Separation of Sulfur Species in Water by Co-Electroosmotic Capillary Electrophoresis with Direct and Indirect UV Detection

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SEPARATION OF SULFUR SPECIES IN WATER BY CO-ELECTROOSMOTIC CAPILLARY ELECTROPHORESIS WITH DIRECT AND INDIRECT UV DETECTION

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Co-electroosmotic capillary electrophoresis (co-CZE) with both direct and indirect UV detection was investigated for the separation of sulfur species. With direct UV detection, the separation of $S_2O_3^{2-}$, SO_4^{2-}, SO_3^{2-}, HS^- was possible using 20 mM phosphate electrolyte containing 0.75 mM tetradecyltrimethylammonium bromide (TTAB) and 15% acetonitrile. To obtain optimal peak shape and sensitivity using indirect UV detection, a range of background electrolytes (BGEs), including benzoate, phthalate, 2,6-pyridinedicarboxylate (2,6-PDCA) and trimellitate, were examined as the BGEs. Of all the BGEs, 2,6-PDCA gave high selectivity and indirect UV response due to its mobility matching to that of sulfur species and its high absorptivity. Detection limits in range of 3–6 μM were obtained using either direct UV or indirect UV detection. The proposed CZE methods were used for the determination of sulfur species in water samples, and provided fast separation of sulfur species in less than 5 min.

Keywords: Co-CZE; Sulfur species; Direct and indirect UV detection; Water sample

INTRODUCTION

The rapid increase in the level of environmental pollution has increased the importance of speciation analysis, especially since different species can have significantly different effects in environmental and biological systems [1–4]. Sulfur-containing species commonly play an important role in many environmental cycles and can exhibit toxicity and also affect the behaviour of metal ions in the environment [1–3]. Sulfur speciation in environmental samples provides information useful in understanding the environmental and biological behaviour of sulfur; for example, reduced forms of sulfur entering the environment from industrial effluent can influence the bioavailability of heavy metals [4].

Sulfur species presented in environmental matrices are often accompanied by other inorganic anions, and therefore ion chromatography (IC) with various detection techniques has been most extensively used for the determination of sulfur species [5–9].

In the IC approach, both anion exchange and ion-interaction chromatographic methods can be used to determine sulfur species. These methods are dependent on the nature of the sulfur species. For example, both anion-exchange and ion-interaction chromatographic methods are more suited for the separation of sulfide, sulfite, sulfate and thiosulfate [5–9], while ion-interaction chromatography is often used for the separation of polythionates due to the generally weaker analyte-stationary phase interaction [8].

Due to high separation efficiency, an alternative method for sulfur speciation is capillary electrophoresis (CZE). The separation of most sulfur species, including sulfite, sulfide, sulfate and thiosulfate, can be achieved using CZE with either direct or indirect UV detection [10–14]. To provide fast electrophoretic separation, the co-electroosmotic capillary electrophoresis (co-CZE) mode frequently coupled with UV detection is often used for the separation of these species [10–14]. Direct UV detection allows for the detection of sulfide, thiosulfate, sulfite and polythionates [10,11], while indirect UV detection is used for the detection of anions such as sulfate that show little direct UV absorbance [12–14]. To achieve optimal peak shape and sensitivity, the background ion and sulfur species should have a similar electrophoretic mobility [15,16]. The background chromophoric ions previously used for the indirect UV detection of sulfur species include chromate [14], pyromellitate [12], sulfosalicylic acids [12,17] and naphthalenetrisulfonate [18]. However, there are only a few reports on co-CZE coupled with direct and indirect UV detection of sulfur species. It is of interest to compare both UV detection modes for sulfur species, and find a new background electrolyte (BGE) for indirect UV detection that exhibits improved selectivity and sensitivity.

In this article, we systematically investigated the use of co-CZE with both direct and indirect UV detection for sulfur speciation. During co-CZE with direct UV detection, parameters affecting the selectivity such as electrolyte pH, and the EOF modifiers were examined, while during co-CZE with indirect UV detection, a new background chromophoric ion was sought, including various aromatic carboxylates and 2,6-pyridine-dicarboxylate (2,6-PDCA). The new background electrolytes were evaluated and a new BGE was used for the separation of sulfur species to give the reasonable selectivity and sensitivity. Finally, the proposed methods were demonstrated for the determination of sulfur species in water samples.

EXPERIMENTAL

Reagents and Solutions

All reagents were obtained from Sigma and Aldrich (Sydney, Australia), and were of analytical grade and used without further purification. Standards of the sulfur species tested were prepared daily from 10 mM stock solutions by dilution with Milli-Q water. Electrolytes required for CZE were prepared by dissolution of an appropriate amount of NaH_2PO_4 or aromatic carboxylate in Milli-Q water contained appropriate amounts of tetradecyltrimethylammonium bromide (TTAB) and organic solvents. All electrolytes were filtered through Millipore 0.45 μm membrane filters and degassed in an ultrasonic bath prior to use. Electrolyte pH was adjusted with 0.1 M NaOH or 0.1 M H_3PO_4.

Instrumentation

All CZE experiments were preformed using a Quanta 4000 (Waters, Milford, USA). The system was controlled by Millennium (Waters, Milford, USA) software. Separation was carried out on fused-silica capillaries with $55\,cm \times 50\,\mu m$ I.D. total length (48.5 cm effective length). The UV detector was set at 185 nm for the direct detection and at 214 nm for the indirect detection.

Procedures

Prior to use, a new capillary was pretreated with the following cycles: 0.1 M NaOH for 10 min, 0.01 M NaOH for 10 min, deionized water for 15 min and then an electrolyte for 20 min. The capillary was rinsed with electrolyte for 2 min between each run. Samples were injected in the hydrostatic mode for 30 s. The capillary was held at 25°C, and the applied voltage was constant at $-20\,kV$. Benzyl alcohol [0.05% (v/v)] was used as a neutral marker for the determination of electroosmotic flow. The electroosmotic mobility was calculated using the equation in described in [19]. Identification of each solute was verified by spiking with known standards. Water samples were centrifuged (4000 rpm for 3 min) and then filtered through a $0.45\,\mu m$ membrane filter to removal particles in sample before analysis.

RESULTS AND DISCUSSION

Co-CZE with Direct UV Detection

In our previous study, we showed that the co-CZE separation and detection of anions with weak UV absorbance at 185 nm was possible using a phosphate electrolyte [20]. For this reason, phosphate was also considered here as the electrolyte. In addition, its medium mobility matched that of the anions of interest and it had a relatively high buffer capacity. Since thiosulfate is decomposed in acidic media and both EOF and mobility are determined by the electrolyte pH, manipulation of electrolyte pH was necessary [10–15]. Furthermore, co-CZE was used for the separation of sulfur species using cationic surfactants to achieve a fast separation with indirect UV detection [11,12], and had showed the type of cationic surfactants or the organic solvent in the electrolyte considerably impacted on the separation selectivity. Hence, changes in cationic surfactants, the electrolyte pH and the concentration of acetonitrile in the electrolyte were all investigated.

Two EOF modifiers, CTAB and TTAB, were added to 20 mM phosphate electrolyte of pH 7.5 to examine the separation selectivity. When CTAB was added to the buffer, the migration time of the solute and the separation resolution were reduced due to the higher EOF ($3.93 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$). However, this was improved by the addition of TTAB to the buffer due to its lower EOF ($3.06 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$). Since a better resolution between solutes was obtained using TTAB as the EOF modifier, it was used in the electrolyte for the separation of the sulfur species. These results indicate that the separation selectivity of anionic solutes in co-CZE mode can be manipulated by the addition of various cationic surfactants to the buffer. The influence of the cationic surfactants on the observed selectivity was due to different alkyl chain length [21,22]. However, this study shows that at concentrations above 0.75 mM

TTAB did not change the EOF because the surface of the capillary is fully coated by TTAB [23,24].

Electrolyte pH has a significant effect on solute mobility, and it therefore affects the separation selectivity [25]. In this case, 20 mM phosphate and 0.75 mM TTAB was used for the electrolyte. Figure 1 shows the effect of electrolyte pH on the effective mobility of solute and the EOF. The effect of pH on mobility appeared to be pronounced for sulfite and sulfide because changes to the effective charge and charge/mass ratio occurred at or near their pK_a (SO_3^{2-}: 1.89, 7.21, HS^{2-}/S^{2-} 6.9; 12.9) [12]. In contrast, the mobilities of thiosulfate and sulfate were nearly constant during variation of the electrolyte pH. Furthermore, the EOF slightly decreased in magnitude with the electrolyte pH, this is due to the increased the ionic strength of the electrolyte as the electrolyte pH was increased [24,25].

The influence of acetonitrile (ACN) on the mobility of solute and the EOF was studied by adding ACN to a 20 mM phosphate electrolyte containing 0.75 mM TTAB at pH 7.0. Figure 2 shows that the effective mobility of the sulfur species
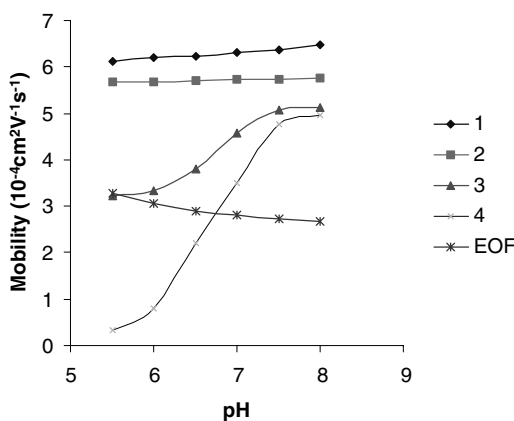
FIGURE 1 Influence of electrolyte pH on the effective mobility of sulfur species and the corresponding EOF. (1) $S_2O_3^{2-}$; (2) SO_4^{2-}; (3) SO_3^{2-}; (4) S^{2-}. Conditions: capillary, fused silica capillary 50 μm × 55 cm (L: 48.5 cm); electrolyte, 20 mM potassium phosphate, 0.75 mM TTAB; applied potential, −20 kV; hydrostatic injection: 30 s, UV detection at 185 nm. Capillary temperature, 25°C.
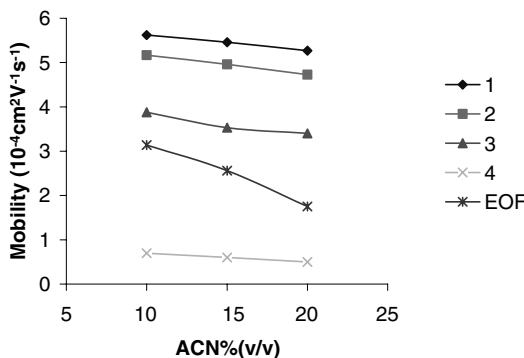

FIGURE 2 Influence of acetonitrile on the effective mobility of sulfur species and the corresponding EOF. (1) $S_2O_3^{2-}$; (2) SO_4^{2-}; (3) SO_3^{2-}; (4) S^{2-}. Conditions: electrolyte, 20 mM potassium phosphate, 0.75 mM TTAB at pH 7.0. Other conditions as in Fig. 1.

decreased with increasing amounts of acetonitrile in the electrolyte. The impact of the solvent on the effective mobility resulted from the variation of the pK_a related to the species transfer activity coefficient, leading to changes in the mass to charge ratio [26]. In addition, the decrease in EOF results from a low value for the zeta potential of the capillary wall upon addition of organic solvent to the electrolyte [27]. In view of the selectivity and the migration time of the solutes, an optimum electrolyte containing 20 mM phosphate, 15% (v/v) ACN and 0.75 mM TTAB at pH 7.0 was used to effectively separate sulfur species as shown in Fig. 3. All sulfur species were well-resolved using UV detection at 185 nm. The migration was in the order thiosulfate, sulfate, sulfite and sulfide. Peak area and concentration was linear in the concentration range 0.01–0.50 mM with correlation coefficients in the range of 0.994–0.999. The detection limits (S/N = 3) ranged from 3 to 7 μM and the reproducibility for the peak area (RSD% $n = 5$) from injecting a 0.1 mM standard mixture ranged from 1.6 to 3.2% as listed in Table I.

Direct UV detection was capable of determining sulfur species in mining leaching water as shown in Fig. 4. Only SO_4^{2-} (0.16 mM) and SO_3^{2-} (0.09 mM) were presented in the sample. To confirm the possible application of the method, spiking was done with a 50 μM standard mixtures and the recovery was tested. The recoveries of 91.2–101.5% for the test solutes were achieved. However, NO_3^- presented in the
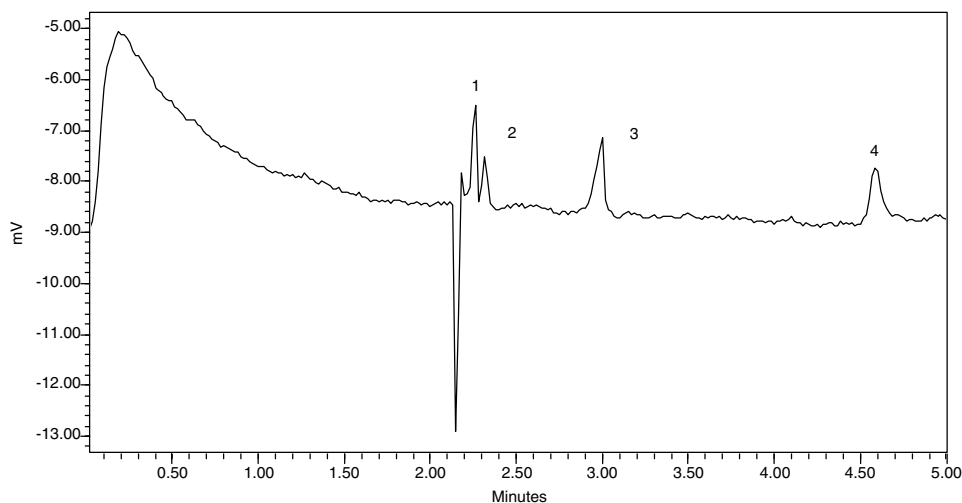

FIGURE 3   Electropherograms of sulfur species (0.10 mM) obtained in a 20 mM KH_2PO_4 and 0.75 mM TTAB at pH 7.0 containing 15% (v/v) acetonitrile. Peak identity: (1) $S_2O_3^{2-}$; (2) SO_4^{2-}; (3) SO_3^{2-}; (4) S^{2-}. Other conditions as in Fig. 1.

TABLE I   The performance of co-CZE with direct UV for the sulfur species

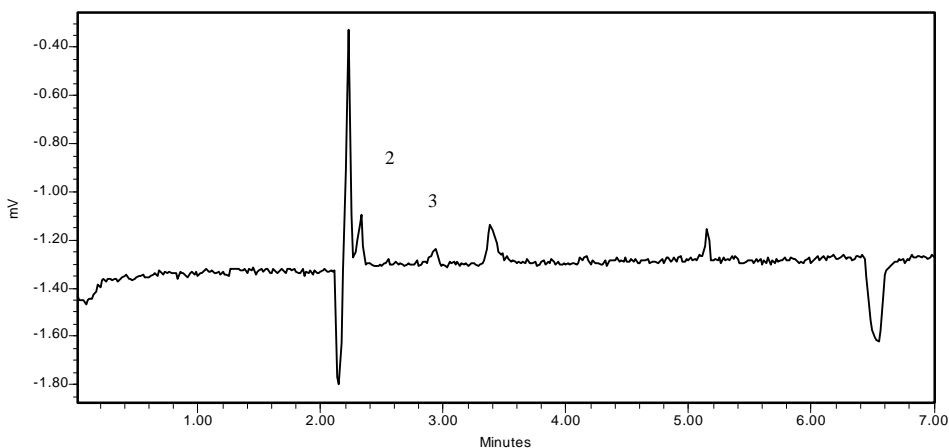| Species	Regression line	Coefficient	Detection limit (μM)	RSD% (peak area, n = 5%)
$S_2O_3^{2-}$	$y = 4.0 \times 10^4 x + 5.4 \times 10^2$	0.999	5.0	1.6
SO_4^{2-}	$y = 1.9 \times 10^4 x + 5.2 \times 10^2$	0.996	7.0	2.7
SO_3^{2-}	$y = 1.9 \times 10^4 x + 4.0 \times 10^2$	0.999	3.0	2.9
S^{2-}	$y = 6.7 \times 10^4 x + 4.1 \times 10^2$	0.994	5.0	3.2

FIGURE 4   Typical electropherogram obtained from ground water. Other conditions as in Fig. 3.

sample interfered with the determination of $S_2O_3^{2-}$ because of their similar migration time. The advantage of direct UV detection is less interference from non-absorbing species presented in water samples. In addition, the fast separation of these species was obtained by the proposed method.

Co-CZE with Indirect UV Detection

A common background electrolyte used in indirect UV detection of sulfur species is chromate (pH 7–9). However, the sulfide cannot be detected with a chromate BGE because of sulfide oxidation [14]. Alternative BGEs are aromatic carboxylic or sulfonic acids. It was reported [12,14] that pyromellitate, naphthalenetrisulfonate and sulfo-salicylic acid were used as BGEs for the indirect UV detection of sulfur species. To obtain optimal peak shape and sensitivity, the sulfur species should have an electro-phoretic mobility similar to that of the background ion and a lower molar absorptivity than the background ion. Aromatic carboxylic acids and 2,6-PDCA can also be used as BGEs for the separation of anions and organic acids with indirect UV detection [28–30], and may be useful for sulfur species. Hence, the aromatic carboxylic acids and 2,6-PDCA were evaluated to search for a new BGE.

The aromatic carboxylates, including benzoate, phthalate, trimellitate and 2.6-PDCA, were evaluated as BGEs for the separation of sulfur species with indirect UV detection at 214 nm. Figure 5 shows the electropherograms obtained using various BGEs, containing 10 mM aromatic carboxylate and 0.75 mM TTAB at pH 7.0, for (a) benzoate, (b) phthalate, (c) 2.6-PDCA and (d) trimellitate. Of all the BGEs, the best resolution and sensitivity for sulfur species was achieved using 2,6-PDCA as the BGE, since its mobility matched closely those of the sulfur species, and it had a high molar absorptivity as shown in Table II. In contrast, benzoate had a lower mobility than that of the test solutes, and lead to poor resolution; for example, comigration of thiosulfate and sulfate, sulfite and sulfide. Similar studies have used different BGEs for the separation of a wide range of solutes [15,31–33]. Phthalate, having a medium mobility, also does not match well the solute mobility and gave poor peak shapes of sulfide obtained using these as BGEs. Although trimellitate
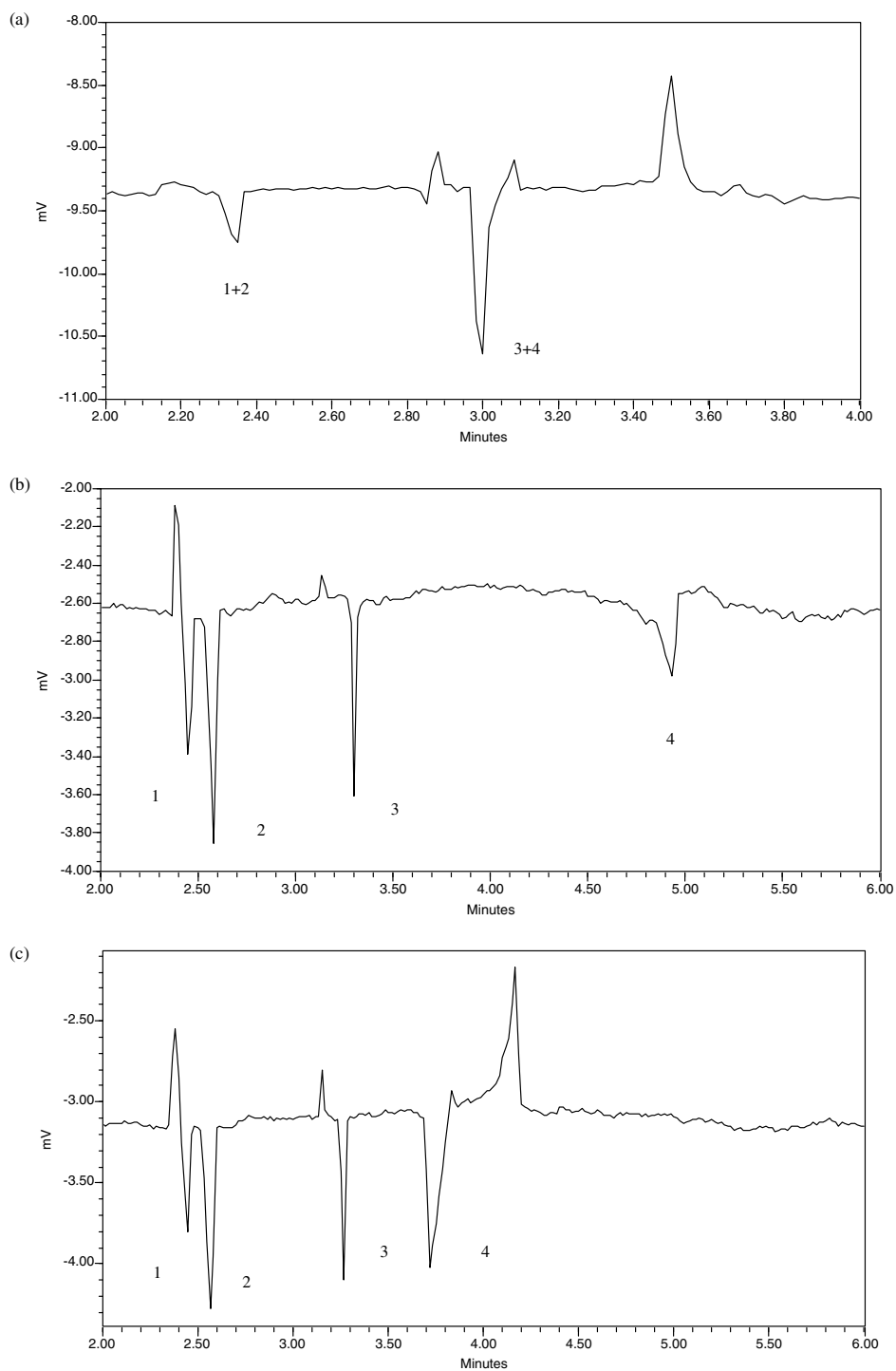
FIGURE 5 Electropherograms of sulfur species (0.20 mM) obtained in a 10 mM aromatic carboxylate and 0.75 mM TTAB at pH 7.0. (1) $S_2O_3^{2-}$; (2) SO_4^{2-}; (3) SO_3^{2-}; (4) S^{2-}. (a) Benzoate; (b) phthalate; (c) 2.6-PDCA; (d) trimellitate. Other conditions as in Fig. 1.
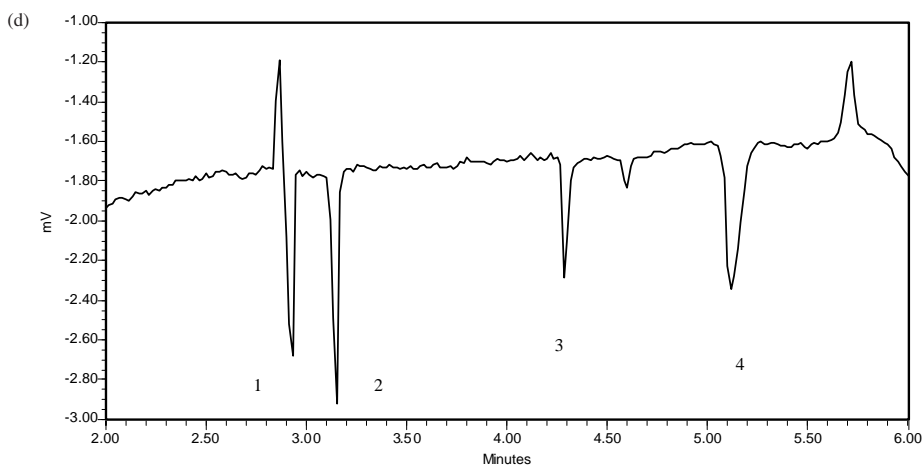
(d)

FIGURE 5   Continued.

TABLE II   The mobility, UV absorptivity and pK_a value (data from [17,31,32])

Species	Mobility	Molar absorptivity $(10^{-4}\,cm^2\,V^{-1}\,s^{-1})$	pK_a $(1\,molar^{-1}\,cm^{-1})$
Benzoate	2.67	44880 (192 nm)	4.21
Phthalate	4.12	27160 (186 nm)	2.95; 5.41
Trimellitate	4.73	7147 (254 nm)	2.52; 3.84; 5.20
2,6-PDCA	4.45	43680 (192 nm)	2.16; 6.92
$S_2O_3^{2-}$	6.48	3500 (210 nm)	0.6; 1.7
SO_4^{2-}	5.77	–	−3; 1.98
SO_3^{2-}	5.13	–	1.89; 7.21
S^{2-}	4.96	8000 (230 nm)	6.99; 12.9

–, Not available.

matched well the mobility of the sulfur species, it had lower molar absorptivity (Table II), which made it unsuitable for indirect UV detection. Severe variation of migration time (Fig. 5a–d) results from the use of the various chromophore ions and their unbuffered electrolyte [34]. The indirect UV detection sensitivity followed the order of 2.6-PDCA > trimellitate > phthalate > benzoate. Generally, indirect UV detection sensitivity decreased with decreasing the molar absorptivity of the BGEs. For example, 2,6-PDCA gave higher detection sensitivity than that of trimellitate and phthalate due to its higher molar absorptivity. This result is in agreement with other studies [15]. 2.6-PDCA also gave good resolution of sulfur species. In view of selectivity and sensitivity, 2,6-PDCA was therefore considered a suitable new electrolyte.

During indirect UV detection, both electrolyte pH and 2,6-PCDA concentrations impact on selectivity and sensitivity [28–30,34]. These conditions therefore need to be optimised. The effective mobility of SO_3^{2-} and HS^- significantly increased with increasing electrolyte pH between 6.0 and 8.0 (Fig. 6) because pH was near their pK_a, leading to ionisation of solutes [31]. In contrast, the EOF remained constant because of the increase in the ionic strength of the electrolyte as the pH increased [24,25]. When the concentration of TTAB was held at 0.75 mM TTAB and the 2,6-PDCA concentrations
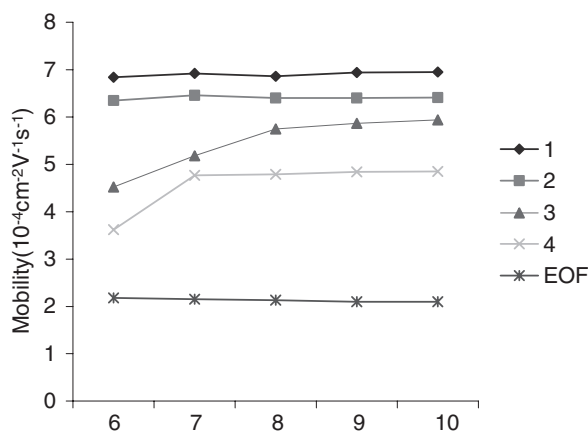
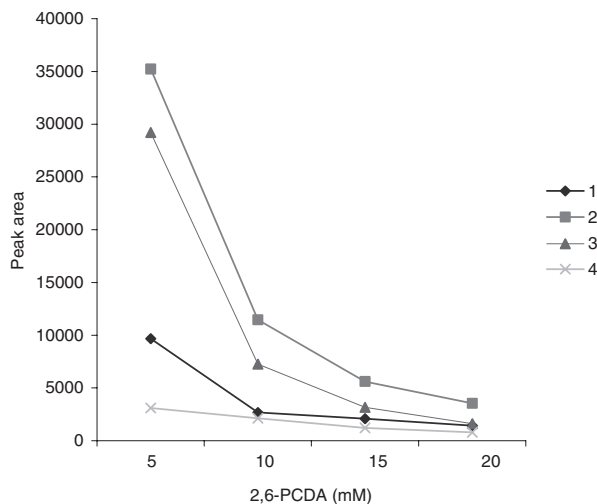FIGURE 6   The effect of the electrolyte pH on the mobility and the EOF. Other conditions as in Fig. 5.

FIGURE 7   The effective of the 2,6-PCDA concentrations on the detection sensitivity. Other conditions as in Fig. 5.

varied from 1 to 20 mM, the changes in the detection sensitivity was observed with increasing concentration of 2,6-PCDA (Fig. 7). The peak area significantly decreased as the concentration increased from 5 to 10 mM. However, the general decrease in peak area as the concentration was increased from 5.0 to 20 mM due to increase in the background absorbance [15]. This suggests that the mobility of sulfur species is almost constant, while the EOF decreased as the concentration of 2,6-PCDA was increased. Higher concentrations favour fast separation, but at the expense of the decreased sensitivity. For consideration of the detection sensitivity and the selectivity, 5 mM PDCA and 0.75 mM TTAB at pH 7.5 was used as the BGE for the optimum separation with good sensitivity and selectivity.

Using this BGE, sulfur species well separated in a short time (Fig. 8). The linearity, detection limit and reproducibility are listed in Table III. The calibration plots for
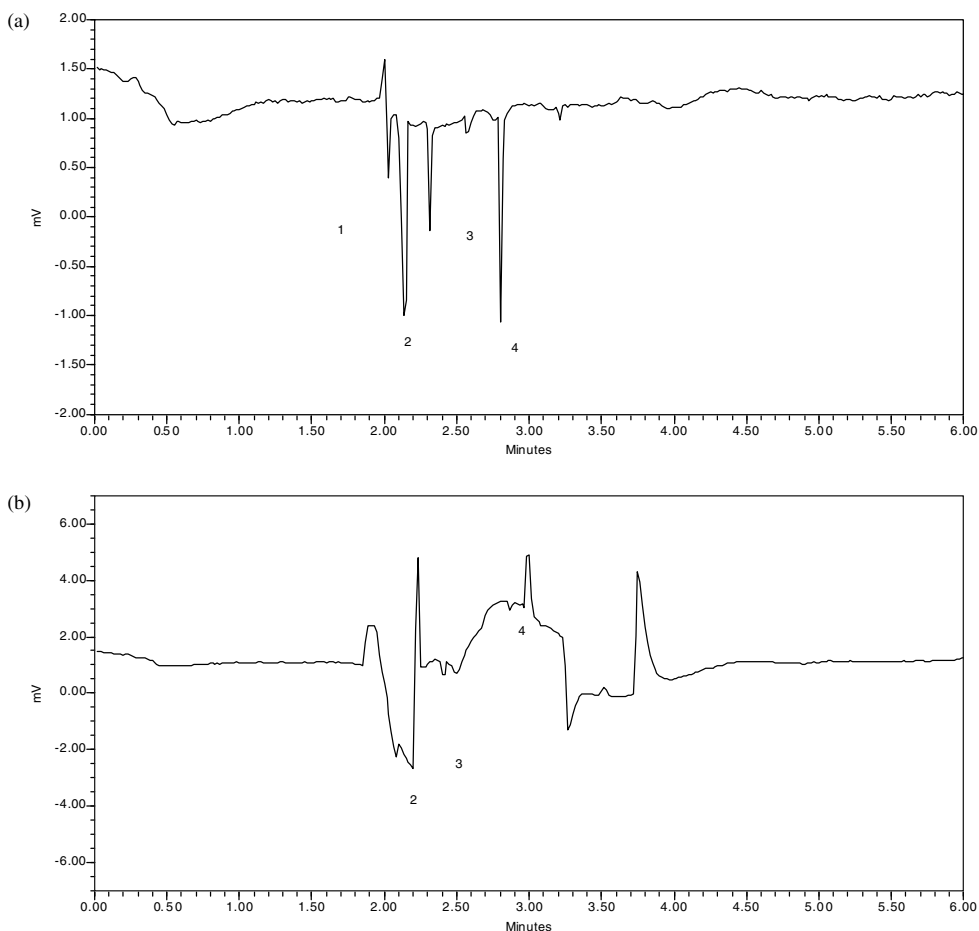
FIGURE 8   Typical electropherograms (a) standard (0.1 mM); (b) wastewater. (1) $S_2O_3^{2-}$; (2) SO_4^{2-}; (3) SO_3^{2-}; (4) S^{2-}. Electrolyte: 5 mM 2,6-PDCA and 0.75 mM TTAB at pH 7.5, other conditions as in Fig. 1.

TABLE III   The performance of co-CZE with indirect UV for the sulfur species

Species	Regression line	Coefficient	Detection limit (μM)	RSD% (peak area, n = 5%)
$S_2O_3^{2-}$	$y = 2.4 \times 10^3 x + 1.5 \times 10^2$	0.998	4.0	2.6
SO_4^{2-}	$y = 4.4 \times 10^4 x + 5.3 \times 10^2$	0.999	2.0	1.7
SO_3^{2-}	$y = 1.1 \times 10^4 x + 4.2 \times 10^2$	0.998	6.0	3.0
S^{2-}	$y = 3.7 \times 10^3 x + 6.3 \times 10^2$	0.996	3.0	2.2

The conditions are the same as in Fig. 5(c).

all solutes were linear over the range 0.01–0.5 mM with correlation coefficients better than 0.996. The detection limits for all solutes ranged from 2 to 6 μM. Recoveries of 88.1–104.8% were obtained by spiking 50 μM of a standard mixture to the sample. However, the separation of $S_2O_3^{2-}$ was a problem because of the interference of the high concentrations of Cl^- and NO_2^- presented in the sample. This method was applied to the determination of sulfur species in wastewater. Figure 8(b) shows a typical

result for sulfur species in wastewater, where a high concentration of SO_4^{2-} (2.7 mM) and low concentrations of SO_3^{2-} (0.14 mM) and HS^- (0.10) were found.

CONCLUSIONS

The separation of sulfur species using co-CZE was possible with both direct and indirect UV detection. The electrolyte pH and organic modifiers could manipulate the separation selectivity of weak ionic sulfur species (sulfite and sulfide). Compared to direct UV detection, indirect UV detection at 214 nm offered a better sensitivity and resolution of sulfur species due to its high molar absorptivity and mobility close to those of the sulfur species. The proposed methods were useful for the separation of SO_4^{2-}, SO_3^{2-}, HS^-. However, because of the interferences by Cl^- and NO_2^-, the method was not suitable for the determination of $S_2O_3^{2-}$. Both direct and indirect UV detection had relatively poor detection limits (3–8 μM) when using hydrostatic injection, and would therefore not be suitable for the determination of a low concentration of sulfur species. Therefore, sample-stacking techniques for on-line preconcentration are currently being investigated to address this problem.

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