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Analysis of anions in drinking water by capillary ion electrophoresis

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Abstract

Capillary ion electrophoresis (CIE) (Waters' trade name: Capillary Ion Analysis, CIA) is a capillary electrophoretic technique which is optimized for the rapid analysis of low-molecular-mass inorganic and organic ions. An electroosmotic flow modifier (OFM) was added to the chromate electrolyte and a negative power supply was used. Indirect UV detection at 254 nm was used throughout. Analysis of anions in a variety of drinking water samples was done. Anion analysis using this technique is rapid (less than 5.5 min), with little sample preparation required. Comparison of anion amounts found using CIA and conventional suppressed ion chromatography (IC) was done with good correlation between the two techniques.

Keywords: Water analysis; Capillary elctrophoresis; Drinking water; Anions.

1. Introduction

Currently, ion chromatography (IC) is the method for analysis of drinking water samples by the U.S. EPA. However, capillary ion electrophoresis (CIE) is an emerging technology which offers advantages over conventional IC. Some of these advantages include fast analysis times, few moving parts, small compact design, and the ability to rapidly convert from anion to cation analysis in minutes rather than hours by conventional IC. Also, the column used in CIE is an open tubular capillary, which allows for minimal sample preparation and is far less expensive than IC columns. Since the separation is performed using electrolytes there is less solvent consumption than by IC (milliliters as compared to liters). The compact design of the CIE also allows for it to be easily transported or used in a mobile laboratory.

Anion analysis was done using a chromate, high mobility, electrolyte with an osmotic flow modifier (OFM), which has been previously shown to be a sensitive technique for the analysis of anions in a variety of matrices including ground and drinking water [1–7]. OFM was added to the electrolyte as an additive that reverses the normally cathodic direction of the electroosmotic flow (EOF) that is found in fused-silica capillaries. This creates a co-electroosmotic condition that augments the mobility of the analytes. To correct for any migration time shifts, isomigration was used. These migration shifts are found in various chemistries and are due to conductance differences between samples. As the sample conductance increases the ions

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migrate through the capillary faster. This phenomenon is known as reverse electrostacking and has been described previously by Jandik and Bonn [8]. Isomigration is a proprietary feature (U.S. patent pending) which is built into the CIA unit to correct for these conductivity differences. The purpose of this paper is to analyze and compare drinking water samples using both IC and CIE, which have been shown previously to provide comparable information on anions in ground and wastewater samples [6,7].

2. Experimental

2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta 4000 (Waters Corporation, Milford, MA, USA) with a negative power supply. A Hg lamp was used for indirect UV detection at 254 nm. AccuSep polyimide fused-silica capillaries of dimension 60 cm × 75 μm I.D. were used throughout. The IC system employed consisted of a 616 pump, 717 + autosampler and M432 conductivity detector (all from Waters Corporation, Milford, MA, USA). An IC-Pak HR Anion column (75 mm × 4.6 mm I.D.) in conjunction with an Alltech suppressor (Alltech Associates, Deerfield, IL, USA) was used for IC analysis.

Data acquisition was carried out with a Waters Millennium 2010 Chromatography Manager with SAT/IN modules connecting the CE and IC systems to the data station with the signal polarity inverted from the CE. Detector time constant for the CE was set at 0.1 s and the data rate for the CE was 20 points/s and 1 point/s for the IC system. Collection of electropherographic and chromatographic data was initiated by a signal connection between both the CE and manual injector and the SAT/IN module.

2.2. Preparation of electrolytes and mobile phases

High-purity water (Milli-Q) was used to prepare all solutions (Millipore, Bedford, MA, USA). The chromate electrolyte was prepared from a concentrate containing 100 m*M* sodium chromate tetrahydrate (Fisher Scientific, Pittsburgh, PA, USA) and 0.0056 m*M* sulfuric acid (J.T. Baker, Phillipsburg, NJ, USA; Ultrex grade). Osmotic flow modifier (OFM) for reversal of the direction of the electroosmotic flow (EOF) was a 20-m*M* concentrate (CIA-Pak OFM anion BT) obtained from Waters. The working electrolyte for anion analysis consisted of 4.5 m*M* chromate–0.4 m*M* OFM. The working electrolyte was prepared fresh daily and degassed prior to use. CIA methods are covered under U.S. patents 5 104 506, 5 128 055, and 5 156 724. The mobile phase for IC analysis consisted of 1.2 m*M* Na_2CO_3 and 1.2 m*M* $NaHCO_3$ with a flow-rate of 1.0 ml/min.

2.3. Reagents

All standard solutions were prepared by diluting 1000 mg/ml stock solutions containing the individual anions. Concentrated standards were prepared from their salts and were of ACS grade or better.

2.4. Calibration

Duplicate injections of three different levels of standards ranging in value from 1–16 mg/ml were done. Correlation coefficients of 0.99X, with X being a value of 7 or better, were obtained by IC and CIE. A linear fit was used in generating the calibration plot. Samples were diluted in high-purity water and injected in triplicate and R.S.D. information was calculated.

3. Results and discussion

Fig. 1 is an electropherogram (Fig. 1A) and chromatogram (Fig. 1B) of an anion standard by CIE and IC. One important feature that is apparent is the speed of analysis of CIE. Total analysis times of under 5.5 min were achieved by CIE, while analysis of the same sample by suppressed IC took over 22 min. Fig. 2 shows a comparison of the same water sample analyzed

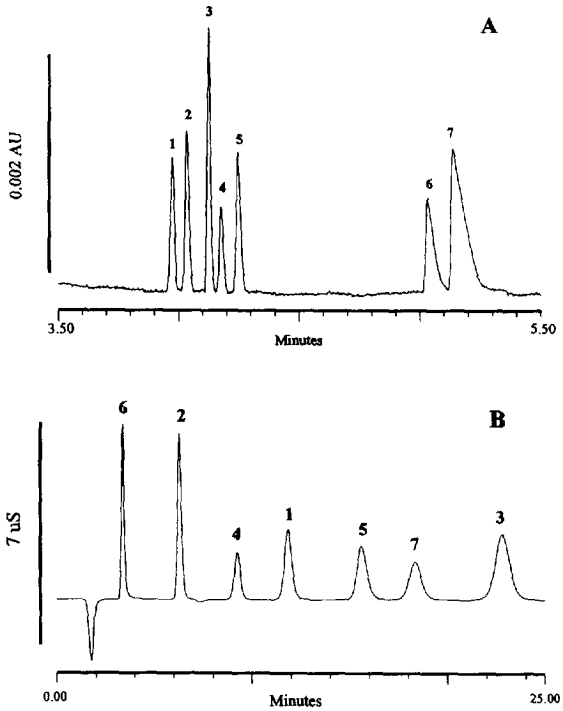

Fig. 1. Anion standard analyzed by CIE (A) and by IC (B). CIE conditions: fused-silica capillary, 60 cm × 75 μm I.D.; voltage 15 kV (negative); 4.5 m*M* chromate–0.4 m*M* CIA-Pak OFM Anion (patented); indirect UV detection at 254 nm; hydrostatic injection (9.8 cm for 30 s). IC conditions: IC-Pak A-HR column; mobile phase: 1.2 m*M* $NaHCO_3$–1.2 m*M* Na_2CO_3; flow-rate: 1.0 ml/min; 100 μl injection; conductivity detection. Peaks: 1 = bromide (4.0 mg/l); 2 = chloride (2.0 mg/l); 3 = sulfate (4.0 mg/l); 4 = nitrite (4.0 mg/l); 5 = nitrate (4.0 mg/l); 6 = fluoride (1.0 mg/l); 7 = hydrogen phosphate (6.0 mg/l).

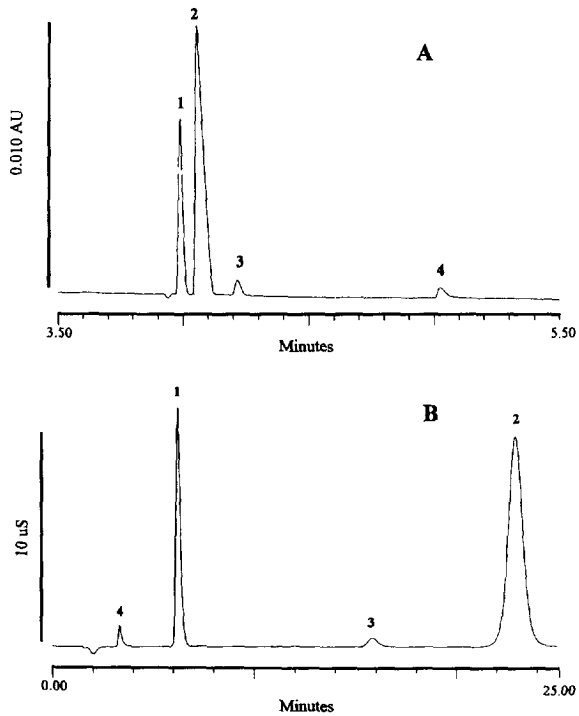

Fig. 2. Drinking water sample No. 1 analyzed by CIE (A) and by IC (B). Sample diluted 1:1 in Milli-Q water. Experimental conditions the same as in Fig. 1. Peaks: 1 = chloride (17.68 mg/l); 2 = sulfate (69.13 mg/l); 3 = nitrate (3.47 mg/l); 4 = fluoride (0.92 mg/l).

by CIE (Fig. 2A) and IC (Fig. 2B). Typical anions found in all samples were chloride, nitrate, sulfate, and fluoride.

One difference between IC and CIE is the peak shape found in CIE, especially for the fluoride and hydrogen phosphate peaks. This non-symmetrical peak shape is due to the electrostacking condition [8,9]. This electrostacking condition requires that the sample zones have a similar ionic strength as the carrier electrolyte. For ions that have different, slower, mobilities than the electrolyte a non-symmetrical peak shape can occur. This peak shape is common in CIE but can lead to confusion when seen by those unaccustomed to these peak shapes. Further, peak identification can be challenging due to the non-symmetrical peak shapes. To correct for this and other features common to CIE analysis, two software options were used. First, the migration time at half peak width was used for identification. This allows any minor time variations in CIE not to interfere with peak identification. Second, time corrected area (peak area/peak migration time) was used for quantitation. This method, which has been discussed previously, corrects for any peak area changes due to migration time shifts [10–12]. These features in conjunction with isomigration were used for calibration of standards and quantitation of drinking water samples. Table 1 is a summary of the amounts found of each anion using both techniques (IC and CIE), with the %R.S.D. shown in parenthesis. As shown in Table 1, comparable results were obtained by CIE as compared to IC.

Table 1

Comparison of drinking water samples analyzed by CIE and IC

Anion	Drinking water sample No. 1		Drinking water sample No. 2	
	Amount by CIE (mg/l)	Amount by IC (mg/l)	Amount by CIE (mg/l)	Amount by IC (mg/l)
Chloride	17.72 (0.06)	17.68 (0.03)	19.87 (0.21)	19.18 (1.23)
Fluoride	0.80 (1.41)	0.91 (0.56)	0.70 (0.60)	0.72 (1.80)
Nitrate	3.54 (1.46)	3.47 (0.82)	3.81 (0.91)	3.77 (0.98)
Sulfate	68.10 (0.22)	69.13 (0.08)	58.56 (0.21)	56.85 (1.16)

%R.S.D. in parenthesis.

4. Conclusions

The results of this work show how CIE, using chromate electrolyte and indirect detection can be used for the analysis of drinking water samples. Comparable results can be obtained using CIE as compared to IC, with faster analysis times possible using CIE. Further, the software and hardware options provided in the CIE instrumentation allow for easier peak identification as well as correction for any migration time shifts.

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