

Sulfur speciation by capillary zone electrophoresis Determination of dithionite and its decomposition products sulfite, sulfate and thiosulfate in commercial bleaching agents

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Abstract

In this paper, a capillary zone electrophoretic (CZE) method was developed for the separation of the sulfur species dithionite ($S_2O_4^{2-}$), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$). A carrier electrolyte (pH 7.0) containing 1.5 mmol L^{-1} pyromellitic (PM) acid, 10 mmol L^{-1} Tris(hydroxymethyl)-aminomethane (Tris), 0.5 mmol L^{-1} diethylenetriamine (DETA) and 0.1% (v/v) formaldehyde (as stabilizer for $S_2O_4^{2-}$ and SO_3^{2-}) allowed the determination of the sulfur anions after 9 min CZE separation with indirect UV detection at 214 nm. The addition of 0.1% (v/v) formaldehyde to the sample solution stabilizes dithionite and sulfite as $HOCH_2SO_2^-$ and $HOCH_2SO_3^-$ anions. The procedure was applied for the determination of dithionite and its decomposition products sulfite, sulfate and thiosulfate in commercial formulations of bleaching agents. Dithionite was found to be the major component of the commercial formulations in concentrations between 30.80 and 33.30% (w/w). As anticipated, sulfite, sulfate and thiosulfate were found to be present as decomposition or by-products in the commercial formulations at concentrations of 14.30–14.80, 5.20–5.70 and 0.30–0.40% (w/w), respectively. The results were found to be in good agreement with those of polarographic and spectrophotometric determinations.

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1. Introduction

Sulfur-containing substances play an important role not only in the metabolism of organism and in environmental cycles, but also in many industrial processes. They are related by various oxidation and reduction reactions, disproportioning processes, and they also affect the behavior of other ions (e.g. heavy metals) especially in the environment [1,2]. The analysis of sulfur species is of interest to control industrial products, waste water and waste products, environmental and biological samples.

Sodium dithionite is widely used as a reductant in industry. It finds use as a bleaching agent in textile and paper industries, in the dyeing of cellulose fibers [3], in the manufacturing of various chemicals, and as a biochemical reductant [4].

Dyeing of cotton fabric with anthraquinone vat dyes like indanthrenes or indigo occurs in an alkaline sodium dithionite solution through a reduction reaction [5]. The concentration of dye in reduced form determines the quality of the dyed textile product and it is highly dependent on the pH and concentration of sodium dithionite. Since sodium dithionite is a relative unstable compound that decomposes to sulfate, sulfite and thiosulfate in aqueous media containing dissolved oxygen, the concentration of reducing agent as well as the concentration of dyeing stuff in the dye bath can change rapidly during the process. Therefore, a relative high excess of these compounds has to be used in textile dyeing processes to avoid having their concentrations drop below the critical concentration [6]. Furthermore, the monitoring of dithionite in solutions used in textile dyeing processes is very important in order to reduce the consumption of reducing agent and to obtain a more friendly environmental process [6].

The addition of dithionite is also routinely made to the wet end process waters in paper and pulp production [7]. Thus, these

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waters may contain large concentrations of sulfur species such as sulfate, sulfite and thiosulfate, which have been found to be corrosive towards the steel used in storage tanks. The formation of thiosulfate in closed water circulation can also reach critical corrosion concentration levels and lead to corrosion problems in paper machines. Therefore, the monitoring of sulfur compounds in paper machine process waters can also be helpful in reducing corrosion and in optimizing consumption of dithionite during the process [8].

Dithionite is also a component of household bleaching agents in formulations which contain typically >30% (w/w) sodium dithionite, and some additives such as soda, sodium carbonate and tensides. Dithionite is extremely air sensitive [9], and the commercial product is always contaminated with other sulfur species, which are present unavoidably as by-products or decomposition products. In the domestic bleaching process of textiles, the commercial product containing dithionite is mixed with water and heated for minutes or even for hours depending on the temperature. During the bleaching process, the dyes present in textiles are decomposed by reduction [10].

In the methods reported in the literature, dithionite has been determined by iodimetric [11,12], potentiometric [13], amperometric [6] and spectrophotometric [13] titrations, Raman spectroscopy [14], spectrophotometry [4], ion-chromatography [15,16], polarography and voltammetry [17–19]. It is well known that the stabilization of sulfur species like dithionite and sulfite is a fundamental requirement for an accurate speciation study. However, almost all the methods cited do not offer a satisfactory stabilization of dithionite and sulfite in the sample, although their reactions with formaldehyde to form $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ stable anions have already been established and reported in the literature [3,11,12,15].

Capillary zone electrophoresis (CZE) is increasingly being used in routine analysis of inorganic and organic ions in environmental and pharmaceutical samples [20]. The use of CZE for the analysis of sulfur speciation offers several advantages such as shorter analysis time (usually less than 10 min) in comparison with ion-chromatography [21–24], and a good selectivity because the separation does not imply any interactions with a solid-phase. Small anions with high electrophoretic mobility, like inorganic sulfur anions, migrate strongly to the anodic capillary end and can be detected there (reversed polarity, because the detector is normally on the cathodic end). The electroosmotic flow, leading to the cathode, can retard or prevent the migration to the anode and need to be suppressed or reversed. That is usually performed by the addition of modifiers (quaternary ammonium salts [25,26], or amines such as diethylenetriamine [27]) to the separation buffer or by rinsing with these modifiers before separation.

Indirect UV detection in CZE is a universal technique to detect non-absorbing anions that requires the presence of a chromophoric compound in the separation buffer providing a background signal [28]. Several buffer substances have been used for indirect UV detection of sulfur-containing anions, including chromate [7,25,29,30], phthalate [31], naphthalenesulfonates [32], pyromellitic acid [27,32] and *p*-aminobenzoate [26].

The aim of this work was to study the capillary electrophoretic separation of dithionite ($\text{S}_2\text{O}_4^{2-}$) and its decomposition products thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfate (SO_4^{2-}), and sulfite (SO_3^{2-}) using pyromellitic acid for the indirect UV detection and formaldehyde as additive in the carrier electrolyte. The use of formaldehyde as stabilizing medium for dithionite has been already studied before [3,12,15,33], and it was applied here for CZE separations. Considerations on the use of stabilizing mediums for the accurate determination of dithionite and sulfite by CZE were presented. The methodology was applied for the sulfur speciation in commercial formulations of bleaching agents used in the household. The results obtained were compared with those of polarographic and spectrophotometric determinations.

2. Experimental

2.1. Instrumentation and apparatus

A BioFocus 3000 capillary electrophoresis system (BioRad) equipped with a program controlled UV-vis detector (190–800 nm) was used. Separations were performed using an uncoated fused-silica capillary tube of 50 cm \times 75 μm I.D. (CS-Chromatographie Service GmbH), with 25 kV of applied voltage. Indirect detection was performed at the anodic side by the measurement of absorbance at 214 nm. A BioFocus integrator program with reversed polarity was used to obtain positive peaks and to record all data.

The solutes were injected in the hydrodynamic mode from the cathodic compartment by pressure (5 psi s = 3.44×10^4 Pa s). All experiments were conducted at 25 °C.

The spectrophotometric measurements were performed using a Perkin-Elmer Lambda 40 UV-vis spectrophotometer with 1 cm matched silica cells.

The polarographic measurements were performed using a Metrohm 693 VA Processor in combination with a 694 VA Stand (all from Metrohm, Herisau). The three-electrode configuration was consisted of the static mercury drop electrode (SMDE) from multi mode electrode (Metrohm) as working electrode, an Ag/AgCl reference electrode with a 3 M KCl filling solution and a platinum wire as auxiliary electrode.

2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade. Water was purified by a NANOpure II system (Barnstead). Sodium sulfite, sodium sulfate, sodium thiosulfate, sodium hydroxide, potassium chromate, diethylenetriamine (DETA) and 30% hydrochloric acid were obtained from Merck. Sodium dithionite (85%), Tris(hydroxymethyl)-aminomethane (Tris), pyromellitic acid (PM) and formaldehyde solution (36.5%) were obtained from Fluka. Sodium formaldehyde sulfoxylate (Rongalite), and sodium formaldehyde bisulfite were obtained from Aldrich.

100 mg L⁻¹ standard solutions of the sulfur anions $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , SO_3^{2-} , $\text{HOCH}_2\text{SO}_2^-$, and $\text{HOCH}_2\text{SO}_3^-$ were prepared just before their use by dissolving the appropriate amount of

sodium salts in water. 100 mg L⁻¹ S₂O₄²⁻ standard solution was prepared by dissolving the appropriate amount of the sodium salt in a 0.1% (v/v) formaldehyde aqueous solution.

A solution containing 1.5 mmol L⁻¹ PM, 10 mmol L⁻¹ Tris, 0.5 mmol L⁻¹ DETA and 0.1% (v/v) formaldehyde (pH 7.0, adjusted with 0.1 mol L⁻¹ NaOH) was employed as carrier electrolyte. A solution containing 9.5 mmol L⁻¹ K₂CrO₄ (Merck), 1.0 mmol L⁻¹ DETA and 0.1% (v/v) formaldehyde (pH 7.0, adjusted with hydrochloric acid 30%) was tested as carrier electrolyte in the optimization step of the work. The electrolyte solutions were filtered through a 0.45 μm membrane filter and degassed for 30 min under vacuum prior to use.

2.3. Analytical procedure

The capillary was rinsed with water for 10 min and with a 0.1 mol L⁻¹ NaOH solution for 15 min, and then equilibrated with the carrier electrolyte for 40 min at the beginning of each day. After each electrophoretic separation, the capillary was rinsed for 2 min with water, 3 min with a 0.1 mol L⁻¹ NaOH solution and 4 min with carrier electrolyte (same composition as the running electrolyte).

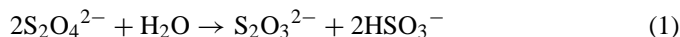
For the determinations using commercial formulations, dithionite-based bleaching agents employed for textiles were used as samples. The commercial samples had the following composition according to the manufacturers: sodium dithionite >30%, soda, anionic tenside and perfume (manufacturer A); sodium dithionite >30%, sodium carbonate, stabilizers and perfume (manufacturer B). For the analyses, 5 mg of the product was dissolved in 50 mL of a 0.1% (v/v) formaldehyde aqueous solution for stabilization. All samples used for the analyses were filtered through a 0.45 μm membrane filter before the measurements. The concentrations of S₂O₃²⁻ and SO₄²⁻ in the samples were determined by the standard addition method (*n* = 5). The determination of S₂O₄²⁻ and SO₃²⁻ concentrations was made by standard additions (*n* = 5) of HOCH₂SO₂⁻ and HOCH₂SO₃⁻ solutions, respectively. The concentration of SO₃²⁻ was calculated by taking the difference of the total HOCH₂SO₃⁻ (S₂O₄²⁻ + SO₃²⁻) concentration from the HOCH₂SO₂⁻ (S₂O₄²⁻) concentration. The final concentration of SO₃²⁻ and S₂O₄²⁻ in the sample was then recalculated from the HOCH₂SO₂⁻ and the HOCH₂SO₃⁻ concentrations.

3. Results and discussion

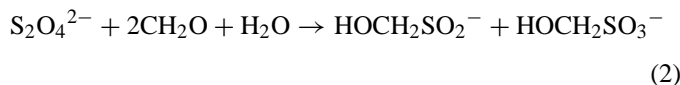
3.1. Stabilization of dithionite and sulfite for capillary zone electrophoretic speciation studies

The stabilization of sulfur species that undergo decomposition in solution prior to the analysis seems to be the most important step in speciation studies. In a previous work [34], we described a systematic study of different conditions for sulfite stabilization in aqueous solution as well as the capillary electrophoretic separation of sulfite, sulfate, thiosulfate and peroxodisulfate. A good stabilization for sulfite has been achieved by adding 5% (v/v) propanol as stabilizer to both the carrier electrolyte and the sample solution [34].

The determination of dithionite is very difficult due to its extreme sensitivity to oxygen in aqueous solution, and to the spontaneous decomposition of such solutions even with the exclusion of oxygen [35]. This decomposition depends strongly on the pH, and at pH values close to 7 the main decomposition reaction can be represented by the equation [36,33]



However, the stabilization of dithionite in aqueous solution can be achieved by adding formaldehyde both to the carrier electrolyte and sample solution. It is well known that formaldehyde converts S₂O₄²⁻ rapidly and quantitatively into the hydroxymethanesulfinate and hydroxymethanesulfonate anions, which are stable species in aqueous solution [3,11,12]



The addition of formaldehyde to sulfite aqueous solutions can also lead to its stabilization as hydroxymethanesulfonate anion [3,34]



The stabilization of S₂O₄²⁻ in solution and its electrophoretic separation under stable conditions could not be achieved by using other stabilizing mediums, like those employed for sulfite stabilization in aqueous solution [34]. A systematic study with these stabilizing mediums and others described elsewhere for polarographic determinations [33] showed that dithionite was not stabilized during the electrophoretic separation, so that the electropherograms were always composed of sulfite, sulfate and thiosulfate peaks. This behavior was also observed in other procedures without the adding of stabilizers prior to the separation of dithionite [8,27,37].

Therefore, the accurate determination of the unstable sulfur species dithionite and sulfite by CZE should always include appropriated stabilizers in both the carrier electrolyte and the sample solution. Table 1 summarizes the experimental conditions for determination of dithionite and sulfite in the presence of decomposition products by CZE, considering the systematic study performed with different stabilizers described previously [34] and in this work.

3.2. Capillary zone electrophoretic separation of dithionite, thiosulfate, sulfate and sulfite using formaldehyde as stabilizer

The separation of S₂O₄²⁻ from other sulfur oxyanions by ion chromatography has already been reported in the literature [2,15,38]. To the best of our knowledge, the simultaneous separation of dithionite and its main decomposition products sulfite, thiosulfate and sulfate has not been performed by CZE yet. Thus we have studied the possibility to separate these sulfur anions by CZE using two different carrier electrolytes for the indirect UV detection. The carrier electrolytes were composed of Tris buffer, DETA as electroosmotic flow modifier, formaldehyde as stabilizer, and pyromellitic acid or chromate as UV-absorbing

Table 1
Summary of experimental conditions for determination of dithionite and sulfite in stabilized forms by CZE

Sulfur species	Sub-products	Stabilizer	Migration time	Working electrolyte
SO_3^{2-}	SO_4^{2-}	Propanol [34] or Formaldehyde [34]	3.5 min (as SO_3^- ion) 6.5 min (as $\text{HOCH}_2\text{SO}_3^-$ ion)	$\text{K}_2\text{Cr}_2\text{O}_4$ 9.5 mmol L^{-1} DETA 1 mmol L^{-1} Propanol 5% (or formaldehyde 1%) pH 10.3
SO_3^{2-} $\text{S}_2\text{O}_4^{2-}$	SO_4^{2-} SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$	Formaldehyde Formaldehyde	6.2 min (as $\text{HOCH}_2\text{SO}_3^-$ ion) 6.2 min (as $\text{HOCH}_2\text{SO}_3^-$ ion) 7.8 min (as $\text{HOCH}_2\text{SO}_2^-$ ion)	PM 1.5 mmol L^{-1} DETA 0.5 mmol L^{-1} Tris 10 mmol L^{-1} Formaldehyde 0.1% pH 7.0

probe (see Section 2). Since $\text{HOCH}_2\text{SO}_3^-$ ions can partly dissociate in alkaline medium to give SO_3^{2-} and CH_2O [15,38], the carrier electrolytes were buffered at pH 7.0 to assure a successful stabilization of all the sulfur species in the electrophoretic system.

Chromate ion, which has a high electrophoretic mobility ($0.72 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$), is ideally suited for detecting rapidly migrating anions. Pyromellitic acid (PM), a polycarboxylic acid with a lower mobility ($0.55 \text{ cm}^2 \text{ kV}^{-1} \text{ s}^{-1}$), has also been successfully employed [1]. In this work, we have found that a carrier electrolyte at pH 7.0 containing 1.5 mmol L^{-1} PM, 10 mmol L^{-1} Tris, 0.5 mmol L^{-1} DETA and 0.1% (v/v) formaldehyde allows the separation of $\text{S}_2\text{O}_4^{2-}$ (as $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ anions) and its main decomposition products SO_3^{2-} (as $\text{HOCH}_2\text{SO}_3^-$ anion), $\text{S}_2\text{O}_3^{2-}$ and SO_4^{2-} , as shown in Fig. 1. However, the separation of the species $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ could not be achieved by using the same electrolyte system (pH 7.0) with chromate as UV absorbing probe, and the electropherograms presented only one peak at 6.2 min.

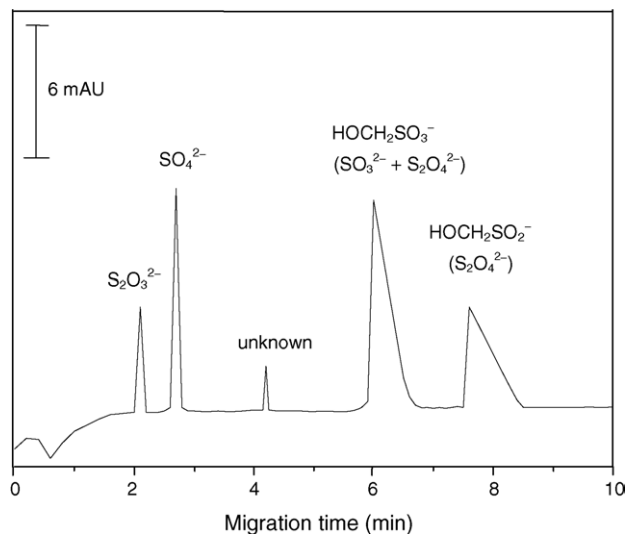


Fig. 1. Electropherogram of a mixture containing $\text{S}_2\text{O}_4^{2-}$ (100 mg L^{-1}), $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} and SO_3^{2-} (each 50 mg L^{-1}) in 0.1% (v/v) formaldehyde solution; carrier electrolyte: PM 1.5 mmol L^{-1} , DETA 0.5 mmol L^{-1} , Tris 10 mmol L^{-1} , formaldehyde 0.1% (pH 7.0); separation voltage: -25 kV ; separation temperature: 25°C ; UV-detection: 214 nm (indirect); sample injection: hydrodynamic ($5 \text{ psi} = 3.44 \times 10^4 \text{ Pa}$); capillary: uncoated fused-silica ($50 \text{ cm} \times 75 \mu\text{m}$).

A possible explanation for the absence of a $\text{HOCH}_2\text{SO}_2^-$ peak in this carrier electrolyte is that chromate may act as an oxidizing medium, converting $\text{HOCH}_2\text{SO}_2^-$ partially or totally to SO_4^{2-} ions during the electrophoretic separation. The increased peak observed for SO_4^{2-} using this carrier electrolyte can support this fact. However, this fact was not systematically investigated in this work, since the separation of $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ was successfully achieved in the carrier electrolyte containing pyromellitic acid (PM).

As neither sulfate nor thiosulfate react with formaldehyde in water, dithionite and sulfite can be stabilized and selectively separated from these sulfur species as $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ anions. Therefore, as both $\text{S}_2\text{O}_4^{2-}$ and SO_3^{2-} ions react with formaldehyde in aqueous solution to form the $\text{HOCH}_2\text{SO}_3^-$ anion according to (2) and (3), the peak at 6.2 min observed in the electropherogram (Fig. 1) represents not only the $\text{S}_2\text{O}_4^{2-}$ concentration, but also the SO_3^{2-} concentration in solution. Nonetheless, the peak at 7.8 min obtained for $\text{HOCH}_2\text{SO}_2^-$ anion is selective for $\text{S}_2\text{O}_4^{2-}$ (2) and can be used for their accurate determination. It means that the SO_3^{2-} concentration in solution can be determined indirectly by taking the difference of the total $\text{HOCH}_2\text{SO}_3^-$ concentration (equivalent to SO_3^{2-} and $\text{S}_2\text{O}_4^{2-}$ anions) from the $\text{HOCH}_2\text{SO}_2^-$ concentration (equivalent to $\text{S}_2\text{O}_4^{2-}$ anion). An unknown peak at 4.3 min can also be identified in the electropherogram, but without interference on the peaks obtained for the sulfur species. Since this peak is also observed in the electropherogram obtained for a 0.1% (v/v) formaldehyde solution (blank measurement), it may be attributed to an unknown anionic species present as impurity in the reagent.

The detection limits for determination of the sulfur anions by CZE using the PM carrier electrolyte were calculated using the threefold baseline noise and slope of the calibration function of each sulfur anion ($2\text{--}10 \text{ mg L}^{-1}$) and they were found to be 0.80 mg L^{-1} ($\text{S}_2\text{O}_4^{2-}$), 1.0 mg L^{-1} (SO_3^{2-}), 0.45 mg L^{-1} (SO_4^{2-}) and 0.6 mg L^{-1} ($\text{S}_2\text{O}_3^{2-}$).

4. Analytical application

The CZE method described above was applied for the determination of dithionite and its decomposition products sulfite, sulfate and thiosulfate in commercial formulations of bleaching agents used in the household. For this purpose, two formula-

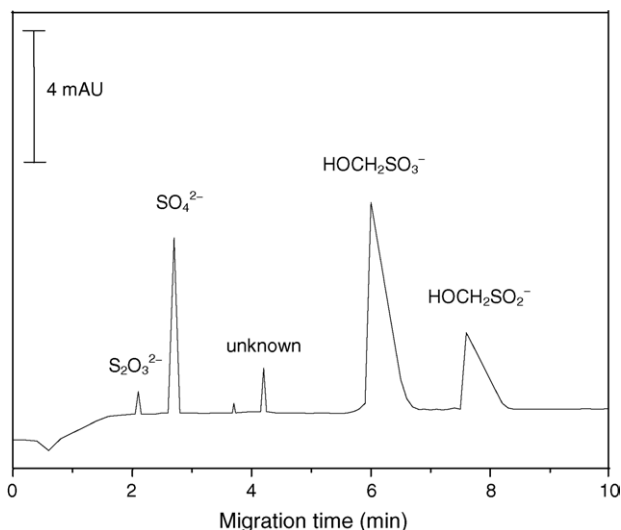


Fig. 2. Electropherogram of a dithionite-based commercial bleaching agent; sample: 5 mg in 50 mL of 0.1% formaldehyde solution; carrier electrolyte: PM 1.5 mmol L^{-1} , DETA 0.5 mmol L^{-1} , Tris 10 mmol L^{-1} , formaldehyde 0.1% (pH 7.0); other parameters as described in Fig. 1.

tions from different manufactures were analyzed. Fig. 2 shows the electropherogram obtained for a 5 mg bleaching agent sample stabilized in a 0.1% (v/v) formaldehyde solution. As it can be seen, sulfite, sulfate and thiosulfate are present in the sample as decomposition products of dithionite. The presence of these sulfur species in all the sample electropherograms may be related to the decomposition of dithionite to *meta*-bisulfite and thiosulfate at solid state [39,40]. The presence of sulfite and sulfate as decomposition products or by-products may be related to the subsequent decomposition of *meta*-bisulfite.

The experimental results obtained by the proposed CZE method were compared to those obtained by polarographic and spectrophotometric methods described in previous works [33,41,42]. The results shown in Table 2 were found to be in good agreement concerning the dithionite and thiosulfate concentrations determined by the comparative methods. The results have also shown that the analyzed samples contained dithionite in concentrations close to that described by the manufactures (>30% sodium dithionite), while sulfite, sulfate and thiosulfate

Table 2
Determination of dithionite, sulfite, sulfate and thiosulfate in commercial formulations of bleaching agents ($n = 3$)

Sample	Sulfur species (%) ^a			
	$\text{S}_2\text{O}_4^{2-}$	$\text{S}_2\text{O}_3^{2-}$	SO_4^{2-}	SO_3^{2-}
Manufacturer A				
CZE	30.80 ± 1.0	0.40 ± 3.0	5.20 ± 2.0	14.30 ± 2.0
Polarography	31.10 ± 1.0	0.47 ± 2.0	–	–
Spectrophotometry	29.40 ± 1.0	–	–	–
Manufacturer B				
CZE	33.30 ± 1.0	0.30 ± 2.0	5.70 ± 1.0	14.80 ± 1.0
Polarography	35.10 ± 0.7	0.33 ± 3.0	–	–
Spectrophotometry	34.80 ± 1.3	–	–	–

^a Values (%) expressed in w/w.

were also present in the samples as decomposition products or by-products.

5. Conclusions

Capillary zone electrophoresis with indirect detection at 214 nm using 1.5 mmol L^{-1} pyromellitic acid, 10 mmol L^{-1} Tris, 0.5 mmol L^{-1} DETA and 0.1% (v/v) formaldehyde (pH 7.0) as carrier electrolyte provides a rapid separation of dithionite (as $\text{HOCH}_2\text{SO}_2^-$ and $\text{HOCH}_2\text{SO}_3^-$ anions), sulfite (as $\text{HOCH}_2\text{SO}_3^-$ anion), sulfate and thiosulfate. The stabilization of dithionite and sulfite ions in the sample is very important if accurate determinations are to be achieved. After the stabilization in the sample using formaldehyde, dithionite can be determined in the presence of its decomposition products after 9 min CZE separation. The method allowed the determination of dithionite, sulfite, sulfate and thiosulfate in commercial formulations of bleaching agents. The results obtained with the proposed method were found to be in good agreement with those of polarographic and spectrophotometric determinations, which also prove the accuracy of the procedure. The CZE method described may be useful for application in other particulate samples (e.g. from textile and paper industries) where the rapid monitoring and control of dithionite and/or its decomposition products is necessary, such as those already described in other recent works [6,8].

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