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Versatility of capillary electrophoresis of anions with a high-mobility chromate electrolyte

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Abstract

Capillary ion electrophoresis (Waters' trade name: Capillary Ion Analysis) is a capillary electrophoretic technique which is optimized for the rapid analysis of low-molecular-mass inorganic and organic ions. Indirect UV detection at 254 nm was used throughout. An electroosmotic flow modifier was added to the chromate electrolyte and a negative power supply was used. Analysis of anions in a variety of samples with differing matrices was investigated. Examples discussed include trace level anions in power plant water (ng/ml) and μg/ml level of anions in intermediate and concentrated sulfonated dyes. Anion analysis using this technique is rapid (less than 5 min), with little sample preparation required. The same electrolyte composition, with only minor variations, was used for all samples. Both hydrostatic mode of injection for ppm level analysis and electromigration mode of injection for trace level analysis was used.

1. Introduction

Anion analysis using a chromate, high-mobility, electrolyte with an osmotic flow modifier (OFM) has been previously shown to be a sensitive technique for the analysis of anions [1–3]. The purpose of this paper is to show examples of specific applications using this high-mobility electrolyte. 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.

The first example is of low-level anion analysis, part-per-billion (ppb), for sulfate and nitrate in water samples from a coal fired power plant. Current ion chromatographic (IC) techniques require extensive trace enrichment and run times of approximately 12–15 min. Capillary ion electrophoresis (CIE) (Waters' trade name: Capillary Ion Analysis, CIA) allows for fast (less than 5 min) analysis times. Electromigration was used as an injection mode since it has been shown to be a good injection mode for low level anion analysis [2]. Sodium octanesulfonate was added as well, as an electromigrative additive to improve the trace enrichment process [2]. OFM, in the hydroxide form, was added to the chromate electrolyte. The hydroxide form of the OFM was used so as to make final the working electrolyte pH more alkaline than it is in the normal bromide form.

The second set of examples is μg/ml level anion analysis of intermediate and concentrated

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sulfonated dyes. For these samples a chromate electrolyte was used as well, with OFM added in the standard Br form [4]. IC was also employed, in the analysis of the sulfonated dyes for comparison purposes.

2. Experimental

2.1. Instrumentation

The capillary electrophoresis (CE) system employed was the Quanta 4000 (Waters Chromatography Division of Millipore, 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 6000A pump, U6K manual injector and M431 conductivity detector (all from Waters). An IC-Pak A Anion column was used for IC analysis. A borate–gluconate mobile phase was used [4].

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

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). OFM for reversal of the direction of the EOF was a 20 m*M* concentrate (CIA-Pak OFM anion BT) obtained from Waters. For low-level trace enrichment analysis the OFM was converted to the hydroxide form by passing the OFM through an ion-exchange resin (AG1-X8, OH form; Bio-Rad, Richmond, CA, USA). The working electrolyte for low-level analysis consisted of 7 m*M* chromate–0.7 m*M* OFM-OH. For μg/ml-level analysis OFM was added without any pretreatment [4]. The working electrolyte for standard, μg/ml-level analysis, consisted of 5 m*M* chromate–0.5 m*M* OFM-BT, pH 8.1 [5]. All working electrolytes were prepared fresh daily and degassed prior to use.

2.3. Reagents

All standard solutions were prepared by diluting 1000 μg/ml stock solutions containing the individual anions. For the CIE and IC analysis of the sulfonated dyes the same standard solutions were used. For trace-level analysis all samples and solutions were stored in pre-rinsed plastic ware. Sodium octanesulfonate (VHG Labs., Manchester, NH, USA) was added to standards and samples for trace enrichment (100 μl per 100 ml solution). To prevent contamination from handling, disposable, non-talc, gloves were worn.

2.4. System operation

Two sample carousel configurations were employed for the CE system. The 13-position carousel used 4-ml (45 × 15 mm) polypropylene Sunvials (Sunbrokers, Wilmington, NC, USA) for electrolytes and samples. The 20-position carousel used 600-μl polypropylene centrifuge tubes (Waters) for sample vials and 20-ml HDPE sample side electrolyte vials (Waters). Receiving side electrolyte vials were 20-ml glass scintillation vials (Waters) for both carousels. The 13-position carousel was used for ng/ml-level analysis since the larger sample vial size allowed for easier rinsing of the vials and minimized contamination. The 20-vial carousel was used for μg/ml-level analysis.

3. Results and discussion

3.1. Low-level analysis (ng/ml)

For the analysis of low-level anions using trace enrichment techniques a water blank must be run and the amounts adjusted for any anions present which are to be quantitated [2]. Duplicate injections of three different levels of standards ranging in value from 8–36 ng/ml was done. Correlation coefficients of 0.999, for both anions calibrated, was calculated using a linear fit. Fig. 1 is an electropherogram of an anion standard. The samples analyzed from the power plant were found to contain extremely low amounts of anions. Fig. 2 is an example electropherogram of one of the samples. At these low levels the anions were below the intercept of the calibration curve with the exception of sulfate, in Fig. 2, which was 9 ng/ml. All samples were well below the 15 ng/ml limit set by the plant. Other peaks in the electropherograms correspond to unidentified anions or small organic acids.

3.2. μg/ml level analysis of dyes

Sulfate analysis was of the most interest since it is involved in the manufacturing of the sul-

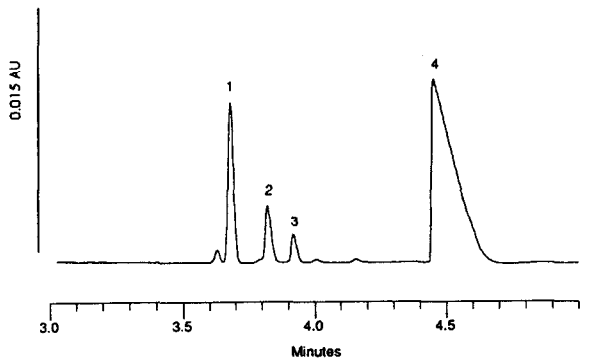

Fig. 1. Electropherogram of anion standard. CIE conditions: Fused-silica 60 cm × 75 μm I.D. capillary; voltage 15 kV (negative); 7 m*M* chromate–0.7 m*M* CIA-Pak OFM Anion (patented) OH form; indirect UV detection at 254 nm; electromigration injection (5 kV for 45 s). Peaks: 1 = chloride (contaminant); 2 = sulfate (16 ng/ml); 3 = nitrate (13 ng/ml); 4 = carbonate (contaminant).

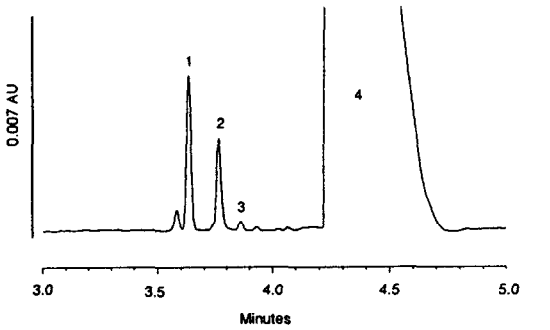

Fig. 2. Electropherogram of boiler sample (neat). CIE conditions as in Fig. 1. Peaks: 1 = chloride (not quantitated); 2 = sulfate (9 ng/ml); 3 = nitrate (< 5 ng/ml); 4 = carbonate (not quantitated).

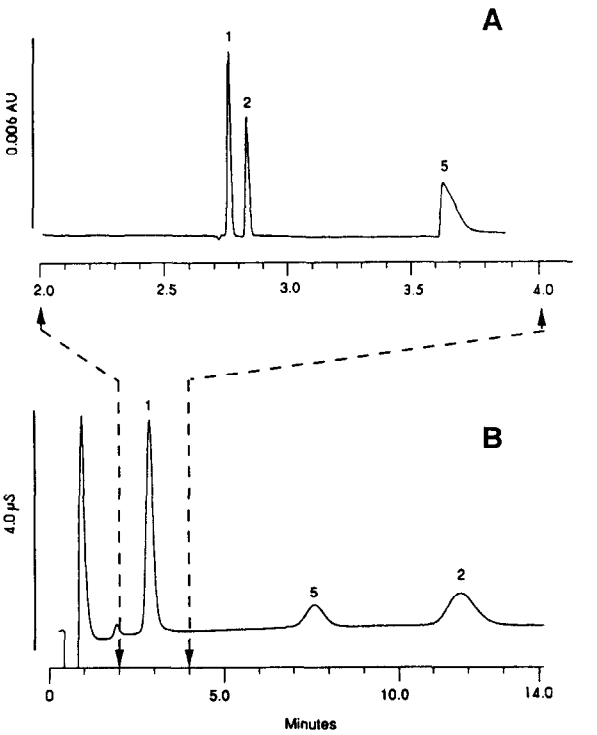

Fig. 3. 10 μg/ml chloride, sulfate and phosphate standard. (A) Electropherogram. Conditions, capillary: 60 cm × 75 μm I.D.; voltage: 18 kV (negative); 4.5 m*M* chromate–0.5 m*M* CIA-Pak OFM Anion-BT, pH 8.1; indirect UV at 254 nm; hydrostatic injection (10 cm for 30 s). (B) Chromatogram from IC system. Conditions, column: Waters IC-Pak Anion A; eluent: modified borate–gluconate, flow-rate: 1.2 ml/min, detection: conductivity. Peaks: 1 = chloride; 2 = sulfate; 5 = phosphate. One noticeable advantage of CIE is in the time of analysis as compared to IC.

fonated dyes. Other anions, chloride and phosphate, were quantitated as well for comparison purposes with IC. As mention previously, CIE offers the ability to analyze for anions fairly quickly (about 5 min). Fig. 3 exemplifies this since one CIE run can be done in less than 4 min. In this case if sulfate was the only anion of interest the run could be stopped at 3 min and the capillary purged briefly to replenish the capillary with electrolyte and another analysis started. A linear calibration curve was plotted for duplicate injection of three different levels of standards from 5–25 μg/ml. Correlation coefficients, for both IC and CIE, were 0.999 for all anions calibrated. Figs. 4 and 5 are of different in-process dyes. As can be seen in Fig. 5, CIE was able to easily detect phosphate in the blue dye sample. Table 1 shows a comparison between CIE and IC for the two samples analyzed. As can be seen the values determined from both techniques agreed quite well. One disadvantage

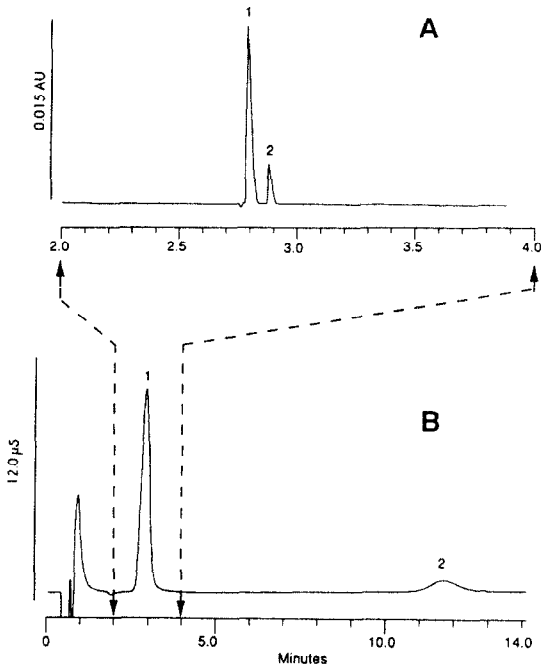

Fig. 4. Intermediate green dye. Diluted 1:50 with high-purity water. Conditions as in Fig. 3. (A) Electropherogram. (B) Chromatogram from IC. Peaks: 1 = chloride; 2 = sulfate. Amounts found listed in Table 1.

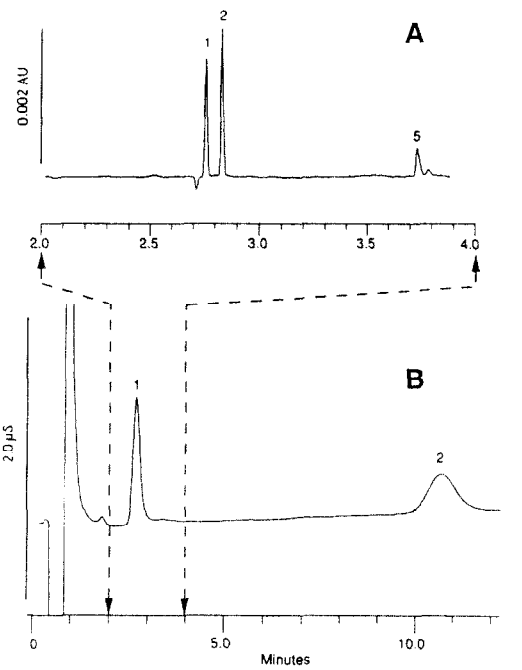

Fig. 5. Concentrated blue dye. Run neat. Conditions as in Fig. 3. (A) Electropherogram. (B) Chromatogram from IC. Peaks: 1 = chloride; 2 = sulfate; 5 = phosphate. Amounts found listed in Table 1.

of IC for the analysis of sulfonated dyes was that the dyes tended to adhere to the column causing column degradation and loss of resolution. This could be seen by the column effluent which became discolored from the dyes and remained discolored for several column volumes after the run. Even with a pre-column the analytical column still degraded quite rapidly. With CIE there was no apparent loss of efficiency over time since the capillary is hollow and the purge incorporated at the end of the run flushed the capillary with new electrolyte.

4. Conclusions

The results of this work show how CIE, using chromate electrolyte and indirect detection can be used for a variety of samples. CIE offers the advantage over IC for rapid analysis of anions as well as no noticeable sample adsorption as was seen with the sulfonated dyes on the IC column.

Table 1
Quantitative results of sulfonated dyes by CIE and IC

	Cl^-	R.S.D. (%)	SO_4^{2-}	R.S.D. (%)	HPO_4^{2-}	R.S.D. (%)
CIE (average amount in μg/ml, n = 2)						
Blue dye	2.78	0.94	4.69	0.56	0.89	1.55
Green dye	1897	0.87	503	1.32	N.D.[a]	–
IC (average amount in μg/ml, n = 2)						
Blue dye	2.64	0.67	4.33	0.03	N.D.	–
Green dye	1909	0.13	497	0.27	N.D.	–

[a] N.D. = None detected.

Work continues in our laboratory investigating additional applications for CIE. As of now, CIE offers a complementary method of analysis and in some cases a superior and less expensive means of analysis than IC.

5. Acknowledgement

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5. References

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