Simultaneous ion chromatography of inorganic anions together with some organic anions and alkaline earth metal cations using chelating agents as eluents

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ABSTRACT

The possibility of the simultaneous separation of inorganic and some organic anions and alkaline earth metal cations was investigated on two silica gel-based anion exchangers with the chelating agents ethylenediaminetetraacetic acid (EDTA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), ethylene glycol bis(2-aminoethyl ether) tetraacetic acid (EGTA) and diethylenetriamionepentaacetic acid (DTPA) as eluents. The retention times (t_R) of all the inorganic and organic anions decreased with increasing pH and concentration of the eluents, whereas for the alkaline earths the t_R *vs.* pH plots were "bell-shaped", which indicated that alkaline earths could be separated either as metal cations or as chelating anions, depending on the pH and concentration of the eluent, but with almost the same sequence Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}.

Under the experimental conditions EDTA and DCTA were usually applicable for the simultaneous separation of inorganic and some organic anions and alkaline earth metal ions, whereas EGTA and DTPA were more suitable for inorganic and organic anions but not good for alkaline earth metal ions.

The proposed method was used for the simultaneous determination of some inorganic and organic anions and alkaline earth metal ions in natural samples such as drinking water, mineral water, brine and spinach juice, with satisfactory results.

INTRODUCTION

For the simultaneous determination of inorganic anions and cations[1–11], particular attention has been focused on single-column ion chromatography with

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chelating agents as eluents. Yamamoto *et al.*[9] effected the separation of inorganic anions and Ca and Mg cations on an anion-exchange column with EDTA (see *Reagents and solutions* for full names) as eluent and conductivity detection. Matsushita[10] separated inorganic anions and some divalent metal ions by using DCTA as eluent and UV detection. An ion-chromatographic method using chelating agents and selctive UV detection for the same purpose was recently described[11].

With regard to the simultaneous determination of organic and inorganic anions, only a few publications have considered non-suppressed single-column ion chromatography. Cortes[12] separated some inorganic and organic anions by using an "amino column" and UV detection, Skelly[13] separated glycolic acid, NO_2^- and NO_3^- by a reversed-phase system and Haddad and Croft[14] separated acetate, lactate, chloride and phosphate on a polymeric anion column with UV detection.

In this study, an attempt has been made to separate simultaneously some inorganic and organic anions and all the alkaline earth metal cations, for which the chelating agents EDTA, DCTA, EGTA and DTPA were systematically investigated as eluents on the silica gel-based anion-exchange columns Nucleosil SB and Nucleosil Anion II with both conductivity and UV detection.

EXPERIMENTAL

Apparatus

The instrumentation consisted of an a high-performance liquid chromatographic pump (Model 2200, Bischoff, Leonberg, F.R.G.), an Ion Chromatograph 690 conductivity detector (Metrohm, Herisau, Switzerland), a UV detector (Biotronik, Maintal, F.R.G.) and a Chromato-Integrator (Merck/Hitachi, Darmstadt, F.R.G.).

The separation columns used were Nucleosil 10 SB (250 × 4 mm I.D.) and Nucleosil 10 Anion II (250 × 4 mm I.D.) (Macherey, Nagel & Co., Düren, F.R.G.).

Reagents and solutions

The eluents were prepared by dissolving 1–3 mmol of EDTA (ethylenediaminetetraacetic acid; Titriplex II), DCTA (1,2-diaminocyclohexanetetraacetic acid; Titriplex IV), EGTA (ethylene glycol bis(2-aminoethyl ether)tetraacetic acid; Titriplex VI) and DTPA (diethylenetriaminepentaacetic acid; Titriplex V) in 1 l of deionized, distilled water followed by adjusting the pH to a certain value between 4 and 8 with lithium hydroxide solution. Before use all eluents were filtered through a 0.2-μm membrane filter. Stock solutions of inorganic and organic anions and alkaline earths were prepared from the salts at concentrations of 1 mg/l, then diluted to the desired concentrations.

All reagents were of analytical-reagent grade and used without further purification.

Chromatographic conditions

Unless stated otherwise, the chromatographic experiments were performed at a flow-rate of 2 ml/min and the sample volume used was 100 μl. The sensitivity of the conductivity detector was set at 2 μS/cm and the integrator attenuation was set at 5. The sensitivity of the UV detector was 0.16–0.08 a.u.f.s. and the detection wavelength length was 205 nm. The separation systems, including the separation columns, the concentrations, pH values and flow-rates of the eluents are summarized in Table I.

TABLE I

THE SEPARATION SYSTEMS

Column	Eluent	Concentration (mmol/l)	pH	Flow-rate (ml/min)
Nucleosil SB	EDTA	1, 2, 3	4.2–8.0	2
	DCTA	1, 2, 3	4.5–7.5	2
	EGTA	1–5	4.4–8.0	2
	DTPA	1, 2	4.5–7.5	2
Nucleosil Anion II	EDTA	1	4.0–6.0	2
	DCTA	1.5	4.5–7.0	1

RESULTS AND DISCUSSION

Effect of pH and concentration of the eluent

The active species of EDTA and aminopolycarbonic acids as eluents are their anions, which are dependent directly on the pH and concentration of the eluent. The effects of pH and concentration eluents were therefore systematically investigated.

Considerating the stability of the silica-based exchangers and the solubility of the aminopolycarbonic acids, the pH of the eluents was adjusted to a certain value between 8 and 4. Plots of retention times *vs.* pH of EDTA and DCTA eluents on both
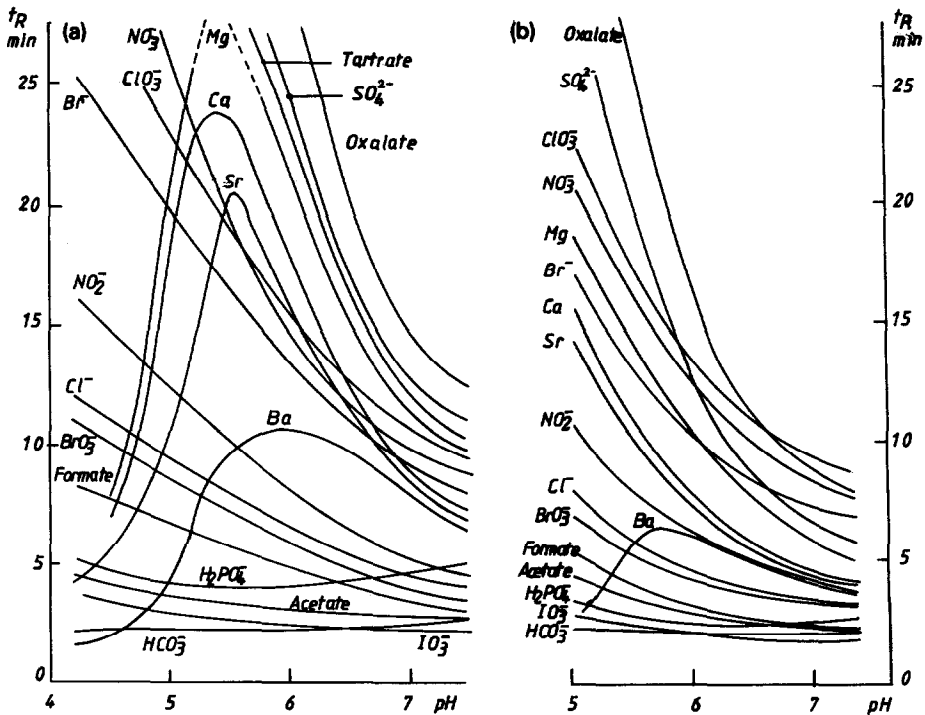

Fig. 1. Effects of pH and concentration of eluents. Column: Nucleosil SB (250 × 4 mm I.D.). Eluent, EDTA, (a) 1 mmol/l and (b) 3 mmol/l; flow-rate, 2 ml/min; conductivity detection. t_R = Retention time.

TABLE II

RETENTION TIME OF SOME INORGANIC AND ORGANIC ANIONS AND ALKALINE EARTH METAL CATIONS ON THE NUCLEOSIL SB COLUMN

Conditions: Nucleosil 10 SB column (250 × 4 mm I.D.); flow-rate, 2 ml/min; conductivity detection.

Retention time (min)

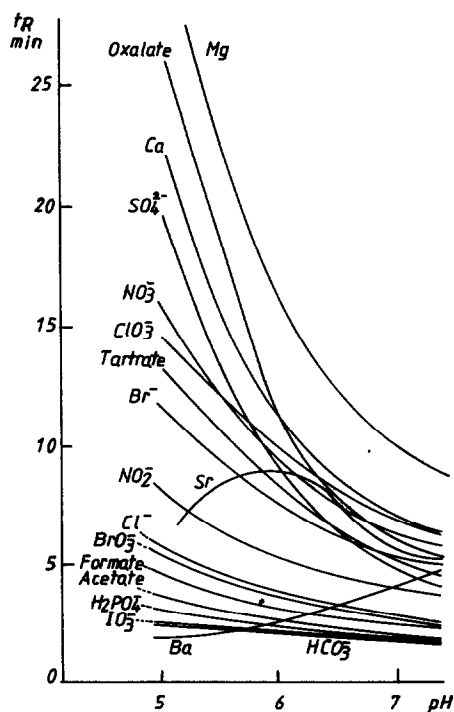| Ion	EDTA			DCTA			EGTA		DTPA	
	1 mM, pH 6.0	1 mM, pH 7.0	3 mM, pH 6.0	2 mM, pH 5.0	2 mM, pH 6.0	2 mM, pH 7.0	2 mM, pH 7.7	3 mM, pH 7.7	2 mM, pH 4.5	2 mM, pH 6.0
F⁻			2.90	4.80	2.50	2.40	3.90	3.30		
HCO₃⁻	2.80	2.80	2.42	2.41	2.42	2.40	4.90	4.22		
IO₃⁻	3.02	2.63	2.50	2.90	2.32	2.24	5.33	4.60		
H₂PO₄⁻	4.21	5.00	2.94	3.33	3.30	3.20	16.4	14.8	3.90	4.73
BrO₃⁻	5.80	4.80	5.02	5.90	4.32	3.63	8.52	7.60	5.21	
Cl⁻	6.11	4.54	5.12	6.22	4.33	3.80	8.65	7.32	5.12	3.70
NO₂⁻	8.22	6.01	7.05	8.32	5.80	4.75	11.2	8.90	7.40	4.80
Br⁻	12.5	9.80	11.0	12.2	8.40	7.11	18.4	14.9	9.40	7.03
ClO₃⁻	15.9	10.9	14.5	15.3	9.70	9.20	23.5	19.0	10.3	8.80
NO₃⁻	14.6	10.1	13.2	14.7	10.0	8.50	20.8	16.5	12.0	6.94
SO₄²⁻	25.5	12.9	13.2	23.3	10.2	7.10	18.9	18.0	16.1	8.50
Acetate	4.20	3.00	3.30	3.90	3.11	2.52	4.62	4.03	3.22	2.71
Formate	4.80	3.32	3.63	4.80	3.42	3.01	5.21	4.70	4.90	2.90
Propionate	4.40	3.90	3.93	4.60	3.30	2.90	5.40	4.60	3.50	2.91
Pyruvate	6.50	3.50	3.75	5.60	4.30	3.2	6.90	5.90	4.10	3.20
Tartrate	25.0	13.9	13.2	25.5	11.6	7.20	21.0	20.0	12.9	9.5
Oxalate	32.4	15.5	17.0	29.0	14.2	8.30	25.0	23.0	13.7	12.0
Ba²⁺	5.5	8.8		2.2	3.0	4.3				
Sr²⁺	15.5	9.20		13.2	13.7	8.80				
Ca²⁺	16.5	8.40	7.70	28.3	15.3	9.02	13.4			
Mg²⁺	23.0	12.0	11.4			12.7	4.5			

Fig. 2. Influence of pH of DCTA. Column: Nucleosil SB (250 × 4 mm I.D.). Eluent, DCTA (3 mmol/l); flow-rate, 2 ml/min; conductivity detection.
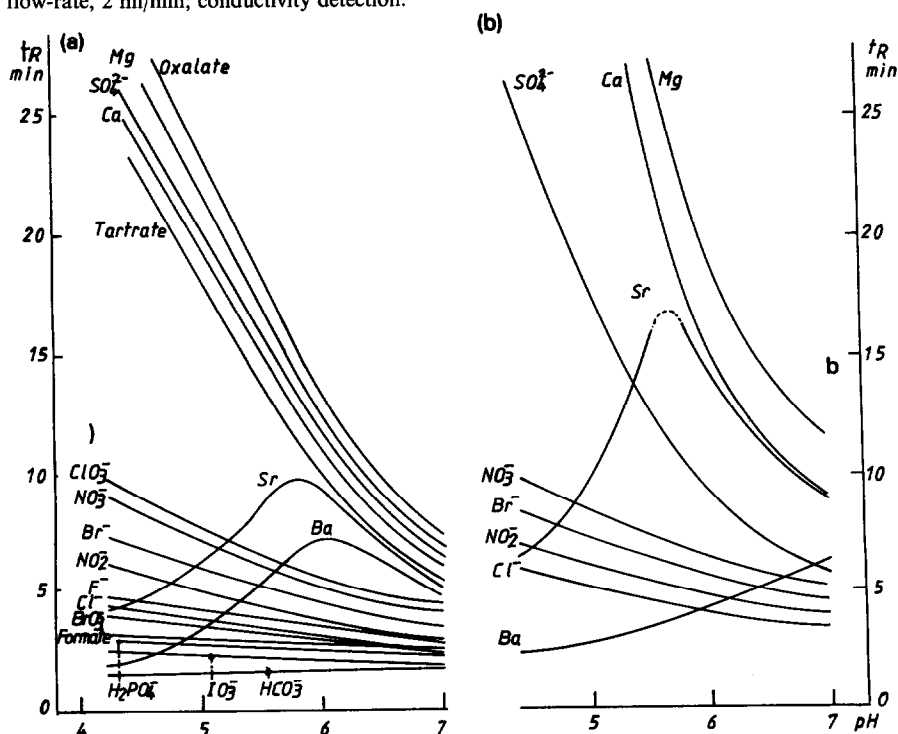

Fig. 3. Influence of pH of eluents. Column: Nucleosil Anion II (250 × 4 mm I.D.). Eluent: (a) 1 mmol/l EDTA at 2 ml/min; (b) 1.5 mmol/l DCTA at 1 ml/min. Conductivity detection.

TABLE III

COMPARISON OF RETENTION TIMES OF VARIOUS IONS ON THE NUCLEOSIL ANION II AND NUCLEOSIL SB COLUMNS WITH EDTA AS ELUENT

Elution conditions: 1 mmol/l EDTA, pH 6.0, flow-rate 2 ml/min.

Column	Retention time (min)									
	Acetate	Formate	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	Oxalate	Ca^{2+}	Mg^{2+}
Nucleosil Anion II	2.1	2.9	3.2	4.0	4.8	5.7	12.0	14.1	11.0	12.5
Nucleosil SB	3.1	4.8	6.1	8.0	12.2	14.5	25.0	30.0	18.1	22.5

columns are shown in Figs. 1, 2 and 3. The retention times of some inorganic and organic anions and alkaline earth metal ions on the Nucleosil SB column with EDTA, DCTA, EGTA and DTPA as eluents are partly summarized in Table II. For inorganic and organic anions the retention times decreased regularly with increase in the pH of the eluent, characterized by a negative slope of the plots, whereas for the alkaline earth metal ions the retention time $vs.$ pH plots were "bell-shaped", which indicated that the alkaline earths should be separated either as metal cations before the top of the diagram with a positive slope or as chelating anions after the top characterized by the negative slope when the pH and the concentration of the eluents become high enough.

Fig. 1 also shows the dependences of the retention times on the concentration of EDTA. For the elution of inorganic and organic anions and also alkaline earth metal ions all the retention times decreased regularly with the increasing EDTA concentration. However, among the alkaline earths only Ba^{2+} showed "bell-shaped" plots at all EDTA concentrations in the range 1–3 mmol/l. Near the top of the diagram the alkaline earths should exist partly as cations and partly as anions, thus causing weak conductivity signals which cannot be used for the quantitative detection. The conductimetric detection of the alkaline earths was therefore possible only within the limits of the range just after or before the top of the diagram.

Comparison between Nucleosil Anion II and Nucleosil SB

The Nucleosil Anion II separation column had a lower capacity than that of the Nucleosil SB column and was suitable for the rapid separation of various anions and Ca^{2+} and Mg^{2+}. In addition, Nucleosil Anion II permitted lower eluent concentrations to be used for the separation and was favourable for trace analysis. However, on this column the elution sequence could not be reversed by changing the pH or eluent concentration. Fig. 3, shows the plots of retention times $vs.$ pH on this column and Table III compares the retention times for various ions on the Nucleosil Anion II and Nucleosil SB columns with EDTA as eluent.

Because of its greater capacity, the Nucleosil SB column could be suitable for the separation of more ions. Moreover, on this column it is possible to change the elution sequence of some ions. For example, by using EDTA as eluent SO_4^{2-} was eluted after Ca^{2+} and Mg^{2+} (see Fig. 4). However, SO_4^{2-} could be eluted before Ca^{2+} and Mg^{2+} if DCTA was used instead of EDTA as the eluent on the same column (see Fig. 5). The elution sequence of some ions could be reversed by changing the pH and eluent concentration. For example, the elution sequence of NO_3^- could be changed step by step from NO_3^-, Ca^{2+}, Mg^{2+}, SO_4^{2-} (eluent 1 mmol/l EDTA, 5.3 < pH < 6.6) through Ca^{2+}, NO_3^-, Mg^{2+}, SO_4^{2-} (pH > 6.6) and Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-} (2 mmol/l EDTA, pH < 6.3) to Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^- (3 mmol/l EDTA, pH > 6) by increasing the concentration and pH of EDTA as shown in Fig. 1.

It is of interest that the elution sequence of the alkaline earths in all these separation systems generally remained Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+} (except when using EGTA as eluent, when Mg^{2+} was always eluted before Ca^{2+}), which is the opposite of that in separation systems involving cation exchangers[15–17].

On the Nucleosil SB column with EDTA or DCTA as eluent, $H_2PO_4^-$ was generally eluted before Cl^-, but with EGTA as eluent $H_2PO_4^-$ was far behind Cl^- (see Fig. 6). A separation of acetate, formate, pyruvate, Cl^-, NO_2^-, $H_2PO_4^-$, SO_4^{2-} and NO_3^- was thereby achieved (Fig. 6). However, EGTA was not suitable for the elution
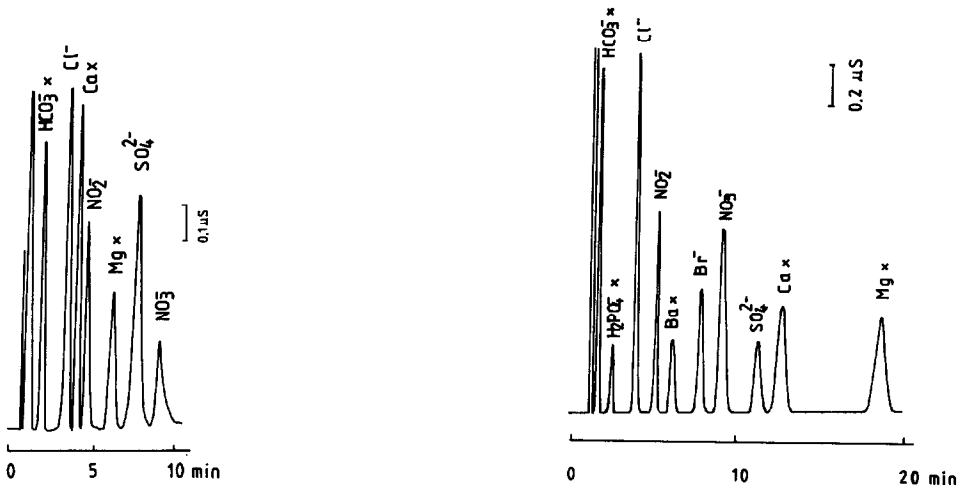
Fig. 4. Rapid separation of main inorganic anions, Ca^{2+} and Mg^{2+} with EDTA as eluent. Column: Nucleosil SB. Eluent: 2 mmol/l EDTA, p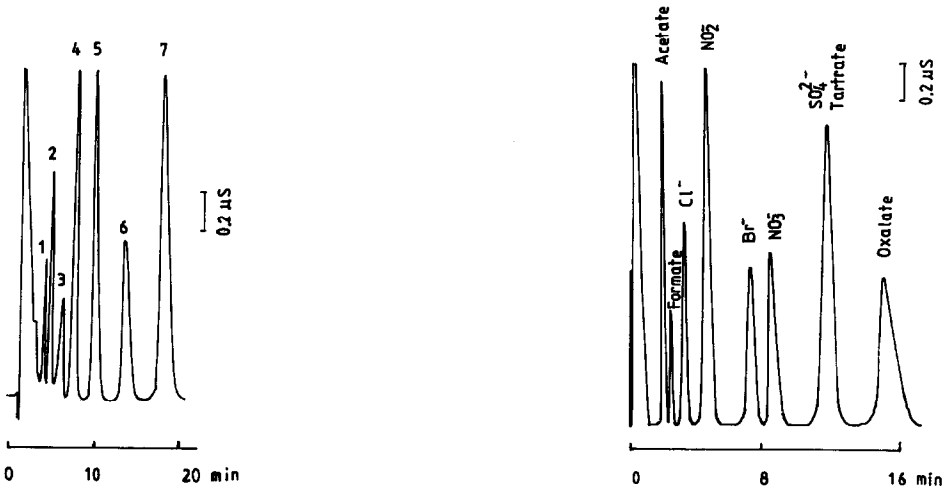H 7.5, flow-rate 2 ml/min. Conductivity detection, sensitivity = 1 μS/cm. Concentrations: HCO_3^- 40, Cl^- 35, Ca^{2+} 20, NO_2^- 20, Mg^{2+} 8, SO_4^{2-} 30, NO_3^- 20 mg/l. × = Reversed negative signal.

Fig. 5. Simultaneous IC of inorganic anions and alkaline earth metal ions with DCTA as eluent. Column: Nucleosil SB. Eluent: 1 mmol/l DCTA, pH 7, flow-rate 2 ml/min. Conductivity detection. × = Reversed negative signal.

Fig. 6. Chromatographic separation of inorganic and organic anions with EGTA as eluent. Column: Nucleosil SB. Eluent: 4 mmol/l EGTA, pH 7.0, flow-rate 2 ml/min. Conductivity detection. 1 = Acetate; 2 = formate; 3 = pyruvate; 4 = Cl^-; 5 = NO_2^-; 6 = $H_2PO_4^-$; 7 = SO_4^{2-}.

Fig. 7. Chromatographic separation of inorganic and organic anions with DTPA as eluent. Column: Nucleosil SB. Eluent: 1 mmol/l DTPA, pH 7.5, flow-rate 2 ml/min. Conductivity detection.
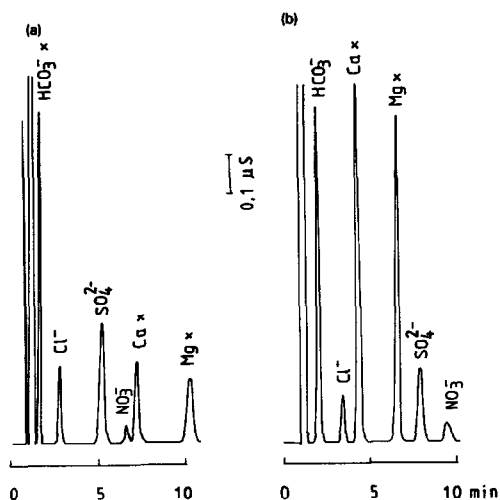
Fig. 8. IC analysis of mineral water with DCTA and EDTA as eluents. Column: Nucleosil SB. Eluent: (a) 3 mmol/l DCTA, pH 6.75, flow-rate 2 ml/min; (b) 2 mmol/l EDTA, pH 7.5, flow-rate 2 ml/min. Conductivity detection, sensitivity = 1 μS/cm, attenuation = 5. Concentrations found: HCO_3^- 180, Cl^- 4.2, NO_3^- 2.0, SO_4^{2-} 7.8, Ca^{2+} 40.2, Mg^{2+} 19.0 mg/l. $\times$ = Reversed negative signal.

of the alkaline earths because of peak broadening owing to the slow chelating reaction.

With DTPA as eluent, NO_3^-, SO_4^{2-}, tartrate and oxalate could be better separated than with other eluents, but DTPA was not suitable for the separation of the alkaline earths for the same reasons as given above for EGTA. A chromatogram for the separation of acetate, formate, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, tartrate and oxalate is shown in Fig. 7.
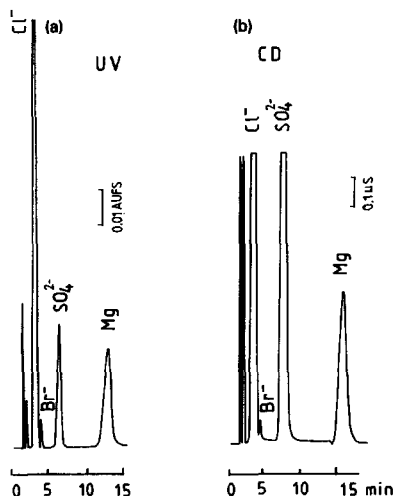

Fig. 9. IC analysis of brine with UV and conductivity detection. Column: Nucleosil Anion II. Eluent: (a) 1 mmol/l DCTA, pH 6.6, flow-rate 1.5 ml/min; (b) 1 mmol/l DCTA, pH 6.0, flow-rate 1.5 ml/min. Detection: (a) UV detector, 205 nm, Range = 0.16 a.u.f.s., attenuation = 4; (b) conductivity detector, sensitivity = 1 μS/cm, attenuation = 5. Concentrations found: Br^- 0.8, Cl^- 220, SO_4^{2-} 80, Mg^{2+} 72 mg/l. $\times$ = Reversed negative signal.
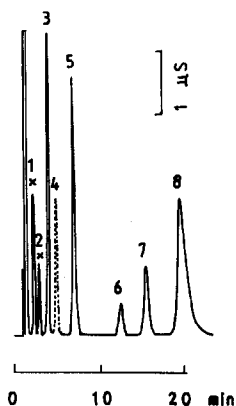
Fig. 10. IC analysis of spinach juice. Column: Nucleosil Anion II (from a batch with higher capacity). Eluent: 3 mmol/l EDTA, pH 5.4, flow-rate 2.5 ml/min. Conductivity detection, sensitivity = 5 μS/cm, attenuation = 4. Concentrations found: 1 = $H_2PO_4^-$ 40; 2 = acetate 20; 3 = Cl^- 45; 4 = NO_2^- 33 (dashed line, reduced from NO_3^- overnight); 5 = NO_3^- 33; 6 = Mg 35; 7 = SO_4^{2-} 32; 8 = oxalate 126. $\times$ = Reversed negative signal.

Application

The proposed method was applied to for the simultaneous determination of some inorganic and organic anions and alkaline earths metal ions in natural samples.

Fig. 8 shows the IC analysis of a mineral water with the Nucleosil SB column and a conductivity detector using EDTA and DCTA as eluents, giving different elution sequence for Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-} and different signal strengths for Ca^{2+} and Mg^{2+}.

Fig. 9 shows the IC analysis of a brine sample in which the trace amount of Br^- present could be successfully separated from the large amounts of Cl^-, SO_4^{2-} and Mg^{2+}. It can be seen that the UV detector was more suitable than the conductivity detector for the detection of trace Br^-.

Fig. 10 shows the chromatogram of freshly squeezed spinach juice which was diluted and filtered first through double-folded filter-papers and then through a 0.2-μm membrane filter. An unexpectedly complete separation and simultaneous determination of oxalate, acetate, Cl^-, NO_3^-, SO_4^{2-} and alkaline earths in this spinach sample was achieved. The sample solution of the spinach juice was not stable and the NO_3^- was enzymatically reduced to NO_2^- if the solution was allowed to stand overnight.

In conclusion, this IC method is a simple, versatile and practical technique for the simultaneous determination of various inorganic and organic anions and metal cations, and may find new applications in the analysis of environmental, food, drink and biomedical samples. An IC determination of urate, oxalate, SO_4^{2-}, Cl^-, Ca^{2+}, Na^+, NH_4^+, K^+, etc., in renal calculi has been achieved and will be reported separately.

ACKNOWLEDGEMENT

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