ELSEVIER

Journal of Chromatography A, 696 (1995) 349–352

JOURNAL OF CHROMATOGRAPHY A

Short communication

Separation of fast anions by capillary electrophoresis without flow reversal

G.W. Tindall*, R.L. Perry

Research Laboratories, Eastman Chemical Company, Kingsport, TN 37662, USA

First received 22 July 1994; revised manuscript received 16 November 1994; accepted 14 December 1994

Abstract

Anions with high electrophoretic mobilities (fast anions) cannot easily be separated on bare silica columns by capillary electrophoresis unless the electroosmotic flow is reversed. The materials used to reverse flow limit the selection of indirect chromophores as well as complicate the direct detection of ions that do not need indirect detection. The availability of columns permanently coated to reduce electroosmotic flow could provide the means to separate fast anions without the need for a flow reversal agent. Useful separations of fast anions were achieved on commercially available silane-coated columns. These columns were particularly useful for the analysis of anions that could be detected by direct detection.

1. Introduction

Numerous applications of capillary electrophoresis have been reported for the determination of anions [1–9]. Bare silica capillaries are normally used and their surface is negatively charged at the pH typically used for separation. A corresponding positive charge in the capillary electrolyte results in bulk flow (electroosmotic flow) when voltage is applied. The net velocity of an anion is the vector sum of its electrophoretic velocity and its electroosmotic flow velocity. In anion analysis, an electroosmotic flow modifier may be added to reverse the direction of this flow. If the detector end of the capillary is positive, the electrophoretic and electroosmotic velocities are toward the detector. This configuration provides rapid separation of a wide variety of ions.

Quaternary salts, for example myristyltrimethylammonium bromide, can be used to reverse flow. The use of a quaternary salt, in combination with chromate as an indirect chromophore, has been described by Jones et al. [10] for anion analysis. A disadvantage of this approach, other than limitations imposed by the patent, is compatibility of the indirect chromophore with the quaternary salt. Vanadate, for example, forms a precipitate with some quaternary salts used for flow reversal [9].

Flow reversal is unnecessary for the separation of many anions, for example aliphatic and aromatic acids [8]. By using small-diameter columns and high pH, electroosmotic flow velocity is faster than the electrophoretic mobility of many anions and they will reach the detector in reasonable times even though their electrophoretic

* Corresponding author.

0021-9673/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0021-9673(94)01229-6

migration is away from the detector. However, without flow reversal some very fast anions cannot be practically analyzed because the vector sum of their electrophoretic velocity and flow velocity is small [6]. For example, if the detector is negative, they migrate away from the detector nearly as fast or faster than flow toward the detector. In these cases the analysis time is unacceptably long or impossible because the analyte never reaches the detector. Reducing electroosmotic flow would result in practical separation times for these anions.

Additives such as water-soluble polymers have been reported to slow electroosmotic flow, but we were unable to significantly slow flow at neutral or basic pH. However, there are now a variety of coated columns available. High coverage of the silica surface should result in much reduced flow. The objective of this investigation was to evaluate coated (low flow) columns for fast anion analysis.

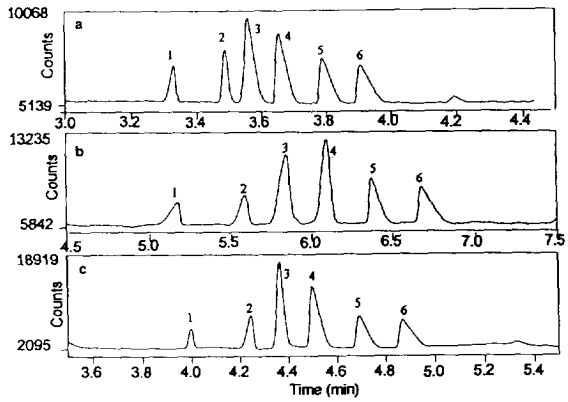

Fig. 1. Separation of fast anions with various indirect chromophore-electrolytes. Capillary: 72 cm (50 cm to detector) × 50 μm I.D. DB-1. Voltage: + 25 kV at detector end. Column temperature: 30°C. Sample injection: 5 s by vacuum at 5 in.Hg (1 in.Hg = 3386.38 Pa). (a) 4 m*M* Sodium chromate, 270 nm; (b) 7.5 m*M* sodium vanadate, 254 nm; (c) 7.5 m*M* sodium iodide, 226 nm. Peaks: 1 = thiosulfate; 2 = bromide; 3 = chloride; 4 = sulfate; 5 = nitrite; 6 = nitrate. Concentration: 10 mg/l.

2. Experimental

The 270A-HT electrophoresis instrument was manufactured by PE-ABI (Foster City, CA, USA). A 0.05-μm film thickness DB-1 (C_1 phase), 72 cm × 50 μm I.D. column made by J & W Scientific (Folsom, CA, USA) and CElect-H50 (C_1 phase), H150 (C_8 phase) and H250 (C_{18} phase) 72 cm × 50 μm columns made by Supelco (Bellefonte, PA, USA) were used for anion separations. Separations were made with the detector end of the column at + 25 kV and a column temperature of 30°C.

3. Results and discussion

Fig. 1 shows the separation of six fast ions on the DB-1 column. The ions all separate in a relatively short time and can be detected with a variety of indirect chromophore-electrolytes. One advantage of not using a quaternary salt electroosmotic flow modifier is the freedom to use any indirect chromophore that is compatible with the column and analytes. Factors to consider when choosing the indirect chromophore have been discussed [11]. The best dynamic range for separation will be achieved when the mobilities of the analyte and electrolyte match. The molar absorptivity and mobility of the indirect chromophore will affect sensitivity. The electrolyte should not react with any of the analytes of interest. Therefore, we do not recommend iodide for the determination of thiosulfate because it may contain iodine as an impurity or as a result of electrolysis.

Fig. 2 shows the separation of the six fast anions on the Supelco columns with chromate as the electrolyte. These columns differ in column coating which affects their charge and electroosmotic flow. Increased flow results in improved resolution, but at the expense of longer analysis time. This effect can be seen by comparing the separation of bromide and iodide on the DB-1 column and the H50 column (Fig. 3). This H50 column has slightly higher flow resulting in slightly longer migration times and higher resolution for iodide and bromide. The length of a column can be adjusted to optimize analysis time and resolution.

We found column life was typically limited by

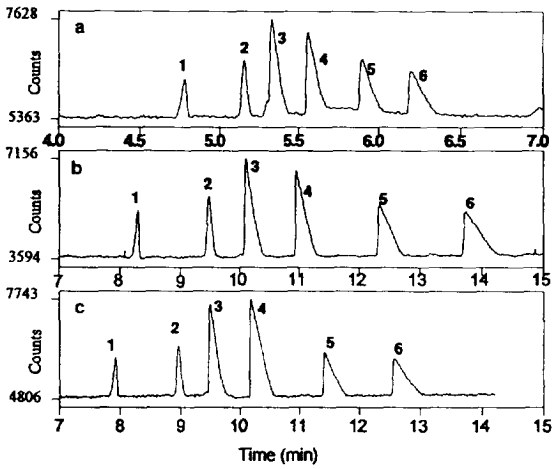

Fig. 2. Separation of fast anions on various Supelco capillaries. Capillary: 72 cm (50 cm to detector) × 50 μm I.D. Voltage: + 25 kV at detector end. Electrolyte: 4 m*M* sodium chromate. Detector: 270 nm. Column temperature: 30°C. Sample injection: 5 s by vacuum at 5 in.Hg. (a) CElect-H50, (b) CElect-H150, (c) CElect-H250. Peaks: 1 = thiosulfate; 2 = bromide; 3 = chloride; 4 = sulfate; 5 = nitrite; 6 = nitrate. Concentration: 10 mg/l.

stability of the coating. The columns investigated show some initial instability that results in slightly increasing migration times, but the times stabilize after a few runs. The lowest flow columns evaluated in this investigation have remained stable for weeks of use at neutral or slightly basic pH. However, the coatings are not stable at very high or low pH. When the coating starts to hydrolyze, as evidenced by increasing migration times, flow can increase in a matter of hours to a point where separation time is too long to be practical.

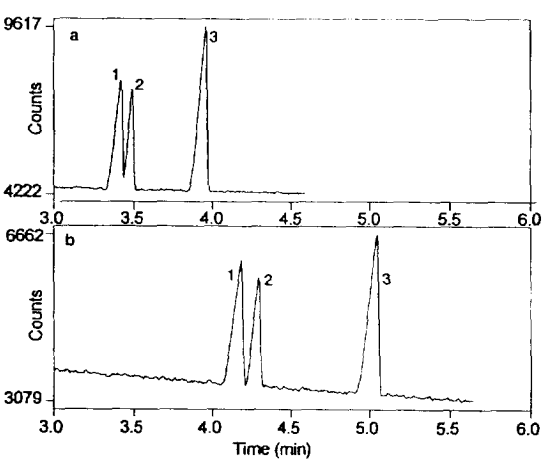

Fig. 3. Comparison of the separation of bromide and iodide on the DB-1 (a) and CElect-H50 (b) columns. Capillary: 72 cm (50 cm to detector) × 50 μm I.D. Electrolyte: 10 m*M* sodium phosphate (pH 7). Detector: 200 nm. Voltage: + 30 kV at detector end. Column temperature: 30°C. Sample injection: 5 s by vacuum at 5 in.Hg. Peaks: 1 = bromide; 2 = iodide; 3 = nitrate. Concentration: 10 mg/l.

Electrolyte concentration affected the separation in several ways. A higher electrolyte concentration produced better peak shapes at high analyte concentrations, but reduced sensitivity. The wavelength must be chosen to optimize absorbance once peak shape and sensitivity are optimized [11]. All the columns had some amount of electroosmotic flow that was slowed by increased electrolyte concentration. Migration times of anions decreased with increasing concentration of electrolyte, as a result of decreased flow, which under the conditions used is away from the detector. Electrolyte concentration also affected mobility (see Ref. [12], p. 407). When the ionic strength of the electrolyte is increased, divalent ions are slowed more than monovalent ions. As a result, electrolyte concentration affects selectivity in cases where anions of different charge are present in the sample. An example of this effect is illustrated in Fig. 4. At low electrolyte concentration sulfate migrates to the detector faster than chloride. As the electrolyte concentration is increased, sulfate mobility is reduced more than chloride and their positions in the electropherogram reverse. Because the electroosmotic flow decreases, both ions reach the detector quicker.

The use of the coated columns is particularly advantageous for the determination of anions that do not require an indirect chromophore. Tetraalkylammonium salts are typically available as the bromide salt. The bromide must be exchanged for a UV-transparent ion for direct determination of anions with flow reversal. This inconvenience is avoided by using coated columns. With direct detection, the baseline typically has less noise, consistent with the observation of Wang and Hartwick [13] that fluctuation in chromophore-electrolyte concentration is the

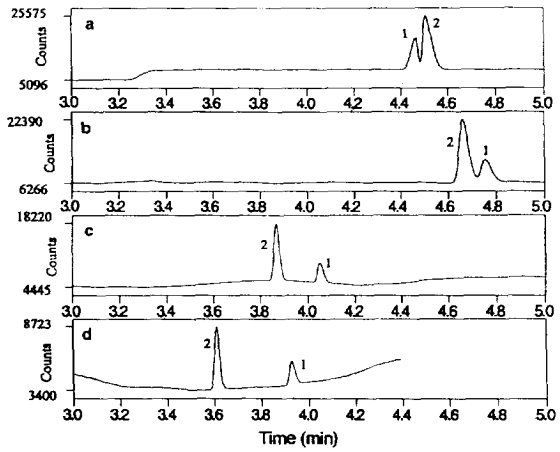

Fig. 4. Comparison of the effects of electrolyte concentration on selectivity. Capillary: 72 cm (50 cm to detector) × 50 μm I.D. DB-1. Detector: 226 nm. Voltage: +25 kV at detector end. Column temperature: 30°C. Sample injection: 5 s by vacuum at 5 in.Hg. Sodium iodide concentration: (a) 2 m*M*, (b) 5 m*M*, (c) 10 m*M*, (d) 20 m*M*. Peaks: 1 = sulfate; 2 = chloride. Concentration: 10 mg/l.

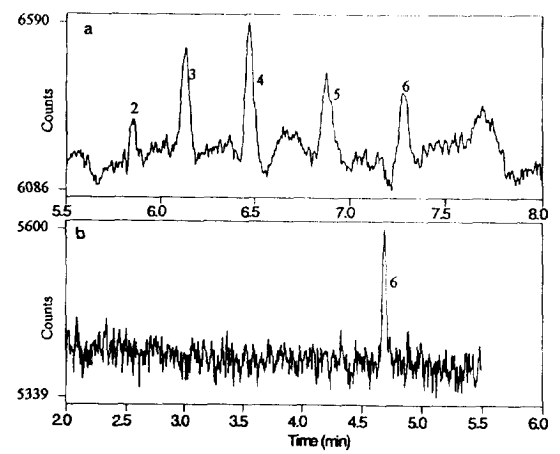

Fig. 5. Comparison of baseline noise with indirect and direct detection. Capillary: 72 cm (50 cm to detector) × 50 μm I.D. CElect-H50. Column temperature: 30°C. Sample injection: 5 s by vacuum at 5 in.Hg. Peaks: 2 = bromide; 3 = chloride; 4 = sulfate; 5 = nitrite; 6 = nitrate. (a) Indirect, conditions: 7.5 m*M* sodium iodate, detector at 226 nm, all components at 0.3 mg/l; (b) direct, conditions: 10 m*M* phosphate, pH 7, detector at 210 nm, nitrate concentration 0.15 mg/l.

noise limiting factor with indirect detection. An example of the improved baseline with direct detection is shown in Fig. 5. While the high-frequency noise attributed to the detector is similar for direct and indirect detection, the baseline with indirect detection has low-frequency fluctuations that makes accurate integration of low-concentration peaks difficult.

Acknowledgements

The authors thank both J & W Scientific and Supelco for providing the columns used in this investigation.

References

[1] K.D. Altria and C.F. Simpson, *Chromatographia*, 24 (1987) 527.
[2] S. Hjertén, K. Elenbring, F. Kilar, J. Liao, A.J.C. Chen, C.J. Siebert and M. Zhu, *J. Chromatogr.*, 403 (1987) 47.
[3] X. Huang, J.A. Luckey, M.J. Gordon and R.N. Zare, *Anal. Chem.*, 61 (1989) 766.
[4] B.F. Kenny, *J. Chromatogr.*, 546 (1991) 423.
[5] T. Wang and R.A. Hartwick, *J. Chromatogr.*, 589 (1992) 307.
[6] P. Jandik, W.R. Jones, A. Weston and P.R. Brown, *LC·GC*, 9 (1991) 3.
[7] M.W.F. Nielen, *J. Chromatogr.*, 588 (1991) 321.
[8] G.W. Tindall and R.L. Perry, *J. Chromatogr.*, 633 (1993) 227.
[9] P. Jandik and W.R. Jones, *J. Chromatogr.*, 546 (1991) 431.
[10] W.R. Jones, P. Jandik and M. Merion, *US Pat.*, 5 104 506 (1992).
[11] G.W. Tindall, D.R. Wilder and R.L. Perry, *J. Chromatogr.*, 641 (1993) 163.
[12] J.C. Reijenga and E. Kenndler, *J. Chromatogr. A*, 659 (1994) 403.
[13] T. Wang and R.A. Hartwick, *J. Chromatogr.*, 607 (1992) 119.