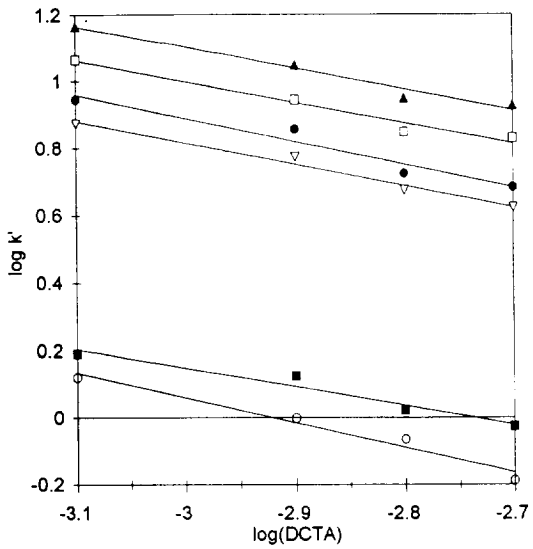

Fig. 1. Log(capacity factor) vs. log(DCTA concentration). ○ = $BaDCTA^{2-}$; ■ = FeDCTA ; ▽ = $SrDCTA^{2-}$; □ = $CuDCTA^{2-}$; ▲ = $ZnDCTA^{2-}$; ● = $HgDCTA^{2-}$.

of DCTA species show that 67% of [$HDCTA^{2-}$] and 33% of [$HDCTA^{3-}$] are present at pH 5.8, giving an "effective charge" of −2.33. These results suggest that mechanisms other than pure ion exchange could be active during the separation process. Haddad and Jackson [17] discussed several examples in which steric and activity effects and/or ion-pair formation could explain the observed behaviour.

3.2. Effect of pH

Changes in the pH range produce variations in the proportions of the anionic species in the eluent, as expected from the DCTA acid dissociation constants ($pK_1 = 2.43$, $pK_2 = 3.52$, $pK_3 = 6.12$ and $pK_4 = 11.70$) [16]. In addition, the conditional stability constants of metal chelates are often strongly dependent on pH owing to the acid–base equilibrium of the chelating agent.

Separations were performed at four different pH values, 4.5, 5.0, 5.5 and 5.8, with the eluent concentration fixed at 1.2 m*M*. At pH values lower than 4.5 broader peaks with longer retention times were observed; pH values higher than 6.0 were not tested because this is the upper recommended pH limit for column operation.

Fig. 2a and b show that an increase in the pH of the mobile phase decreases the retention time of some complexed metal anions. The "effective

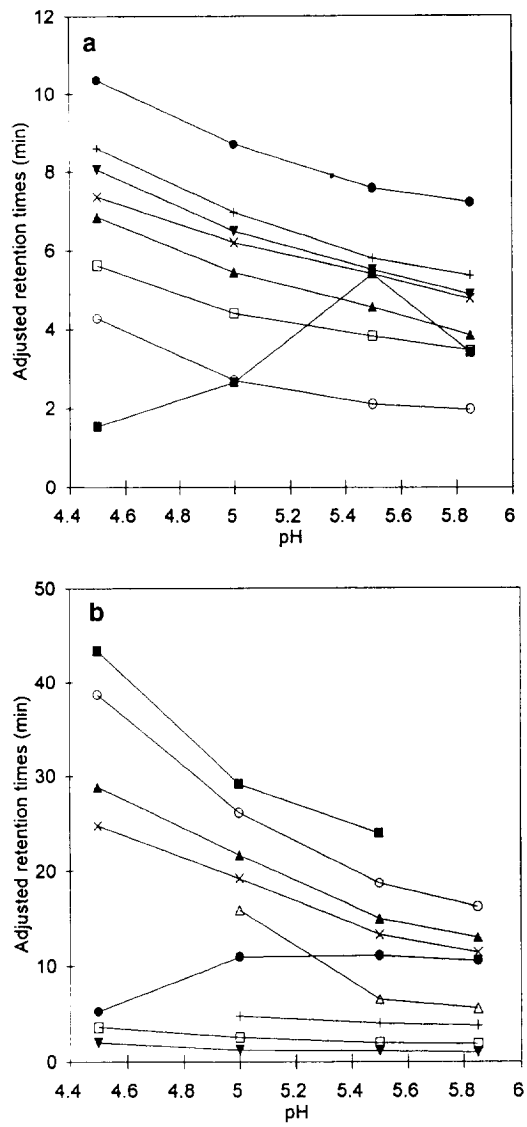

Fig. 2. Adjusted retention time vs. pH of 1.2 m*M* DCTA eluent. (a) Flow-rate, 0.8 ml min^{-1}. ■ = $BaDCTA^{2-}$; × = $FeDCTA^{-}$; ▲ = $YDCTA^{-}$; + = $NdDCTA^{-}$; ▼ = $LaDCTA^{-}$; ● = $CrDCTA^{-}$; ○ = Cl^{-}; □ = NO_3^{-}. (b) Flow-rate, 1.5 ml min^{-1}. × = $CaDCTA^{2-}$; ● = $SrDCTA^{2-}$; + = $CrDCTA^{2-}$; ■ = $MnDCTA^{2-}$; ○ = $CoDCTA^{2-}$; △ = MoO_4^{2-}; ▲ = $CuDCTA^{2-}$; ▼ = Cl ; □ = NO_3^{-}.

charge" of the eluent should increase with increase in pH.

Ba and Sr complexes exhibit lower than expected retention times at pH <5.5. This result means that a considerable dissociation of the complexes occurred at pH <5.5.

3.3. Wavelength selection

In order to investigate the location of the relative absorption maxima, plots of absorbance vs. wavelength for divalent metal complexes were obtained. Some results are depicted in Fig. 3. Other divalent metals not included in Fig. 3 showed a continuous increase in absorbance from 300 to 210 nm, similar to that in the spectrum of the Co(II) complex. An operating wavelength of 210 nm was chosen for divalent cations. However, it is worth mentioning that other wavelengths can be employed to improve the selectivity in particular cases.

A wavelength of 195 nm was selected for trivalent metals because Y(III), La(III), Nd(III) and Gd(III) only produced positive chromatographic peaks below 200 nm. Cr(III) and Fe(III) could be measured at either 210 or 195 nm without significative losses in sensitivity.

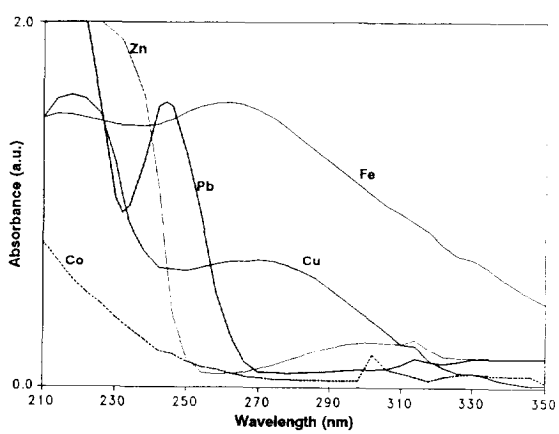

Fig. 3. Absorbance vs. wavelength for some complex anions. Metal concentration, 0.2 m*M*; DCTA/metal molar ratio, 1:1.

3.4. Applications

To establish the elution order of the elements studied, individual retention times were measured at a flow-rate of 0.8 ml min^{-1}. The values obtained and the corresponding detection limits, defined as three times the standard deviation of the baseline noise, are given in Table 1. A detection wavelength of 210 nm was employed for all metals except Y, La, Nd and Gd, for which a 195 nm was utilized.

Chromatograms depicting the behaviour of different metal and anion mixtures are included in Figs. 4 and 5.

The method was also applied to the determination of Ca(II), Mg(II), Cl^-, NO_3^- and SO_4^{2-} in drinking water, as shown in Fig. 6. Chloride and sulfate gave negative peaks because these ions do not absorb UV radiation.

Table 1
Retention times (t_R) and detection limits (D.L.)

Cation complex	t_R (min)	D.L. ($\mu g\,ml^{-1}$)
Ba–DCTA	7.1	0.1
Y–DCTA	7.5	0.3
Fe–DCTA	8.5	0.05
La–DCTA	9.6	0.05
Gd–DCTA	8.7	0.2
Nd–DCTA	9.1	0.04
Cr–DCTA	10.9	0.01
MoO_4^{2-}	12.9	0.02
Mn–DCTA	16.7	0.2
Ca–DCTA	24.6	0.3
Sr–DCTA	24.6	0.3
Hg–DCTA	27.2	0.03
Pb–DCTA	28.8	0.03
Cu–DCTA	32.1	0.03
Cd–DCTA	32.6	0.8
Mg–DCTA	32.7	0.2
Zn–DCTA	35.5	0.4
Ni–DCTA	37.2	0.03
Co–DCTA	38.0	0.03

Mobile phase: 1.2 m*M* DCTA, pH 5.8, flow-rate 0.8 ml min^{-1}.

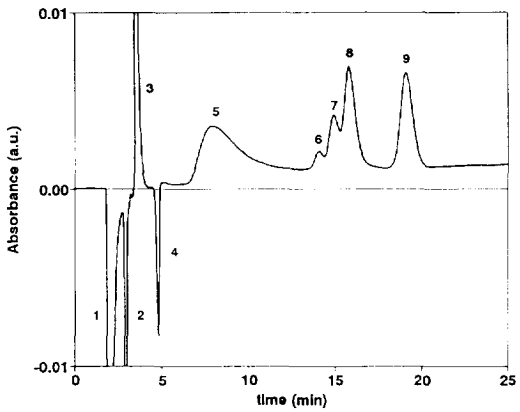

Fig. 4. Chromatogram for some selected metal ions and anions. Observed peaks: 1 = injection; 2 = Cl^-; 3 = NO_3^-; 4 = SO_4^{2-}; 5 = MoO_4^{2-}; 6 = $CaDCTA^{2-}$; 7 = $HgDCTA^{2-}$; 8 = $CuDCTA^{2-}$; 9 = $CoDCTA^{2-}$. [DCTA] = 1.2 m*M* at pH 5.8; flow-rate, 1.5 ml min^{-1}; concentration of each metal ion, 2.5 $\mu g\ ml^{-1}$; detection wavelength, 210 nm.

4. Conclusions

This work has shown the potential of DCTA as a chelating agent for measuring a variety of metals and inorganic anions using ion-exchange chromatography. The concentration of DCTA, the pH of the mobile phase and the detection wavelength can be changed to optimize the conditions for any given application in order to obtain reasonable retention times.

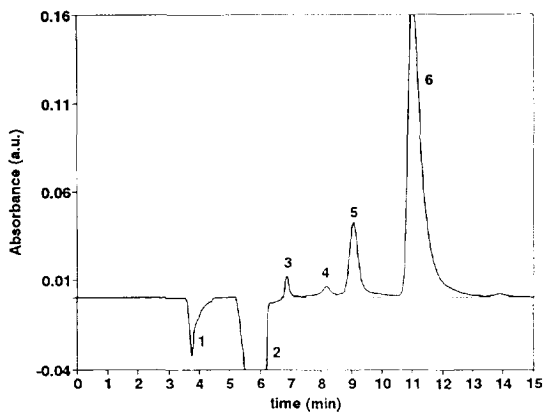

Fig. 5. Chromatogram for some selected metal ions and anions. Observed peaks: 1 = injection; 2 = Cl^-; 3 = $BaDCTA^{2-}$; 4 = YDCTA; 5 = FeDCTA; 6 = CrDCTA. [DCTA] = 1.2 m*M* at pH 5.8; flow-rate, 0.8 ml min^{-1}; concentration of each metal ion, 10 $\mu g\ ml^{-1}$; detection wavelength, 195 nm.

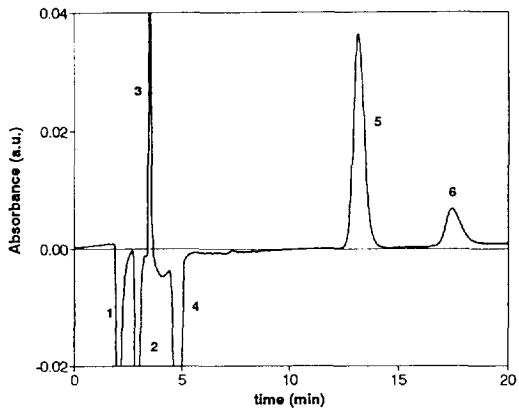

Fig. 6. Chromatogram of drinking water. Observed peaks: 1 = injection; 2 = Cl^-; 3 = NO_3^-; 4 = SO_4^{2-}; 5 = $CaDCTA^{2-}$; 6 = $MgDCTA^{2-}$. Concentrations: Cl^- = 33.0 $\mu g\ ml^{-1}$; NO_3^- = 1.3 $\mu g\ ml^{-1}$, SO_4^{2-} = 58.0 $\mu g\ ml^{-1}$; Ca^{2+} = 20.9 $\mu g\ ml^{-1}$; Mg^{2+} = 4.4 $\mu g\ ml^{-1}$. Other conditions as in Fig. 4.

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