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Sulfur speciation by capillary electrophoresis with indirect spectrophotometric detection: In search of a suitable carrier electrolyte to maximize sensitivity

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Abstract

Various probes have been evaluated as alternative ions to chromate, which is most frequently used in the analysis of small inorganic anions by capillary electrophoresis with indirect UV detection. Sulfur species ($S_2O_3^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$, S(−II)) have been determined. The optimization of the method was particularly focused on S(−II) since this species rapidly yields $S_2O_3^{2-}$ and SO_4^{2-} in the presence of oxidizing agents. Therefore, it could not be analysed by capillary electrophoresis with chromate as the background electrolyte. The alternative probe ions all contain aromatic rings (benzene or naphthalene) to provide the intrinsic background absorbance for indirect detection. They are all fully ionized at the pH chosen for this application (TRIS buffer, pH=8) and the range of their mobilities is large enough to suit the analytes mobilities. They have no oxidizing properties. Transfer ratios have been determined experimentally and compared to calculated values derived from the Kohlrausch regulation function. All experimental values were lower than expected from the calculations, which proves the limitations of the Kohlrausch theory concerning the configuration (electrolyte/analyte) of this study. However, maximizing $(z_A/z_E)\cdot\epsilon_E$ (with z_A and z_E being the charges of the analyte and the probe, respectively, and ϵ_E the molar absorptivity of the probe) and keeping the mobility of the probe close to those of the analytes will give a good hint for the choice of the most suitable UV-absorbing probe. Pyromellitate and naphthalenetrisulfonate, the mobilities of which are close to that of S(−II), give the best sensitivity for this species, with good resolution and sensitivity for all other species.

Keywords: Speciation; Carrier electrolyte; Sulfur; Pyromellitate; Naphthalenetrisulfonate

1. Introduction

Sulfur speciation is of great interest regarding the geochemistry of deep underground fluids: it is a reliable means of determining their oxidation state.

The analysis of several species of the same compound in equilibrium in their natural medium is often tedious because of the possible alteration of their speciation induced by the analytical conditions. One may consider the use of capillary zone electrophoresis (CZE) for the analysis of sulfur speciation, given the following features: the analysis time is short (usually less than 10 min), the pH and ionic strength of the separation medium (electrolyte) can be chosen in accordance with those of the sample matrix, and the selectivity of the separation does not imply interactions with a solid-phase. Furthermore, it is compatible with indirect photometric detection, often used with inorganic transparent species. This separation method has already been investigated for the quantitative analysis of inorganic anions in explosive residues [1] but sulfide can not be detected with the electrolyte used in these experiments (chromate, pH=7.8). Only a higher pH value (pH=11),

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for which the oxidation due to chromate is greatly reduced, could lead to the detection of sulfide in samples from the kraft pulping process [2]. However, these analytical conditions are not satisfactory when applied to underground waters, the pH values of which usually range between 7 and 9. Alternative background electrolytes (BGE) are aromatic carboxylic or sulfonic acids. Naphthalenesulfonates are already known as efficient ion-chromatographic mobile phases [3,4] because of their selective ion-exchange abilities for separating the most common anions as well as their large molar absorptivities that induce good indirect detection sensitivity. Similar reasons were put forward for the choice of benzenedisulfonic acid-based eluents [5]. Successful CZE separations of inorganic anions with indirect UV detection were achieved by introducing benzenetetracarboxylic acid (pyromellitic acid, PM) in the BGE [6]. The net charge of this probe being pH-dependent, its effective mobility can be adjusted to those of the analytes by modification of the pH of the BGE. Naphthalenesulfonates were thoroughly studied as promising probes for capillary electrophoresis with indirect UV detection [7]. It was found that either naphthalenedisulfonate (NDS) or naphthalenetrisulfonate (NTS) could be used, depending on the mobility of the analyte: a closer mobility match between the chromogenic probe and the analyte improved the detection limit of the method.

Theoretical considerations derived from the Kohlrausch theory were discussed by Foret et al. [8] for the selection of a suitable chromophore to be used as carrier electrolyte. Again, it was concluded that mobility was of great importance in the achievement of negligible electromigration dispersion and high detection sensitivity, the best sensitivity being obtained in low-concentration BGE with high absorption. Nielen introduced the response factor (or transfer ratio R) in a theoretical discussion on the quantitative aspects of indirect UV detection in CZE [9]. This parameter measures the extent to which the displacement of the probe by the analyte is complete. It was the basis of a similar study on the evaluation of various benzenecarboxylic acids as carrier electrolytes [10]. Significant deviations were observed between experimental and predicted values and showed the limitations of the Kohlrausch theory applied to the dynamic CZE model.

The objectives of this work were the simultaneous analysis of various sulfur species (namely sulfate SO_4^{2-}, thiosulfate $S_2O_3^{2-}$, tetrathionate $S_4O_6^{2-}$, and sulfide HS^-) using CZE with indirect photometric detection.

1.1. Experimental determination of the transfer ratio in electrophoresis with indirect UV detection

The transfer ratio R is defined as the number of moles of probe co-ions displaced by one mole of analyte ions:

$$R = \frac{[E]^E - [E]^A}{[A]^A} \tag{1}$$

$[E]^E$ and $[E]^A$ refer to the concentration of the probe in the pure BGE and in a sample zone, respectively; $[A]^A$ is the concentration of the analyte in the sample zone.

If we consider a band of solute δl that migrates through the capillary with a constant velocity v_{app}, the width of the peak on the electropherogram (δt on a time scale) (see Fig. 1) is:

$$\delta t = \frac{\delta l}{v_{app}} \tag{2}$$

Electromigration dispersion in the sample migrating zone induces distortions of the corresponding peak. Because of the resulting triangular peak shape, the corrected area A_c, defined as the peak area divided by the migration time t_m, is equal to:

$$A_c = \frac{\delta t \cdot \mathscr{A}_{max}}{2} \cdot \frac{1}{t_m} \tag{3}$$

with $t_m = l_d / v_{app}$, l_d being the length to the detector, and $\mathscr{A}_{max}$ the maximum of absorbance of the peak (see Fig. 1).

Hence, from Eq. (2) and Eq. (3), we get

$$A_c = \frac{\delta l}{2 \cdot l_d} \cdot \mathscr{A}_{max} \tag{4}$$

When operating with direct UV detection, the Beer-Lambert law ensures that

$$\mathscr{A}_{max} = \varepsilon_A \cdot \bar{l} \cdot [A]^A_{max} \tag{5a}$$

where ε_A is the molar absorptivity of the analyte and $\bar{l}$ is the mean optical pathlength through the capillary

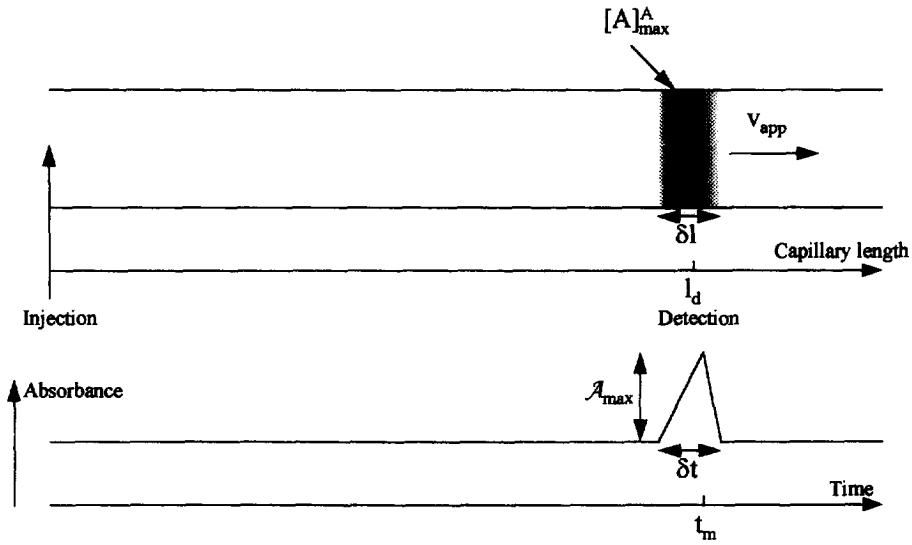

Fig. 1. Schematic diagram of the sample zone passing through the detection window of the capillary and the corresponding electropherogram.

($\bar{l} \approx 0.6 \cdot d_c$ with d_c the diameter of the capillary [8]).

When indirect UV is concerned, the absorbance signal corresponds to the difference between the absorbance of the probe in the BGE and that of the probe in the sample zone, assuming that neither the analyte nor the BGE counter-ion are absorbent.

$$\mathcal{A}_{max} = \varepsilon_E \cdot \bar{l} \cdot [E]^E - \varepsilon_E \cdot \bar{l} \cdot [E]^A_{max} \quad (5b)$$

with ε_E the coefficient of absorption of the BGE co-ion E. Substituting Eq. (1) into Eqs. (5b) leads to:

$$\mathcal{A}_{max} = \varepsilon_E \cdot \bar{l} \cdot R \cdot [A]^A_{max} \quad (5c)$$

Applying Eq. (4) and Eq. (5a) or (5c), we can derive:

$$A_c = \frac{\delta l}{2 \cdot l_d} \cdot \varepsilon_A \cdot \bar{l} \cdot [A]^A_{max}$$

$$= 0.3 \cdot \frac{\delta l}{l_d} \cdot \varepsilon_A \cdot d_c \cdot [A]^A_{max} \quad (6a)$$

with direct detection mode and, similarly

$$A_c = 0.3 \cdot \frac{\delta l}{l_d} \cdot \varepsilon_E \cdot R \cdot d_c \cdot [A]^A_{max} \quad (6b)$$

with indirect detection mode.

Besides, the injected amount of analyte Q_A is totally recovered in the triangular-shaped sample zone that passes through the capillary at the detection window.

$$Q_A = V_{inj} \cdot [A]_{inj} = \frac{\pi \cdot d_c^2}{4} \cdot \delta l \cdot \frac{[A]^A_{max}}{2} \quad (7)$$

Where V_{inj} is the injected volume and $[A]_{inj}$ is the concentration of the analyte A in the injected sample. Finally, combining Eq. (7) with Eq. (6a) or (6b) gives

$$A_c = \frac{2.4 \cdot \varepsilon_A \cdot V_{inj}}{\pi \cdot d_c \cdot l_d} \cdot [A]_{inj} \quad (8a)$$

with direct detection mode and,

$$A_c = \frac{2.4 \cdot \varepsilon_E \cdot V_{inj} \cdot R}{\pi \cdot d_c \cdot l_d} \cdot [A]_{inj} \quad (8b)$$

with indirect detection mode.

Now, if we consider the calibration curve of the probe E, taken as the analyte, in a transparent electrolyte, the corresponding slope of the first order regression fitting is given by

$$\alpha_E = \frac{2.4 \cdot \varepsilon_E \cdot V_{inj}}{\pi \cdot d_c \cdot l_d} \quad (9a)$$

Similarly, the expression of the slope of the cali-

bration curve of a given analyte A in the electrolyte E is

$$\alpha_A = \frac{2.4 \cdot \varepsilon_E \cdot V_{inj} \cdot R}{\pi \cdot d_c \cdot l_d} \quad (9b)$$

If similar experimental conditions are used for both series of data (same capillary, same injected volume, same analytical conditions), the experimental determination of R can be derived:

$$R = \frac{\alpha_A}{\alpha_E} \quad (10)$$

1.2. Kohlrausch's regulation function

Assuming that all the constituents of the BGE and the sample are fully ionized, the following equation can be derived from the Kohlrausch's regulation function [10]:

$$R = \frac{z_A}{z_E} \cdot \frac{m_E}{m_A} \cdot \frac{m_A + m_C}{m_E + m_C} \quad (11)$$

where z is the charge and m the absolute value of the effective mobility of the BGE co-ion E, the counter-ion C, and the sample A.

Several publications have discussed the applications and limitations of this equation [11–17]. Poppe [12] stated that the Kohlrausch theory can not be applied to complicated systems where the BGE contains various protolytic forms in equilibrium. This was experimentally confirmed by Cousins et al. [10] who found only poor agreement between the calculated and experimental determinations of the transfer ratio, even though the operated pH provided full ionization of the BGE components. However, Collet and Gareil [17] have recently shown that surprisingly good predictions could be drawn from the Kohlrausch theory as they applied it to the CZE analysis of cations with indirect UV detection using weak electrolytes and a UV-absorbing counter-ion.

The work described in this paper is part of some general investigations concerning the use and limitations of the Kohlrausch theory to CZE systems.

2. Experimental

2.1. Chemicals, sample and BGE preparation

Tris(hydroxymethyl)aminomethane (TRIS), 1,5-naphthalenedisulfonic acid, tetrahydrate (NDS) and 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid, PM) were obtained from Aldrich. Phthalic acid (PHT) and diethylenetriamine (DETA) were from Merck, as well as sodium thiosulfate ($Na_2S_2O_3$), sodium sulfate (Na_2SO_4) and sodium sulfide, hydrate ($Na_2S \cdot xH_2O$). Sodium tetrathionate ($Na_2S_4O_6$) was from Fluka. Naphthalene-1,3,6-trisulfonic acid (NTS, Fluka), 1,3-benzenedisulfonic acid (BDS, Sigma) and chromic acid (CHR, Merck) were purchased as sodium salts and converted to the corresponding acid by elution through a column filled with Dowex-50W resin, hydrogen form (Sigma). The water used throughout this study was purified with a MilliQ system (Millipore).

Stock solutions of $Na_2S_2O_3$, Na_2SO_4, $Na_2S_4O_6$, and Na_2S, 2 10^{-2} M in degassed water were prepared daily.

The electrolytes were composed of 10 mM TRIS, the chromophore at various concentrations (see Table 1 and discussion), and 0.5 mM DETA as the electroosmotic flow modifier. They were prepared

Table 1
Composition of the BGE and characteristics of the probe ions

Probe E	$[E]^E$ (mM)	z_E	I_{cal} ($\cdot 10^{-3}$)	pH_{cal}	pH_{mes}	m_E ($\cdot 10^{-5}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$)	R.S.D. (%)	λ (nm)	ε_E
CHR	3	2	9.4	8.15	8.10	71.6	1.1	254	2640
PHT	3	2	9.5	8.14	8.10	48.1	0.7	214	9950
PM	1.5	4	15.5	8.15	8.00	55.1	0.9	214	26 200
BDS	3	2	9.5	8.14	8.05	54.3	0.8	214	9950
NDS	3	2	9.5	8.14	8.10	48.1	1.5	214	31 000
NTS	2	3	12.5	8.14	8.00	62.0	1.7	214	31 600

$[E]^E$, concentration of the probe in the BGE; z_E, charge of the probe; I_{cal}, calculated ionic strength of the BGE; pH_{cal} and pH_{mes} calculated and measured pH; m_E, measured effective mobility of the probe; λ, detection wavelength; ε_E, measured molar absorptivity of the probe at the given detection wavelength.

with degassed water and filtered through 0.45 μm filters (Millipore).

2.2. Apparatus, analytical conditions

The CZE apparatus was a Quanta 4000 (Waters) equipped either with a mercury lamp and a 254 nm filter or with a zinc lamp and a 214 nm filter. Two Accusep 60 cm×75 μm I.D. fused-silica capillaries were used in this study; their effective length to the detector window was 52.4 cm.

All sample injections were hydrostatically driven from the cathodic compartment ($\Delta h_0 = 10$ cm for 30 s), which corresponds to an injection volume of ca. 43 nl.

The run voltage was −20 kV except for the determination of the electroosmotic mobility for which it was reversed to +20 kV.

All probe mobilities were determined by injecting them in a transparent electrolyte (3 m*M* H_3PO_4, 10 m*M* TRIS and 0.5 m*M* DETA, pH=8).

Absorptivity determinations were performed with a Lambda5 UV–Vis spectrophotometer (Perkin-Elmer).

3. Results and discussion

3.1. Choice of the BGE

In order to limit the modification of the equilibria that govern sulfur, the pH of the BGE was adapted to that of natural water samples to be analysed, i.e., pH=8. This value ensures that sulfate, thiosulfate, and tetrathionate are fully ionized while the net charge of sulfide (pK_A (H_2S/HS^-)=6.99) is −0.93. The latter will be referred to as S(−II). The pH must be controlled by a non-absorbing buffer with a cationic acidic form and a neutral basic form in order not to interfere with the chromophore. Its acidic form corresponds to the counter-ion (C) of the BGE. Counter-ions of low effective mobility are preferred to minimize the BGE conductivity and thus prevent Joule heating. Furthermore, according to Eq. (11), the transfer ratio depends on the electrophoretic mobility of the counter-ion (m_C). Depending on the relative values of the electrophoretic mobilities of the probe (m_E) and the analyte (m_A), its variations will be as indicated in Fig. 2. A low m_C approximates to

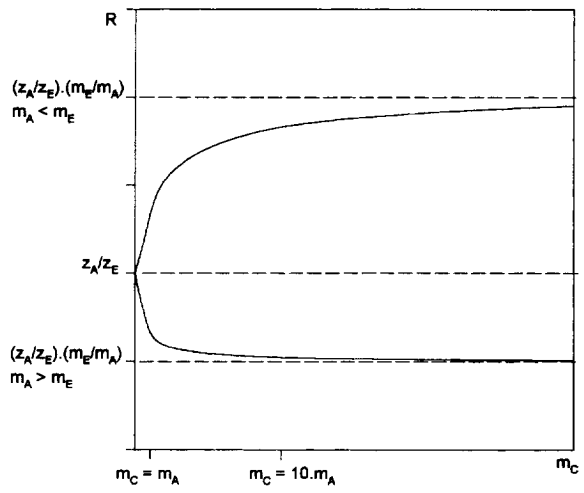

Fig. 2. Variations of the transfer ratio R between an analyte A and a probe E as a function of the mobility of the BGE counter-ion C. In all instances described in this paper, $m_A > m_E$.

the ideal situation where the displacement of the probe by the analyte occurs on an equivalent-per-equivalent basis. In this case, the match between m_A and m_E is of lesser importance, although too loose a match will cause electromigration broadening [8]. Among the frequently used cationic/neutral buffers in CZE that would suit the proper pH-range, TRIS has a relatively low absolute mobility ($m_C^0 = 29.5 \cdot 10^{-5}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ [18]); its pK_A is equal to 8.08.

The co-ion (probe E) has to meet the following requirements: (1) its molar absorptivity must be high in a wavelength range where that of the analytes is low in order to ensure good sensitivity of the indirect detection, keeping its concentration as low as possible, and (2) its mobility must be close to those of the analytes, although it is not a critical parameter in this case. Aromatic carboxylic and sulfonic acids were chosen as the investigated chromophores; they are all fully ionized at pH 8. Their characteristics (mobility, absorptivity) were determined experimentally (Table 1). The mobilities of the analytes were determined experimentally by injection in all six investigated absorbing electrolytes (Table 2).

TRIS concentration was kept equal to 10 m*M* in order to maintain a comparable ionic strength whatever the chromophore; the concentration of the probe was calculated to obtain a final pH of 8.

DETA was added to the BGE. Its role is to moderate the bulk flow due to electroosmosis. Con-

Table 2
Characteristics of the analyte ions

Solute A	m_A ($\cdot 10-5$ cm^2 V^{-1} s^{-1})	R.S.D. (%)
$S_2O_3^{2-}$	77.3	4.6
SO_4^{2-}	70.8	5.1
$S_4O_6^{2-}$	65.3	5.2
S(−II)	63.6	4.4

m_A measured effective mobility of the analyte. The mean value of the electrosmotic mobility was 26.3 (R.S.D. = 9.8%).

trary to other modifiers (like most alkylammonium salts), it does not reverse the electroosmotic flow-rate and its measurement required the reversal of the applied voltage.

3.2. Validity and limitations

R values were determined experimentally according to Eqs. (9a) and (9b) for each analyte-probe set. All but one set of experiments were made with the same capillary (Capillary 1); the experiments with NTS as the BGE were made with a second capillary (Capillary 2) because of the clogging of capillary 1. All calibration curves were linear over the investigated range ($2.5 \cdot 10^{-5}$–10^{-3} M) for both series of experiments (injection of sulfur species with the probes in the BGE and injection of the probes with the phosphate electrolyte). Fig. 3 shows the electropherograms of the four sulfur species, 10^{-4} M each, with PM and NTS electrolytes. $S_4O_6^{2-}$ was injected separately because of the appearance of a precipitate (probably S(0)) when it was added to the same preparation as the other three species.

Fig. 4 shows the linear relationship between the slope α_A and $\varepsilon_E \cdot R$ (R determined experimentally), as expected from Eq. (9b). The expression of the slope is $2.4 \cdot V_{inj} / \pi \cdot d_c \cdot l_d$. One can see that the slopes of the straight lines depend on the capillary. When using the hydrostatic injection mode, V_{inj} is equal to

$$V_{inj} = \frac{\pi \cdot \rho \cdot g \cdot d_c^4 \cdot \Delta h_0 \cdot t_i}{128 \cdot \eta \cdot l_c}$$

where ρ and η are the density and the viscosity (respectively) of the sample matrix, g is the acceleration due to gravity, l_c the total length of the capillary, t_i the injection duration. We can easily derive that the

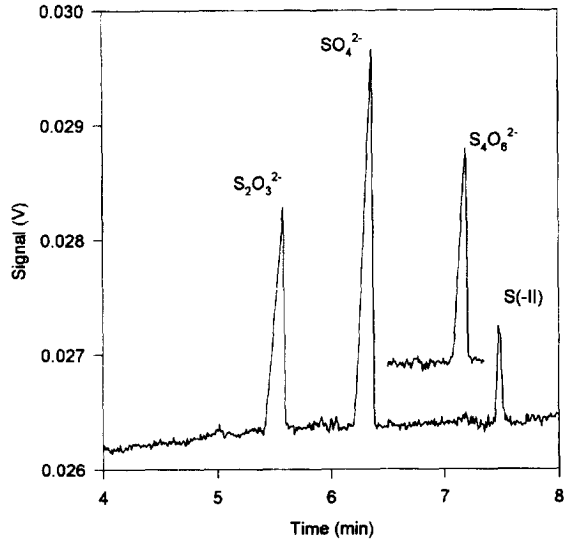

Fig. 3. Electropherogram showing the injection of an aqueous sample of $S_2O_3^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$, and S(−II), 10^{-4} M each, and applying PM as the chromogenic probe of the electrolyte. Analytical conditions: Capillary, fused-silica, 60 cm×75 μm I.D.; Injection, hydrostatic, $\Delta h_0 = 10$ cm for 30 s; Applied voltage, −20 kV; Detection, indirect UV, $\lambda = 214$ nm; Electrolyte, 1.5 mM PM, 10 mM TRIS, 0.5 mM DETA, pH = 8.00.

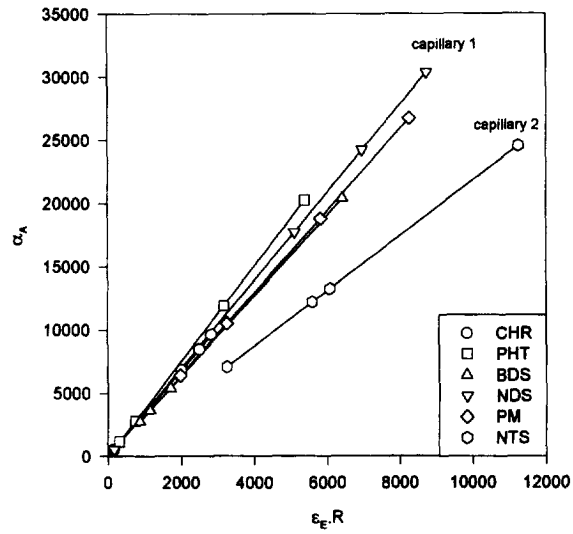

Fig. 4. Evidence of the influence of the capillary inner diameter on the variation of the slope of the analyte calibration curve α_A as a function of $\varepsilon_E \cdot R$. The transfer ratio R is determined experimentally.

slope of the straight lines obtained in Fig. 4 are proportional to d_c^3, all other parameters being identical in all sets of experiments. Injection of the same sample (NTS) in the phosphate electrolyte using both capillaries and comparison of the height of the peaks (see Eqs. (5a)) gave a direct determination of the ratio of the two capillaries inner diameters: $d_{c1}/d_{c2} = 1.17$. Hence, $(d_{c1}/d_{c2})^3 = 1.60$, which is consistent with the calculated value given by the ratio of the slopes in Fig. 4, i.e., 1.56.

The experimentally determined R values were compared with those calculated after Eq. (11) (Fig. 5) using the mobilities from Tables 1 and 2 and that of TRIS taken from published data [18] and corrected for ionic strength and pH. The sets of data determined with the same probe are circled and the name of the probe is given together with its effective mobility.

The data obtained with the CHR electrolyte show good correlation: they are set close to the diagonal line except for S(−II) which undergoes oxidation during the run. All other BGEs yield overestimated calculated R values compared with the experimental ones. A closer look at the data shows that, among the investigated probes, PM gives the best match between experimental and calculated R values. The match gets worse as we move horizontally further away from the diagonal line, that is to say, when NTS, then BDS, PHT and NDS are used. Thus, it appears that the closer the mobilities of the sample and of the probe, the better the experimental R values compared with the expected values as determined after the Kohlrausch theory. There are exceptions to this general remark: CHR and NDS give particularly low experimental transfer ratios with S(−II); as discussed earlier, the use of CHR as BGE leads to severe oxidation of sulfur species during the run, which, in turn, induces a lower apparent value of α_A. The poor correlation with NDS has not been explained.

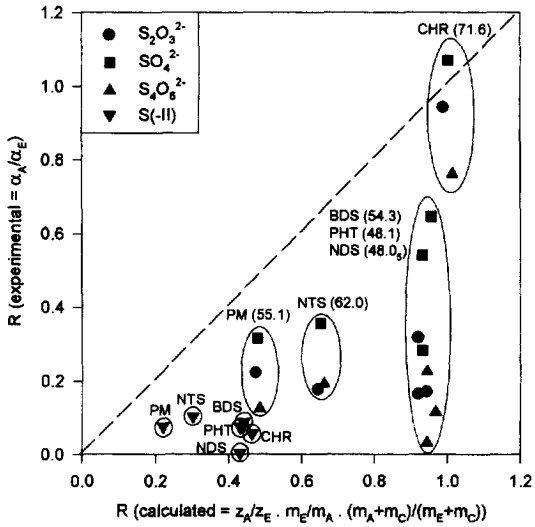

Fig. 5. Correlation between the experimentally determined and the calculated values of the transfer ratio R for each set of analyte/probe.

PM, on the contrary, seems to yield higher experimental R values than expected in consideration of its mobility. This peculiar behaviour was assigned to its probable higher ability to form ionic bonding with cationic species. PM bears a high charge density when fully ionized and may be involved in ion-pairing processes with some cationic constituents of the BGE such as DETA. Evidence of this phenomenon can be given by the comparison of the effective mobilities of the probes as determined experimentally by injecting them in the transparent phosphate electrolyte: we would expect PM mobility to be much higher than that of PHT (or BDS) because it bears twice the negative charge of the latter and is about the same size. However, the mobilities of both probes are similar, showing that the apparent negative charge of PM obviously is lower than 4. Besides, the S(−II) peak in Fig. 3a is nearly symmetrical, suggesting that the effective mobility of PM is similar to that of S(−II) in this particular experiment (e.g., higher than the value obtained by direct injection of the probe in the transparent electrolyte). The difference between the measured mobility of PM and that indirectly observed when PM is used as BGE may be assigned to the PM:DETA stoichiometry in both experiments. The large excess of DETA compared to the injected amount of PM in the experiment designed for mobility determination will displace the equilibrium of complex formation to completeness whereas the 3/1:PM/DETA ratio in the PM-based BGE is unfavourable to ion-pairing interactions. Ionic associations between aromatic anions and quaternary ammonium cations have already been suspected via

observations of mobility alterations [19]. Given these remarks, Eq. (11) should not be used to evaluate the transfer ratios with this probe.

The general discrepancy between calculated and experimentally determined R values can be explained by the modifications of such parameters as the electric field strength, the pH and the ionic strength in the moving sample zone. Beckers studied the simultaneous alterations of these parameters [16] and found that a large difference between the mobilities of the sample and the BGE co-ion, where $m_A > m_E$, causes the transfer ratio to be smaller than unity. In this case, the pH and the ionic strength of the sample zone both increase, as well as the concentration of the BGE counter-ion, while the mobility of the sample component decreases. The larger the difference between the sample and the co-ion mobilities, the more pronounced the modification of the sample zone parameters.

According to Eq. (11), R decreases with (m_A/m_E). Introducing the Debye–Huckel correction for the ionic strength in the expression of the effective mobilities, one comes to the conclusion that, provided the conditions $m_A^0 > m_E^0$ (with m_A^0 and m_E^0 the absolute mobilities of the sample and the BGE co-ion at infinite dilution) and $z_A \leq z_E$ (which includes all the studied cases except CHR), the ratio (m_A/m_E) increases with the ionic strength. Thus, in the sample zone, the ionic strength increase induces a simultaneous increase of (m_A/m_E), that is to say that the co-ion effective mobility undergoes a more rapid decrease than the sample one. The overall effect is the apparent decrease of the transfer ratio.

In the experiments described here, a pH increase does not alter the charge of the BGE co-ion because all probes are already fully ionised at pH 8. It does however modify the charge of the counter-ion TRIS ($pK_A = 8.08$). The mobility of the counter-ion decreases both with pH and ionic strength in the sample zone, which would in turn increase R (Fig. 2). This is all the more so true that m_E and m_A are different. However, the overall experimental reduced R values imply that this effect does not prevail.

3.3. Detection sensitivity

The mobilities of the BGE components were chosen in such a way that the theoretical R value, according to Eq. (11), should be close to that where charge to charge exchange between the sample ion and the BGE co-ion would occur, viz. (z_A/z_E). The sensitivity of the detection, given by the slope α_A of the calibration curve (Eqs. (9b)) should be proportional to $(z_A/z_E)\cdot\varepsilon_E$. Fig. 6 shows that this general trend is observed, despite the overestimated values of the transfer ratio. The data obtained with CHR are supposed to best fit the model and they give the approximate slope of the linear relationship that should be observed. The general trend indicates that sensitivity of the detection does increase with $(z_A/z_E)\cdot\varepsilon_E$ except with NDS which, again, shows unexplained reduced sensitivity (though relatively high compared to the other probes), particularly for S(−II) which is slightly absorbent at the selected wavelength (214 nm). PM and NTS show the best overall results for the analysis of the investigated sulfur species. PM was preferred because of its higher chemical purity that induces lower baseline instability. The limits of detection were calculated by a series of ten injections of low concentrations and were found to be $3\cdot10^{-6}$ M (SO_4^{2-}), $4\cdot10^{-6}$ M ($S_2O_3^{2-}$, $S_4O_6^{2-}$), and $2\cdot10^{-5}$ M (S(−II)).

An example of the analysis of natural water is given in Fig. 7. The water was sampled from a drill hole and transferred to a sealed vacuum-flask. It was opened immediately prior to analysis and the sample

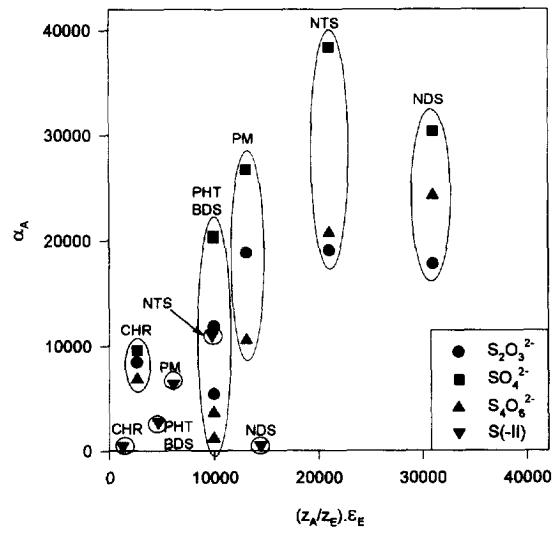

Fig. 6. Optimization of the sensitivity of the detection: variation of the slope of the analyte calibration curve α_A versus $(z_A/z_E)\cdot\epsilon_E$.

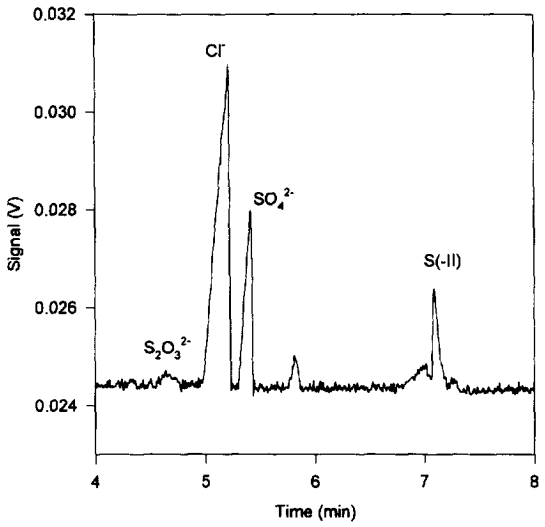

Fig. 7. Analysis of a natural clayey water sampled from a drill hole. The concentrations found were $8.3 \cdot 10^{-5}$ *M* for sulfate and $1.96 \cdot 10^{-4}$ *M* for sulfide. Analytical conditions: Capillary, fused-silica, 60 cm×75 μm I.D.; injection, hydrostatic, $\Delta h_0 = 10$ cm for 30 s; applied voltage: −20 kV; Detection: indirect UV, $\lambda = 214$ nm; Electrolyte: 1.5 m*M* PM, 10 m*M* TRIS, 0.5 m*M* DETA, pH = 8.00.

was put into its vial previously filled with argon. Two peaks corresponding to sulfate and sulfide can be seen. The concentration of thiosulfate was close to the limit of detection of the method.

4. Conclusion

Among the alternative chromogenic probes applied to the analysis of the chosen sulfur species, NTS and PM are best-suited. In this particular case where the mobility of the BGE counter-ion is low, the key parameter to sensitive indirect detection is the molar absorptivity of the probe. The relative match between the mobilities of the analyte and the probe is of lesser importance when only sensitivity is looked at. However, the choice of the BGE should take the mobility parameter into account in order to avoid peak distortion to keep high separation efficiency and lower the detection limits.

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