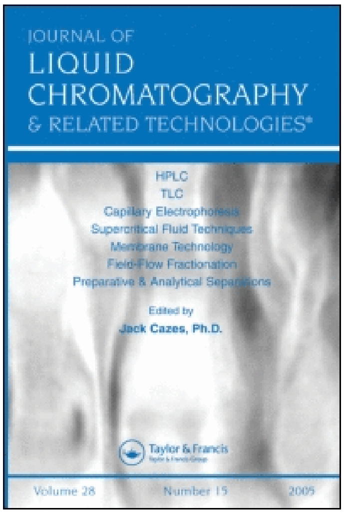

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Abstract: A capillary electrophoresis method using terephthalate as probe ion in indirect photometric detection was investigated. The operating parameters including the pH and concentration of phosphate buffer, the applied potential, and the concentration of terephthalate were studied. Standard solutions containing known concentrations of chloride, sulfate, and fluoride were repeatedly analyzed. The calibration characteristics of analyzing these anions are calculated. The overall accuracy in terms of % recovery is between 95 and 102%. The detection limit ranges from 0.03 to 0.4 mM. The linearity covers more than 100 mM. The reproducibility in terms of % RSD is between 2 and 6%. The sensitivity of analysis ranges from 5.6 for chloride to 28.2 mAu*min/mM for sulfate.

Keywords: Accuracy, Anion, Capillary electrophoresis, Detection limit, Indirect photometric detection, Linearity, Probe ion, Reproducibility, Sensitivity

INTRODUCTION

Capillary electrophoresis (CE) is a powerful separation technique for ion analysis. In terms of actual theoretical plates, CE is at least 10 times more powerful than ion chromatography (IC).[1] However, as an analytical technique, CE requires optimization on more operational parameters to enhance the reproducibility of results. When a fused silica capillary is

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used to analyze anions using CE, the electroosmotic flow (EOF) has to be reversed or suppressed. The direction of EOF in a fused silica capillary is towards the negative electrode, whereas anions migrate towards the positive electrode. If the EOF is not reversed or suppressed, the anions in a capillary may not reach the detector and be observed.

Numerous techniques have been reported to overcome the problem caused by the direction of EOF when analyzing anions. Gross and Yeung analyzed inorganic anions at a low pH, which is associated with low EOF.[2] Tsuda described a method to reverse EOF by adding cetyltrimethylammonium bromide (CTAB) to running buffers.[3] Foret et al. suppressed the EOF by adding Triton X-100 to the buffer for organic and inorganic anion analysis.[4] In another approach, Soga et al. used a polyethyleneglycol coated capillary to suppress the EOF in halide analysis.[5]

In addition to the problem caused by the direction of EOF, inorganic anions generally exhibit poor chromophoric property. In order to analyze these anions, indirect photometric detection is often utilized.[6–12] In the indirect photometric detection, an absorbing probe ion, which has high absorptivity, is added to running buffers. The analyte anion displaces a portion of the probe ion leading to a decrease in background absorbance and a formation of measurable signal.

In this research, CTAB is added to running buffers to reverse EOF and terephthalate is added to the buffer as a probe ion in the indirect photometric detection of a mixture of chloride, sulfate, and fluoride. The parameters, which include the pH and concentration of running buffer, the potential applied to the capillary, and the concentration of terephthalate, are investigated. The calibration characteristics including accuracy, detection limit, linearity, correlation coefficient, reproducibility, correlation coefficient, and sensitivity are calculated and evaluated.

EXPERIMENTAL

Chemicals and Reagents

All chemicals including CTAB, disodium terephthalate, hydrochloric acid, monosodium dihydrogen phosphate, sodium hydroxide, sodium chloride, sodium fluoride, and sodium sulfate were obtained from Aldrich-Sigma (St. Louis, Missouri). The running buffers with three different concentrations: 10, 20, and 30 mM, and with pH ranging from 4 to 10, were prepared from 200 mM monosodium dihydrogen phosphate stock solution. The pH of running buffer was adjusted to the desired value using 1 M NaOH and/or 1 M HCl. Anion solutions, which contain chloride, sulfate, and fluoride ions, with concentrations ranging from 0.01 to 100 mM, were prepared from 200 mM stock solutions of sodium chloride, sodium sulfate, and sodium fluoride. The water used to prepare reagents was ultra pure water (18 mega-ohm/cm) produced from a Hydro's Picosystem (Levittown, Pennsylvania).

Capillary Electrophoresis System

The system used in separating anion mixtures was an Agilent Capillary Electrophoresis (CE) (Palo Alto, California). The system comprises a CE unit with diode array detector. The Agilent Chemstation for CE (version A.06) is used to run, control, acquire, and analyze the data. Separations were carried out on a fused silica capillary with 75 µm ID × 56 cm total length (50 cm effective length). Before each injection, the capillary was preconditioned by flushing with water and the running buffer for 3 minutes, respectively. The sample was introduced into the capillary by a pressure of 30 mbar for 2 seconds. The applied potential was run at −10, −20, and −30 kV. The capillary temperature was thermostatted at 22.0°C. The indirect detection of anions was carried out by a photodiode array detector with a wavelength setting at 500 nm and a reference at 240 nm, which is the λ_{max} of terephthalate. The capillary was post conditioned by flushing with water, 0.1 M NaOH, and water again for 2 minutes, respectively.

RESULTS AND DISCUSSION

Effect of Running Buffer's pH

The comparison of electropherograms run by 20 mM phosphate buffers with pH ranging from 4 to 10 on the anion solution, which contains 100 mM chloride, sulfate, and fluoride, is shown in Figure 1. These electropherograms were obtained at the same conditions of applied potential, injection pressure and time, concentration of running buffer, concentration of probe ion, and concentration of CTAB. This figure illustrates the effect of pH on the separation of the three anions. The three integrated peaks on each electropherogram correspond to chloride, sulfate, and fluoride, respectively. The non-integrated ones are system peaks. The migration times become stabilized at pH 8 and above, and are shorter at low pH for these anions. At a pH below 6, the peak of chloride is flat and barely detected. This is because the running buffers with pH below 6 were adjusted by 1 M HCl to the desired value. The chloride peak starts to emerge at $pH = 6$. Evidently, sulfate has the highest response factor to the indirect photometric detection among these three anions. This indicates that sulfate displaces more probe ion than chloride or fluoride. With the same single charge as chloride, the reason why fluoride

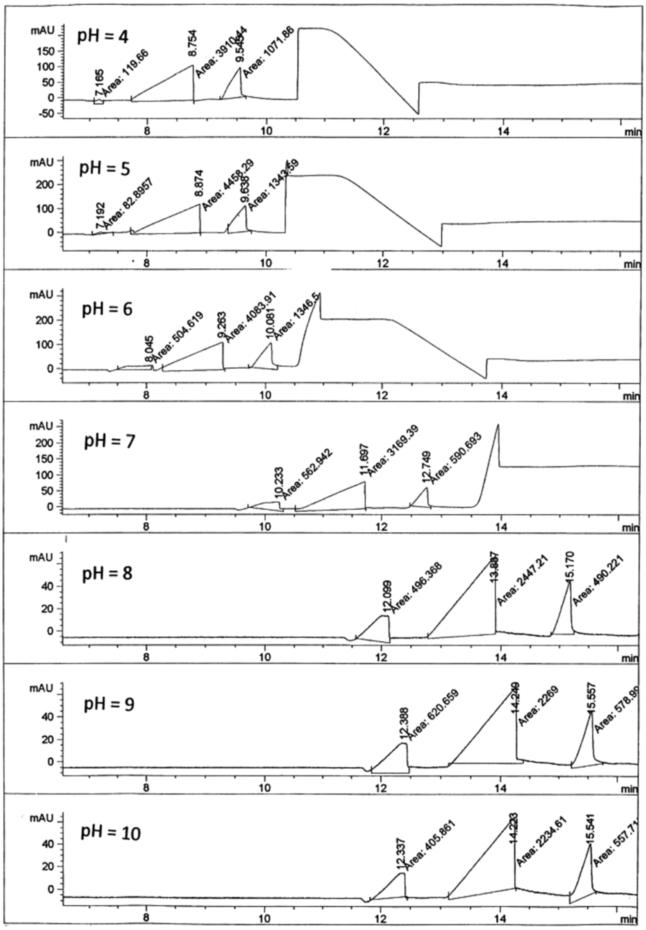

Figure 1. Effect of running buffer's pH on anion analysis (Cl^-, SO_4^{2-}, and F^- 100 mM each), applied potential: −20 kV, injection pressure: 30 mbar 2 s, running buffer: 20 mM phosphate with 0.5 mM CTAB and 7 mM terephthalate.

migrates slower than the double charged sulfate is undetermined. However, this may be due to the strong attraction between fluoride and the positive charged species in the running buffer. Their peak shapes are frontal, which is typical in capillary electrophoresis.

Effect of Running Buffer Concentration

The effect of the running buffer's concentration on the separation of the three anions is illustrated in Figure 2. These electropherograms were run

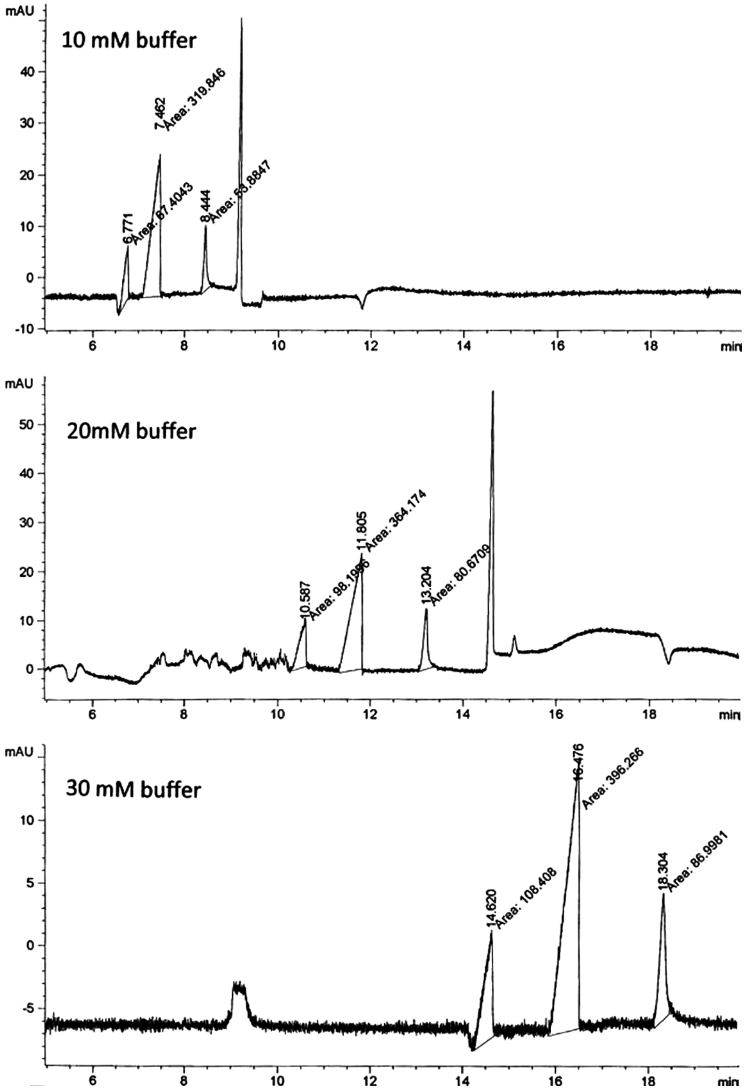

Figure 2. Effect of running buffer's concentration on anion analysis (Cl^-, SO_4^{2-}, and F^- 100 mM each), applied potential: −20 kV, injection pressure: 30 mbar 2 s, running buffer: phosphate with pH = 8, 0.5 mM CTAB, 5 mM terephthalate.

according to the conditions specified in the caption of Figure 2. It is observed, that the migration times of these anions are longer when run by a running buffer with higher concentration. This is probably due to high friction exerted on the anions by the running buffer with high phosphate concentration.

Effect of Applied Potential

The effect of the applied potential on the separation of the three anions is illustrated in Figure 3. The electropherograms were obtained on a solution of 20 mM chloride, sulfate, and fluoride under the parameters listed

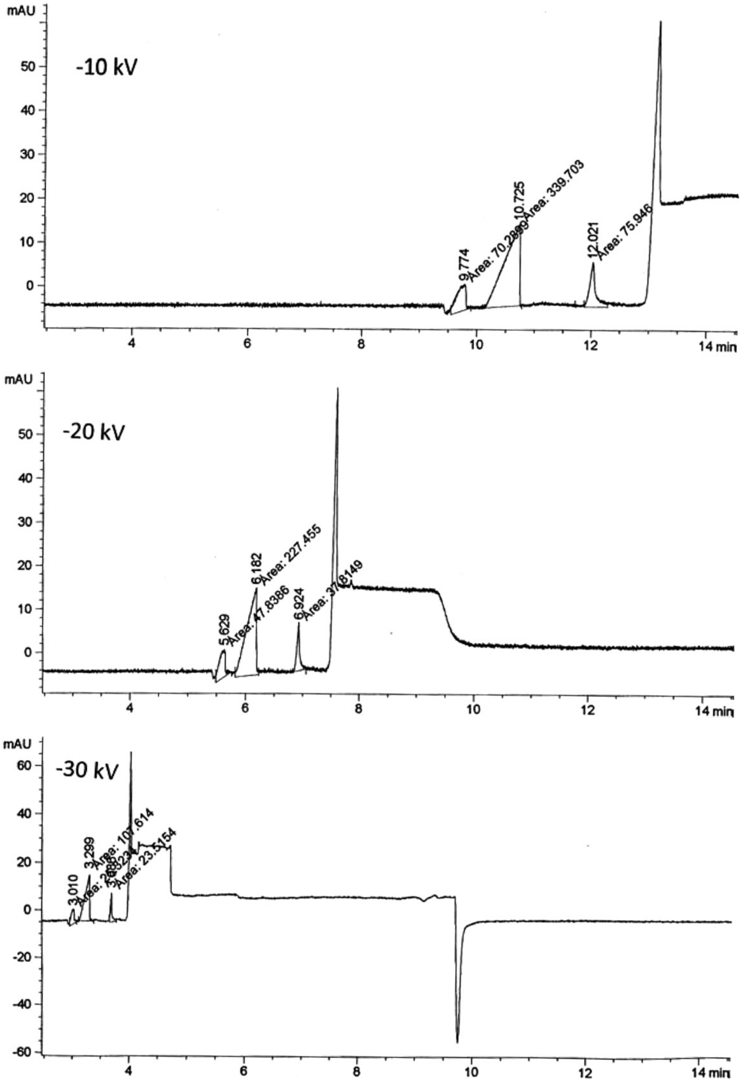

Figure 3. Effect of applied potential on anion analysis (Cl^-, SO_4^{2-}, and F^- 20 mM each), injection pressure: 30 mbar 2 s, running buffer: 10 mM phosphate with pH = 8, 0.5 mM CTAB, and 3 mM terephthalate.

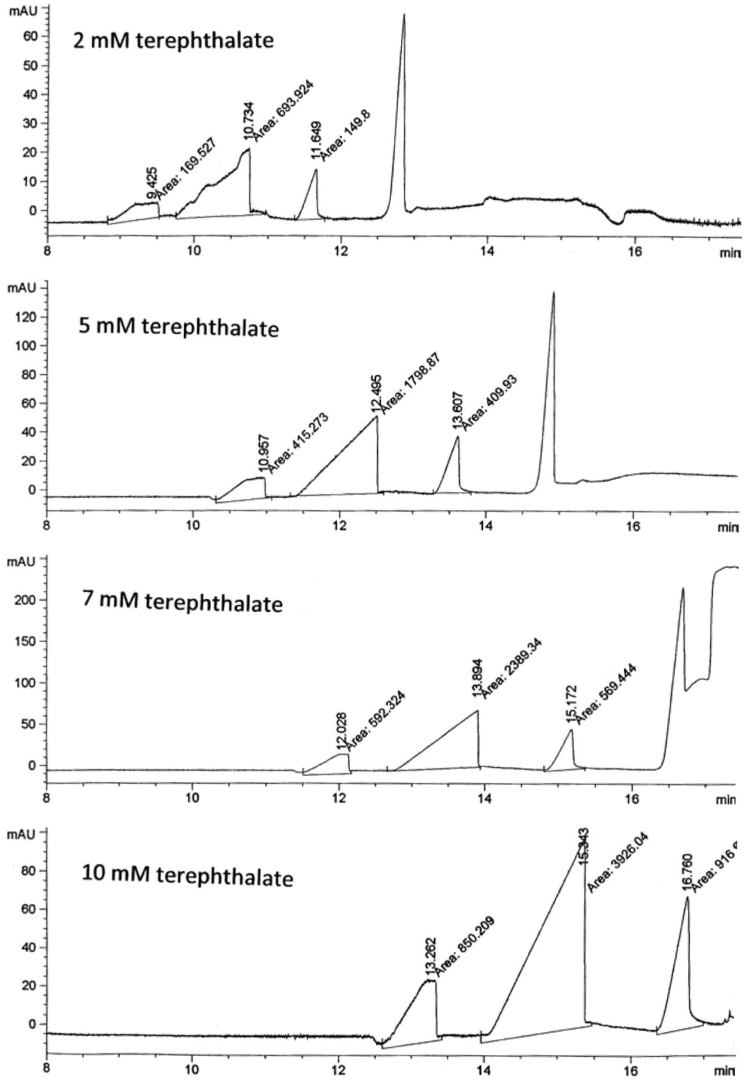

Figure 4. Effect of probe ion's concentration on anion analysis (Cl^-, SO_4^{2-}, and F^- 100 mM each), applied potential: −20 kV, injection pressure: 30 mbar 2 s, running buffer: 20 mM phosphate with pH = 8 and 0.5 mM CTAB.

on the caption of Figure 3. The applied potential was run at three different levels: −10, −20, and −30 kV. The migration times of the three anions are all shortened when the applied potential is higher. The most intense peaks for these anions are observed when CE is run at a potential of – 10 kV. This is due to the broadening of peaks when the migrating velocity is slow. As a result, the peak areas are increased.

Effect of Probe Ion's Concentration

The effect of the probe ion's concentration on the separation of the anions is illustrated in Figure 4. These electropherograms were obtained from the same standard solution (100 mM) using the operating conditions specified on the caption of Figure 4. In the analysis of the same anion solution, the highest response factors are observed on the electropherogram obtained by the running buffer with the highest concentration of the probe ion, terephthalte. It is evident, that increasing the concentration of probe ion will certainly enhance the sensitivity of indirect photometric detection. As a consequence, the high solubility of the probe ion in the running buffer is a critical criterion in choosing a probe ion for indirect photometric detection.

Calibration Characteristics of Analyzing Anions

In order to evaluate the calibration characteristics of analyzing the three anions, a series of anion mixtures, with concentration ranging from 0.01 to 100 mM, were repeatedly run 8 times by a 20 mM phosphate buffer ($pH = 8$). The running buffer contains 7 mM terephthalate and 0.5 mM CTAB. The calibration characteristics, which include accuracy, detection limit, linearity, reproducibility, correlation coefficient, and sensitivity, of the three anions are calculated and summarized in Table 1. The calibration characteristics for analyzing sulfate are the best among these three anions. It is believed that the calibration characteristics of analysis can be enhanced through precisely conditioning the capillary column,

Table 1. The comparison of calibration characteristics for chloride, sulfate, and fluoride

Characteristic	Chloride	Sulfate	Fluoride
Accuracy, % recovery	95–100	98–101	97–102
Limit of Detection, mM	0.4	0.03	0.3
Limit of Quantitation, mM	1.2	0.09	0.9
Linearity, mM	>100	>100	>100
Reproducibility, % RSD	3–6	2–4	3–5
Correlation Coefficient, R^2	0.98	0.99	0.98
Sensitivity, mAu * min/mM	5.6	28.2	6.5

effectively degassing running buffer, and freshly preparing reagents. The detection limits for the anions can be significantly enhanced by increasing the time duration of sample introduction.

In conclusion, terephthalate has proven to be a successful probe ion used in capillary electrophoresis with indirect photometric detection. This technique can be applied to the determination of any anion regardless of its chromophoric properties. The reproducibility of detection can be enhanced through better optimization of operating parameters.

FUTURE STUDY

The effect of increasing the concentration of terephthalate to running buffer will be studied. The approach of using experimental design to optimize instrumental parameters will be researched.

ACKNOWLEDGMENT

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REFERENCES

1. Fritz, J.S. J. Chromatogr. A **2000**, *884*, 261.
2. Gross, L.; Yeung, E.S. J. Chromatogr. **1989**, *480*, 169.
3. Tsuda, T. J. High Resolut. Chromatogr. Chromatogr. Commun. **1987**, *10*, 622.
4. Foret, F.; Fanali, S.; Ossicini, L.; Bocek, P. J. Chromatogr. **1989**, *470*, 169.
5. Soga, T.; Inoue, Y.; Ross. J. Chromatogr. A **1995**, *718*, 421.
6. Kelly, L.; Nelson, R.J. J. Liq. Chromatogr. **1993**, *16*, 2103.
7. Buchberger, W.; Cousins, S.M.; Haddad, P.R. Trends Anal. Chem. **1994**, *13*, 313.
8. Shamsi, S.A.; Danielson, N.D. Anal. Chem. **1994**, *66*, 3757.
9. Macka, M.; Haddad, P.R. Electrophoresis **1997**, *18*, 2482.
10. Johns, C.; Show, M.; Macka, M.; Haddad, P.R. Electrophoresis **2003**, *24*, 557.
11. Haddad, P.R.; Doble, P.; Macka, M. J. Chromatogr. A **1999**, *856*, 145–177.
12. Markuszewski, M.T.; Szczkowska, M.; Siluk, D.; Kaliszan, R. J. Pharm. Biomed. Anal. **2005**, *39* (3–4), 636–642.

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