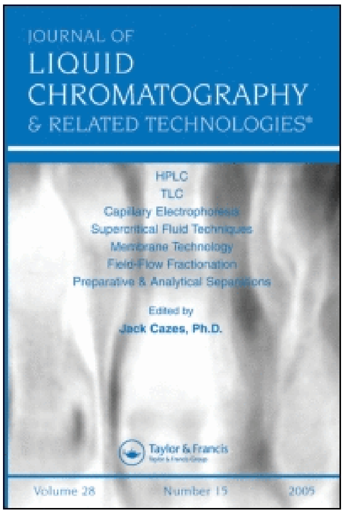

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DETERMINATION OF ANIONS IN WATER SAMPLES BY CAPILLARY ZONE ELECTROPHORESIS WITH INDIRECT UV DETECTION

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ABSTRACT

The separation of anions was performed by capillary zone electrophoresis with indirect UV detection. Optimum conditions for the separation of 12 anions, including the concentration of electroosmotic flow modifier, the concentration of the UV absorbing component and the pH etc. were obtained. This method was applied for the determination of anions in different water samples. The relative standard deviations for the analysis of anions were in the range of 1.2 to 6.9 percent. The detection limits were from 0.12 to 0.84 ppm for the 12 anions.

INTRODUCTION

Ion chromatography (IC) has been widely used to separate and analyze anions since it was introduced into the field of chromatography [1]. The most often and successful application of IC is to separate strong acid anions with conductivity detection [2]. Simultaneous separation of both strong and weak acid anions requires gradient elution to increase peak capacity [3] because of large affinity differences between the strong and weak acid anions to the ion exchange resin. Restrictions have resulted from the specific columns and system complexicity. Inadequate selectivity and efficiency are also potential problems in some applications [1-2].

Capillary zone electrophoresis (CZE) is a relatively new separation method, which is based on the electrophoretic migration of the solutes. CZE has been widely used to separate ionic species with much better efficiency than HPLC and IC. The early application of CZE for the separation of inorganic anions was hampered mainly by the lack of universal detectors. A few studies have been performed using conductivity detector [4-6]. In the past few years, great progress has been made in the separation of inorganic anions using CZE method with indirect detection. The applicability of indirect detection for CZE has been discussed [7,8]. Some works dealing with the separation of organic and inorganic anion have been reported [9-19]. Because of the great influence of electroosmotic flow (EOF) on CZE separations [20], it is often necessary to use EOF modifier to control the EOF and to achieve optimal separation. Excellent separations of anions have been performed by Jones and coworkers [11] using chromate-based electrolyte systems. Optimal conditions for the separation of inorganic and organic anions have been discussed, but the detailed conditions and the EOF modifier were not revealed due to commercial reasons. Another excellent study performed by Harrold *et al* [15] reported on the separation of anions using pyromellitic acid as the UV background providing component and alkyl amine as the EOF modifier.

This paper presents results for the separation of anions using a chromate buffer system with cetyltrimethylammonium bromide as

EOF modifier. The optimum conditions for the separation of organic and inorganic anions were determined. The CZE method developed was applied to the determination of anions in various water samples.

EXPERIMENTAL

Chemicals and materials

Ca 10 mg/ml stock solutions for individual anions were prepared by dissolving a single weighed amount of analytical or better grade sodium or ammonium salt of the anions in deionized water. Standard mixtures at ppm level were prepared by stepwise dilution of the stock solutions fresh daily. Potassium chromate, used as the UV background-providing compound and electrophoresis buffer, was of analytical grade and was obtained from Aldrich (Milwaukee, WI, USA). 14.2 mM cetyltrimethylammonium bromide (CTAB) (Aldrich) solution was prepared by dissolving 0.1293 gram of analytical grade salt in 25 ml water. All solutions were prepared using 18 MΩ water from a Millipore water purification system. All other chemicals and reagents were analytical or better grade. The electrophoresis buffer was prepared from 0.58 M chromate and 14.2 mM CTAB stock solutions daily by stepwise dilutions. CTAB was used as an electroosmotic flow modifier to reverse the electroosmotic flow, so that an electroosmotic flow direction from the cathode to anode was obtained. 1:10 (v/v) high purity nitric acid and 100 mM sodium hydroxide were used to adjust the pH of the electrolyte in the pH study. All the buffers were passed through 0.45 μm membrane filters and degassed by ultrasonication prior to use.

Instrumentation

A home-made capillary electrophoresis system was used for the present investigation. A Spellman model RHR30PN10/RVC high voltage supply with reversible polarity and a maximum capacity of 30 kV was employed. A model UVIS 20 UV detector (Carlo Erba Instruments, Italy) and a piece of fused silica capillary tube of 550 mm total length and 450 mm effective length (from the injection end to the detection window) with 50 μm i.d., were used to perform the separation and determination of anions. On-line detection was carried out through a window by burning off 2 mm of polyimide coating from the capillary tube. Indirect UV detection was performed at 254 nm throughout the experiments. Samples were introduced into the column hydrodynamically by raising the sample vial to a height of 10 cm for 20 or 30 seconds. Samples were introduced into the capillary either from the cathode end when negative polarity power was applied or from the anode end when positive polarity was used. Electropherograms were recorded and processed with a Carlo Erba model PDP 700 integrator. The tap and rain water was passed through a 0.45 μm filter before injection. The mineral water samples were obtained from a supermarket and used for the determination without pretreatment.

RESULTS AND DISCUSSION

Separation of anions with CZE under different electroosmotic flow

When positive polarity power was used to separate anions, no peaks were recorded in the electropherograms except for the water peak. This could be explained by the fact that the electrophoretic flows for anions were in opposite direction to and faster than the electroosmotic flow. In the case that the anions were injected from the anodic end, they could reach the detection cell only when electroosmotic flow overcomes the electrophoretic flows. Since simple anions have relatively large charge to radius ratios, their electrophoretic flows were greater than the electroosmotic flow and hence they would not migrate towards the detector. This is unlike the cases in most CE separations where the electroosmotic flow tends to be great than the electrophoretic flows [21].

When the polarity of the power supply was reversed, anions could reach the anode since their electrophoretic flows were greater than the electroosmotic flow. In such a CZE configuration, of the 12 anions injected into the column, i. e. thiosulphate, bromide, chloride, sulphate, nitrite, nitrate, molybdate, citrate, fluoride, phosphate, carbonate and acetate, the first eight anions were detected and separated within 24 min. The separation is illustrated in Figure 1A. The other anions could not reach the detection window within 1 hour, probably because the electrophoretic flows of these anions were slower than but close to and in opposite direction to the electroosmotic flow (if their electrophoretic flows were much slower than the electroosmotic flow, these anions would be expected to be detectable in a positive polarity CZE configuration [21]), and hence very slow migrations of these anions were expected. To speed up the migration of these anions, CTAB was added to the electrolyte buffer to modify the electroosmotic flow. CTAB concentration was found to affect the migration times of the anions significantly. Figure 1B and 1C show the separation of anions at different CTAB concentrations. At CTAB concentration of 2.0×10^{-5} M, 10 peaks,

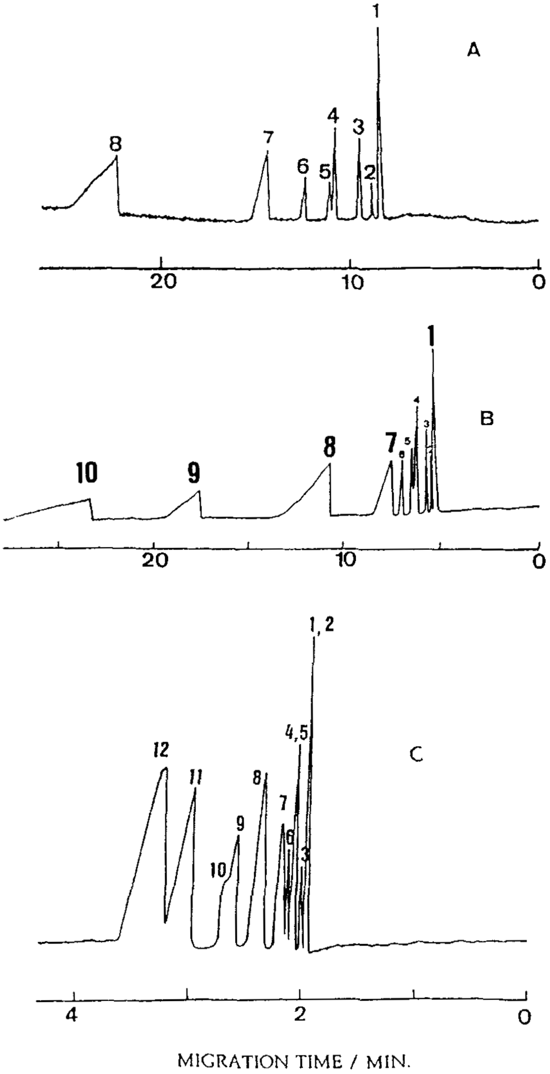

Figure 1. CZE separation of anions at different CTAB concentrations. (A) CTAB = 0 (B) CTAB = 2.0×10^{-5} M (C) CTAB = 6.2×10^{-5} M. CrO_4^{2-} = 5.8 mM; pH = 8.5; 20 kV. CE column, 550 mm X 50 μm i.d. fused silica capillary column (effective length 450 mm). Peak identification. 1 = thiosulphate, 2 = bromide, 3 = chloride, 4 = sulphate, 5 = nitrite, 6 = nitrate, 7 = molybdate, 8 = citrate, 9 = fluoride, 10 = phosphate, 11 = carbonate, 12 acetate.

i.e. the eight peaks obtained in Fig. 1A and fluoride and phosphate, were detected within 25 min and the migration times for all the anions were shortened. At this CTAB concentration, the water peak, used as a marker of the electroosmotic flow, could not be detected in the electropherogram. This indicated that the EOF direction was still from the anode to the cathode, although its speed was hindered by the added CTAB cations which resulted in partial masking of the negative charges of the silanol group on the inner wall of the capillary tube. When CTAB concentration was further increased to 6.2 X 10^{-5} M, all the 12 anions could reach the detection cell, although 3 pairs of anions, i.e. thiosulphate and bromide, sulphate and nitrite as well as fluoride and phosphate, overlapped due to the fast but reversed electroosmotic flow (Fig. 1C). In Fig. 2, the effect of CTAB concentration on the migration times of the anions is shown. It can be seen that the migration times of the anions were greatly shortened by increasing the CTAB concentration to above 4 mM. In subsequent experiments, a CTAB concentration of 4.8 X 10^{-5} M was used to modify the electroosmotic flow and satisfactory separation for the 12 anions was achieved.

The influence of CTAB concentration on the migration times of anions could be explained as follows. At low concentrations of CTAB, the EOF was hampered by the added CTAB cations which reduced the negative charges of the silanol groups on the capillary tube. It was then reversed by the further increases in the CTAB concentration due to the positive charges of CTAB, and finally the reversed EOF reached a maximum when the capillary surface was completed covered by CTAB. This process resulted in the greatest increase in the migration velocities for the anions

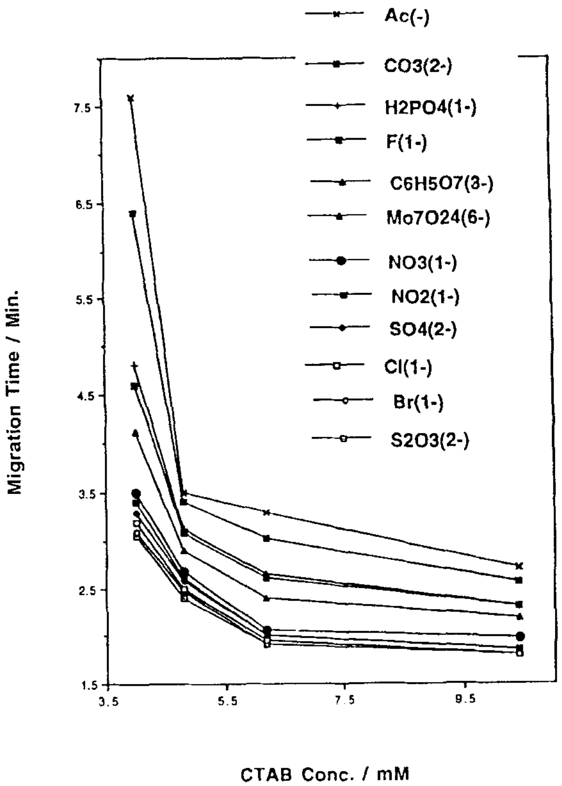

Figure 2. Effect of CTAB concentration on the migration times of anions. Conditions as in Fig. 1.

at low concentration of CTAB in buffer (see Fig. 2), and the increase in the migration velocities at higher concentrations was not so remarkable once the EOF reached a maximum when the surface of the silica capillary was saturated with CTAB.

Effects of chromate concentration on the separation of anions

The effect of chromate on the separation of anions could be attributed to two aspects. The first consideration is the UV detection, which requires a low chromate concentration to achieve high sensitivity in the indirect UV mode. This is becasue the noise level in an indirect UV system is proportional to the concentration of the UV background-providing component [20]. In addition, chromate concentration affects the ionic strength of the electrophoresis buffer. A high chromate concentration increases the current passing through the column, resulting in a high noise level due to inadequate dissipation of the Joule heat. For these reasons, the chromate concentration should be kept low. On the other hand, a decrease in chromate concentration results in a decrease in the efficiency of displacement of the background ions by the sample ions [7], which is a function of the ratios of the analyte to the UV background component. As a result, a low sample loading capacity and narrow linear dynamic range would be expected [15]. Furthermore, if the concentration of chromate is too low, a decrease in the peak efficiency would be obtained, since the CZE efficiency is expected to increase with an increase in ionic strength [22], provided that effective heat dissipation can be achieved. Figure 3 shows the influence of the concentration of chromate on the migration times of the anions. The migration times of the anions increased with an increase in the concentration of chromate due to the slower EOF at higher chromate concentration.

From Fig. 3, the optimum concentration of chromate for the separation of the anions could be found. Although the separation for anions was generally improved at higher chromate concentration, particularly for fluoride and phosphate, as well as for sulphate and nitrate, at chromate concentration of 11.8 mM, the peaks for thiosulphate and bromide overlapped. Figure 4

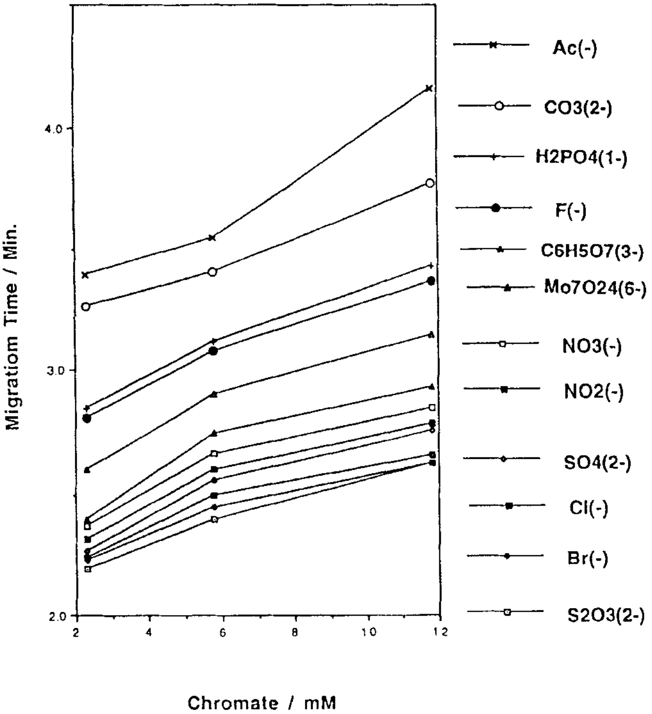

Figure 3. Effect of chromate concentration on the migration times of anions. CTAB = 4.8 X 10^{-5} M. Other conditions and peak identifications as in Fig. 1.

shows the electropherograms of anions at three different concentrations of chromate. It can be seen that the resolution and sharpness of the peaks were significantly affected by changes in the concentraction of chromate. In the present work, chromate buffers at concentrations in the range of 5.8 to 8.2 mM was used as electrophoresis buffers for the separation of anions which provided reasonably good efficiencies and sensitivities.

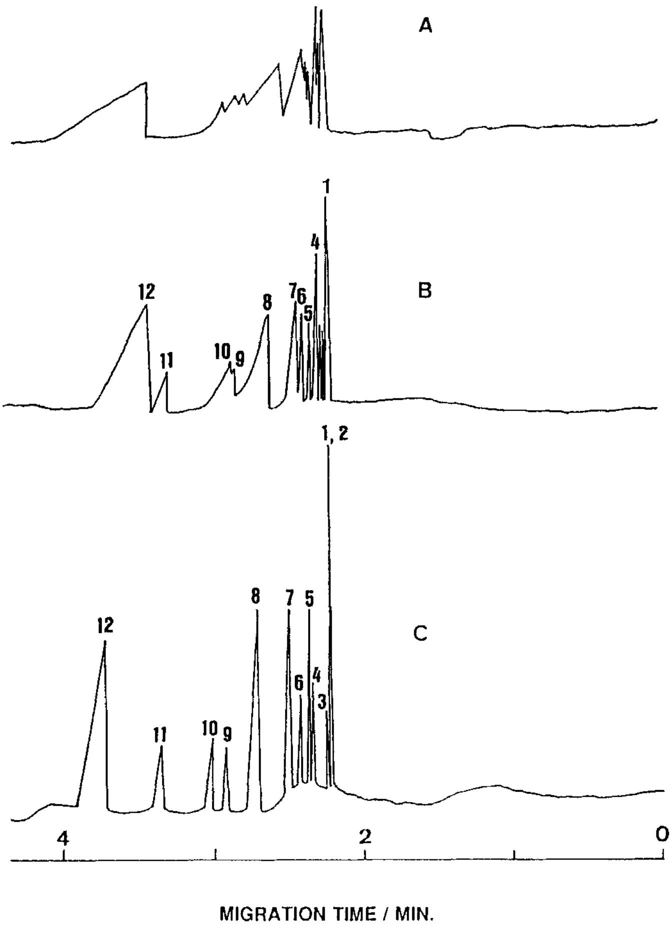

Figure 4. Separation of anions at different chromate concentrations. (A) CrO_4^{2-} = 0.85 mM (B) CrO_4^{2-} = 2.3 mM (C) CrO_4^{2-} = 10.8 mM. CTAB = 4.8 X 10^{-5} M. Other conditions as in Fig.2. Peaks in (A) were not identified, and peak identification in (B) and (C) as in Fig. 2.

Effect of pH of the electrolyte buffer on the separation of anions

The migration times of anions decreased with an increase in pH in the pH range of 7 to 12, mainly due to the slower electroosmotic flow at lower pH (Figure 5). This observation was consistent with an earlier investigation [9]. The 12 anions could be separated within the pH range of 6.5 to 11.5, but bromide comigrated with thiosulphate at pH 11.5 or higher. The migration order for strong acid anions was not changed in this pH range. However, the migration times for the weak acid anions, i.e. carbonate, phosphate and acetate, were affected significantly by changes in pH. This could be explained by the fact that these anions were progressively protonated as the pH of the electrophoresis buffer was decreased. As a result, their electrophoretic velocities became slower since the migration rates of the anions were mainly controlled by the charge to anion size ratio. Fluoride and phosphate, which overlapped with each other at pH higher than 11.5 due to the fast migration of the completely ionized phosphate at high pH, could be separated completely at lower pH. Migration rate of carbonate increased remarkably at pH higher than 9.5, and it migrated ahead of phosphate, fluoride and citrate and just after molybdate at pH 11.5. The migration time for acetate was relatively long in the pH range of 6.5 to 8.5. Figure 6 illustrates the separations of anions at pH 9.5 and 12.0. Since a pH value lower than 6.5 was not applicable because of the change of chemical form of chromate, and pH higher than 12.5 resulted in very noisy baseline, in this investigation, the pH range 7.5 to 10 was used to perform the determination of anions in water samples.

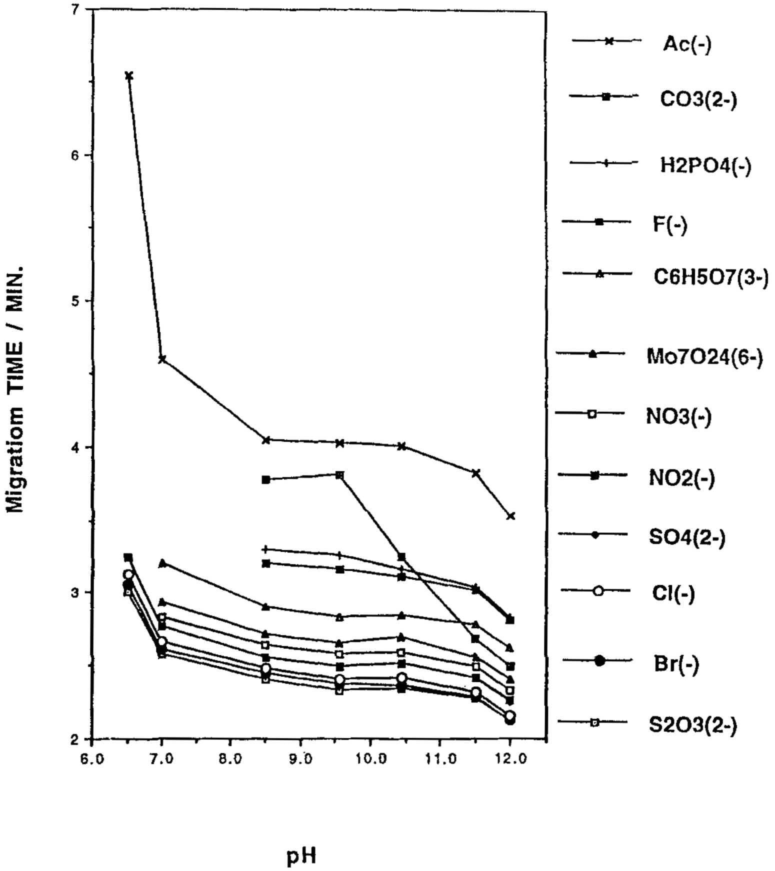

Figure 5. Effect of pH on migration times of anions. CTAB = 4.8 X 10^{-5} M, CrO_4^{2-} = 5.8 mM. Other conditions and peak identification as in Fig. 1.

Figure 7 illustrates a typical CZE separation of 12 anions using the optimal conditions obtained above. 12 anions were separated within a migration time window of 89 seconds.

APPLICATIONS

To demonstrate the usefulness of the CZE method developed, analyses of a variety of samples were performed. The

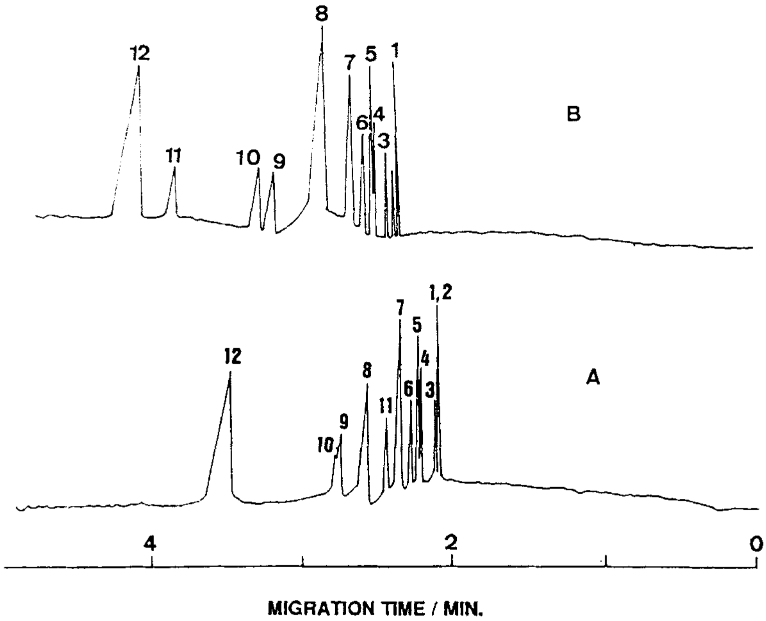

Figure 6. Separation of anions at different pH values. (A) pH =9.5 (B) pH = 12.0 CTAB = 4.8 X 10^{-5} M. Chromate = 5.8 mM. Other conditions and peak identification as in Fig. 1.

electropherograms obtained are shown in Figure 8 to Figure 12. Result of the quantitative analysis are included in Table 1 and II.

Figure 8 is an electropherogram of anions in tap water obtained using an applied voltage of 25 kV and a buffer containing 8.2 mM chromate as the UV absorbing component. Four anions, i.e. chloride, sulphate, nitrate and carbonate, were identified by spiking the sample with standards, and an unknown peak was observed. Figure 9 shows the CZE separation of anions in a commercial mineral spring water. In this and subsequent

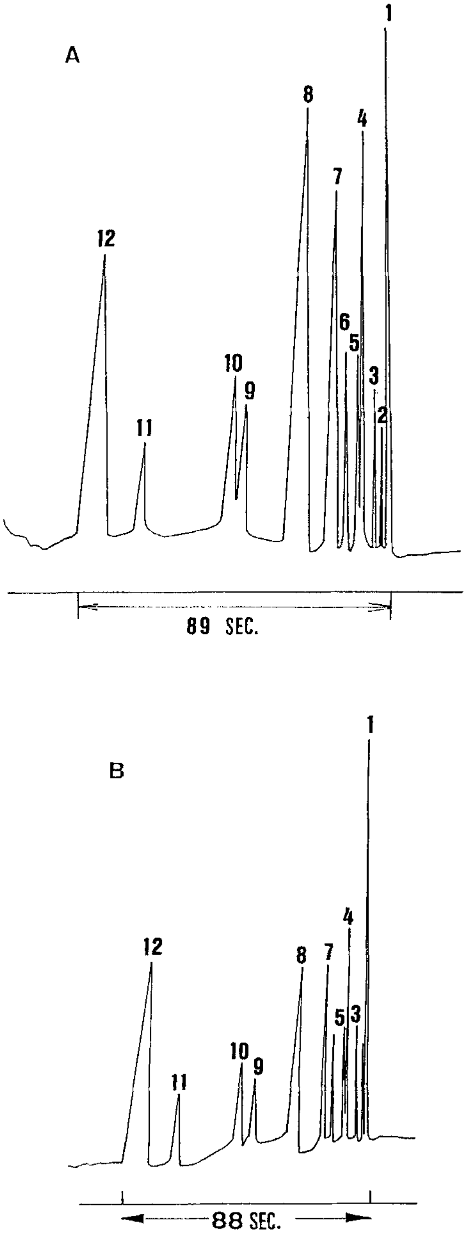

Figure 7. Typical CE separation of anions using the optimal conditions. Peak identifications as in Fig. 1.

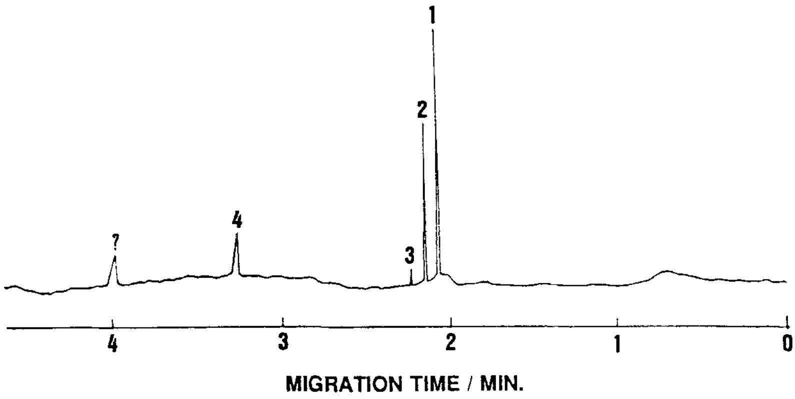

Figure 8. Electropherogram of anions in tap water. peak identification: 1 = chloride, 2 = sulphate, 3 = nitrate, 4 = carbonate, 5 = unknown. Other conditions as in Fig. 7.

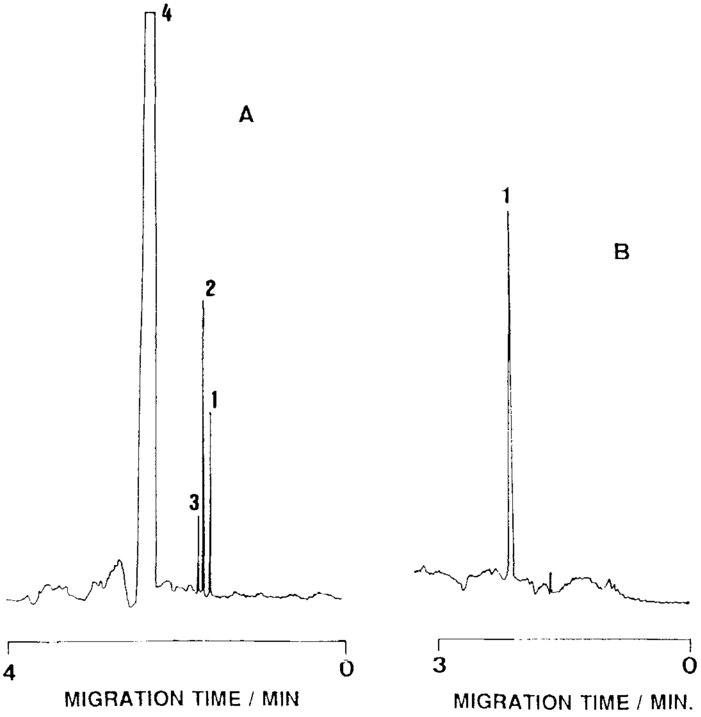

Figure 9. Electropherogram of anions in mineral spring water "Evian". 1=chloride; 2=sulphate; 3=nitrate; 4=bicarbonate. CZE conditions: 8.2 mM Chromate, 4.8 X 10-5 M CTAB, 25 KV applied voltage. Other conditions as in Fig. 1.

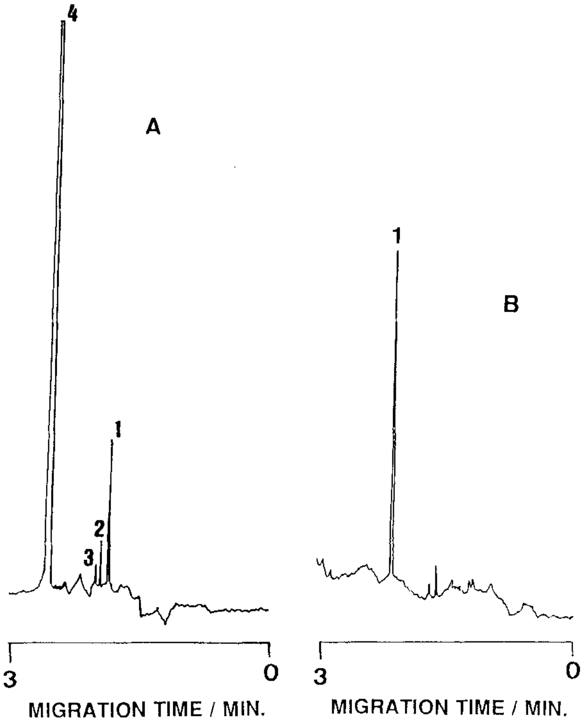

Figure 10. Electropherogram of anions in mineral spring water "Amust". 1=chloride, 2=sulphate, 3=nitrate, 4=bicarbonate. CZE conditions as in Fig. 9.

determinations, the applied voltage was 30 kV and a buffer containing 8.2 mM chromate was used to separate the anions. Very fast separation and high efficiencies for anions were obtained. Figure 10 is the electropherogram for anions in another mineral water sample, the concentrations of anions in the sample in Figure 10 are lower than those in sample in Figure 9. Figure 11 presents the separation of anions in a rain water sample.

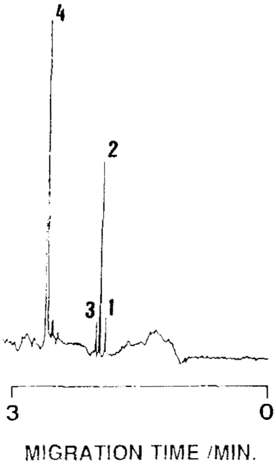

Figure 11. Electropherogram of anions in rain water sample. 1=chloride, 2=sulphate, 3=nitrate, 4=carbonate. CZE conditions as in Fig. 9.

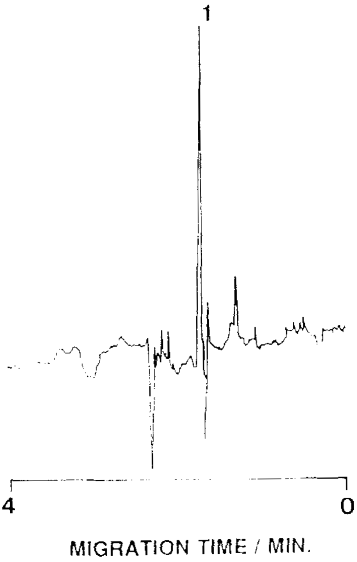

Figure 12. Electropherogram of anions in Pepsi-cola. 1=phosphate. Other conditions as in Fig. 9.

Table I. Analytical Results of anions in water samples.

	Concentration (ppm)				
	Cl^-	SO_4^{2-}	NO_3^-	CO_3^{2-}	PO_4^{3-}
1. tap water:					
Measured value	32.3	31.0		5.0	
R. S. D. (%)	3.6	4.5		2.7	
	(n=4)	(n=3)		(n=4)	
2. Mineral water "Evian":					
Reference value	4	10	1	357	NA
Measured Value	4.9	8.17	1.25	407	NA
RSD (%)	1.2	1.6	4.3	2.4	--
	(n=3)	(n=3)	(n=3)	(n=3)	--
3. Mineral water "Amust":					
Reference value	NA	0.94	0.11	59.1	NA
Measured value	4.0	1.24	ND	59.1	ND
RSD (%)	1.4	6.5	--	2.8	--
	(n=4)	(n=3)	--	(n=3)	--
4. Rain water					
Measured value	0.83	0.53	ND	ND	ND
RSD (%)	6.9	6.1	--	--	--
	(n=3)	(n=3)			
5. Pepsi-cola					
Measured value	--	--	--	--	1052
RSD (%)	--	--	--	--	5.62
					(n=3)

*: Chemical forms for carbonate and phosphate were not determined
NA: not available
ND: not detected

Table II. Detection limits of anions using CE method (ppm)[a].

thiosulphate	0.84
bromide	0.50
chloride	0.17
sulphate	0.16
nitrite	0.42
nitrate	0.25
molybdate	0.80
citrate	0.55
fluoride	0.13
phosphate	0.14
carbonate	0.27
acetate	0.37

[a]: based on 23.5 nl injection

Sulphate was quantitatively determined. It is suggested that the CZE method adopted here could be used for the monitoring of other anions of environmental interest. Figure 12 is the electropherogram of a soft drink (Pepsi-cola) after 40 times dilution. Phosphate was identified and quantitatively determined.

Table I summarizes the analytical results for the determination of anions in water samples with the CZE method. In Table II, the detection limits of the anions are listed. The detection limits were below 1 ppm, and are comparable to those typically obtained by ion chromatography (IC).

The results obtained in the present experiments showed that CZE provides a rapid and reliable method for the determination of anions in aqueous samples. Determination of anions in many different matrices can be readily carried out without the need to perform extensive sample preparations.

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