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Simultaneous determination of inorganic anions and organic acids in amine solutions for sour gas treatment by capillary electrophoresis with indirect UV detection

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Abstract

A new CE method has been developed for the simultaneous determination of selected inorganic anions (bromide, chloride, thiosulfate, nitrite, nitrate, sulfate, thiocyanate, fluoride and phosphate) and organic acids (oxalic, malonic, formic, tartric, acetic, glycolic, propionic, butyric and cyclohexanoic) in amine solutions from sour gas treatment units. An electrolyte composed of 10 mM trimellitic acid, 200 mM Tris (pH 9.0), 0.1% polyvinyl alcohol provides a satisfactory separation of all analytes of interest. The electroosmotic flow is reversed by using hexadimethrine bromide as a semi-permanent positively charged coating, making the electrolyte free of additive. Indirect UV detection at 240 nm is used because of the weak absorbing properties of most of analytes. The addition of 1% diethanolamine in standard mixtures permits to better preserve them, inhibiting potential degradation processes, especially for thiosulfate. The quantification is performed using internal standardization, by which molybdate is used as internal standard. Moreover, the use of relative migration times and the excellent repeatabilities obtained allow unambiguous identification of analytes in real samples by comparison with standard mixture. It has been shown that no significant matrix effect came from the presence of 30% diethanolamine in amine solution samples and the developed method was characterized in terms of calibration linearity and accuracy using recovery tests. In short, the developed method allows the simultaneous and rapid determination, in difficult matrices, of numerous inorganic anions and organic acids characterized by a large range of electrophoretic mobilities.
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Keywords: Amine solutions; Heat stable salts; Capillary electrophoresis; Inorganic anions; Organic acids; Thiosulfate preservation

1. Introduction

Crude oil refining includes steps of catalytic hydrorefining, reforming and hydrocracking, which result in the formation of large volumes of gases containing hydrogen sulfide [1]. Removal of hydrogen sulfide from these gases is obtained by amine washing [2]. Diethanolamine is used for this purpose because of its absorption affinity of hydrogen sulfide. The amine solution (30% diethanolamine in water) is then regenerated by steam stripping before recycling to the absorber. However, over time, amine solutions become deactivated by anions that come from contamination by the make-up water (e.g. chloride, nitrate and nitrite) or that are formed in the treating units as amine degradation by-products (e.g. organic acids) [3]. These anions tie up the amine by forming species named heat stable salts [4], which prevent amine regeneration. When the concentration of any of these heat stable salts exceeds 500 ppm, problems can be expected in the treatment unit such as inefficient hydrogen sulfide removal, corrosion increasing and foaming [3]. Therefore, determination of anions in diethanolamine solutions is very important. The concerned analytes are bromide, chloride, thiosulfate, nitrite, nitrate, sulfate, thiocyanate, fluoride, phosphate, oxalic, malonic, formic, tartric, acetic, glycolic, propionic, butyric and cyclohexanoic acids.

Ion chromatography (IC) is commonly used to monitor inorganic and organic anions in amine solutions. For routine control

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of a few anions, isocratic methods are sufficient. However, in case of determination of all analytes of interest, multiple types of columns with different capacities or gradient methods must be used [5]. Anyway, inorganic anions and organic acids exhibit widely different retentions on anion exchange columns, that lead to long analysis times. In addition, IC lacks selectivity for organic acids which are weakly retained and the elution of polarizable anions such as thiosulfate and thiocyanate, which show strong affinities for anion exchange stationary phases, takes time. Currently, the new anion exchange stationary phases with high capacity allow correct simultaneous separation of numerous inorganic and polarizable anions and a few organic acids, within 35 min [6,7]. Finally, recent developments lead to a spectacular separation of 34 anions under gradient elution conditions with electrolytic generation of an hydroxide eluent [8]. In brief, IC is the analytical method of choice for anions because of its sensitivity, reproducibility and robustness. Perhaps, the only drawbacks of IC are the long time required for a separation, the fairly modest chromatographic efficiencies and the poor duration of the stationary phases.

Capillary electrophoresis (CE) also appears to be a viable technique for the determination of numerous inorganic anions and organic acids in a single run. Indeed, CE offers different selectivities, higher speed of separation and very high separation efficiencies. In addition, in case of samples showing disparate levels of analytes, CE was found more robust than IC [9]. Simultaneous determination of inorganic anions and carboxylic acids has often been achieved in CE with direct UV detection [10]. However, all the analytes of interest do not exhibit sufficient UV absorption, that is why indirect UV detection is usually used for such analyses. Indirect UV detection uses the addition of an absorbing co-ion (called the probe) to the background electrolyte (BGE) and this ion is displaced by the migrating analytes to cause a negative signal for each analyte [11]. The electrophoretic mobility and concentration of the probe are crucial for the separation performance of the method because they influence peak shape and efficiencies. It has been shown that to obtain the sharpest and most symmetrical analyte peaks, and hence the best possible detection limit, the value of the electrophoretic mobility of the probe should match that of the analyte (mobility matching rule) [11]. However, when the task is to separate numerous inorganic anions and organic acids presenting a wide range of electrophoretic mobilities, it is impossible to apply the mobility matching rule. A buffer containing multiple co-ions with different electrophoretic mobilities can be used to overcome this problem, but electropherograms are deteriorated by the presence of system peaks [12]. The other way is to employ a probe that has an intermediate electrophoretic mobility compared to high mobility inorganic anions and low mobility organic acids. An electrolyte based on 2,6-pyridinedicarboxylic acid was used by Soga and Ross to simultaneously separate inorganic anions, organic acids, amino acids, nucleotides and carbohydrates [13–16]. Electrolytes based on p-aminobenzoic [17], phtalic [18], 5-sulfosalicylic [19], trimellitic [20] or 1,3,5-benzenetricarboxylic acid [21] were also successfully used when inorganic anions and organic acids must be simultaneously separated. Trimellitic acid (TMA) was chosen in this work. The separation of anions also needs to suppress or to reverse the electroosmotic flow in order to make all the analytes migrating towards the detection window at the anode extremity. One way is to use a cationic polymer as semi-permanent coating of the capillary. Then, the separation takes place in buffer containing no additives [22]. The semi-permanent coating technique was chosen because additives used for dynamic coating such as cetyltrimethylammonium bromide are known to form ion pairs with polarizable anions, which result in broad peaks with long migration times [23]. Cordova et al. used hexadimethrine bromide as semi-permanent coating and they obtained good repeatabilities for electroosmotic flow velocities for 25 replicates [24].

A lot of CE methods using indirect UV detection exist for the separation of anions, but they are often dedicated only to inorganic anions or organic acids. Indeed, just a few ones are able to simultaneously separate numerous compounds characterized by a large range of electrophoretic mobilities in less than 10 min. The aim of our study was to develop a rapid CE method suitable for the determination of 18 analytes comprising nine inorganic anions and nine organic acids, in diethanolamine solution samples. Diethanolamine solutions contain up to 30% diethanolamine in water and their pH is about 10–11. To our knowledge, it was the first time that CE with indirect UV detection has been applied for this application. First, an appropriate BGE composition was chosen and probe concentration, buffer concentration and pH were optimized. Then, an adequate preparation of standard mixtures was adopted and the specificity of the method was tested through the study of matrix effects. Finally, analyte recoveries in a diethanolamine solution sample from a refinery were studied in order to evaluate the accuracy of the method. The developed method is simple, because of the use of hexadimethrine bromide as a semi-permanent positively charged coating for electroosmotic flow reversal, making the electrolyte free of additive. It is also characterized by an excellent relative migration time repeatability, which allows the unambiguous identification of compounds.

2. Experimental

2.1. Instrumental

CE experiments were performed using an Agilent Technologies ^{3D}CE system (Agilent technologies, Waldbronn, Germany) equipped with a diode-array detector, an autosampler and a power supply able to deliver up to 30 kV. The Agilent technologies ^{3D}CE Chemstation software (rev. A.10.01 [1635]) was used for CE control, data acquisition and data handling.

Unless specified, electrophoretic separations were performed at 25 °C in bare fused-silica extended path length capillaries from Agilent Technologies, of inner diameter (I.D.), effective length (l), and total length (L), respectively equal to 50 μm, 56 cm, and 64.5 cm. The analyses were run in constant voltage mode with negative polarity at −30 kV. Hydrodynamic injection was carried out by using a pressure of 50 mbar for 5 s. The detector was used in the indirect UV detection mode: detection at 350 nm with a bandwidth of 80 nm, reference at 240 nm with

a bandwidth of 10 nm (detection and reference were switched in order to obtain positive peaks).

2.2. Reagents

Chemicals used in this study were all of analytical reagent-grade. Trimellitic (1,2,4-benzenetricarboxylic) acid, Trizma base [tris(hydroxymethyl)aminomethane], polyvinyl alcohol (average molecular weight 30,000–70,000), hexadimethrine bromide, sodium thiosulfate pentahydrate, propionic acid, glycolic acid, sodium nitrite, anhydrous sodium dihydrogenphosphate, cyclohexanecarboxylic acid, butyric acid, and diethanolamine were obtained from Aldrich (Sigma–Aldrich, Steinheim, Germany). Potassium chloride, potassium bromide, potassium nitrate, sodium sulfate, sodium carbonate, sodium molybdate, potassium tartrate acid and sodium formate were obtained from Prolabo (Paris, France). Sodium oxalate and potassium fluoride were obtained from Merck (Darmstadt, Germany). Potassium thiocyanate and malonic acid were obtained from Carlo Erba (Milan, Italy). Anhydrous sodium acetate was obtained from Fluka (Buchs, Germany). The 1 M sodium hydroxide solution was purchased from Agilent Technologies. Freshly distilled water was used for the preparation of all solutions.

2.3. Procedures

2.3.1. Preparation of BGE

The trimellitate-based BGE was prepared as follows: 0.8406 g of trimellitic acid, 0.4000 g of polyvinyl alcohol and 9.6880 g of Trizma base were added to 400 g of water into a glass flask, and the pH was checked to be equal to 9.0. Any modification of this composition will be cited in the text. BGE was sonicated and filtered using a 0.45 μm pore filter before use and it was stored in refrigerator at 4 °C. pH measurements were performed with a glass electrode XG200, a red rod reference electrode (Ag/AgCl) REF201 with a saturated KCl solution in water as salt bridge and a temperature sensor T201 in a pHM210 standard pHmeter with a precision of ±0.02 pH units (all from Radiometer Analytical, France). The electrode was calibrated with pH 4.0, 7.0 and 10.0 with standard solutions from IUPAC.

2.3.2. Modification of electroosmotic flow

Each new fused-silica capillary was flushed (1 bar) with 1 M sodium hydroxide for 20 min. After this preconditioning, the capillary was coated by flushing it with a 10% (w/w) hexadimethrine bromide solution, prepared in distilled water. Then, the capillary was washed with 0.1 M sodium hydroxide for 10 min and with distilled water for 10 min. The use of a 0.1 M sodium hydroxide solution allows the removal of bromide present in the capillary after the coating procedure. Finally, the capillary was flushed with the BGE for 20 min and conditioned under −30 kV for 10 min before analyses. Based on our study, this semi-permanent coating procedure must be performed every 100 injections.

2.3.3. Conditioning and storage of capillaries

Before each injection, the capillary was preconditioned with fresh electrolyte for 3 min. Capillaries were stored after rinsing successively with 0.1 M sodium hydroxide and water for 5 min.

2.3.4. Preparation of standards and samples

Individual stock solutions of analytes and internal standard (molybdate) at 1 g/L were prepared in distilled water, following the recommendations defined by the 6500 EPA method [25]. Standard mixtures at 1, 2, 5, 10, 20 and 30 mg/L in each analyte, which all contain 50 mg/L of molybdate, were obtained by dilution of the individual stock solutions of anions in 1% (w/w) aqueous solution of diethanolamine. This particular preparation of standard mixtures will be discussed further. The real sample of diethanolamine solution from a refinery was diluted by a factor 100 in order to be in the linear range and then spiked with 50 mg/L of molybdate (internal standard).

2.3.5. Methods of identification and quantification of analytes

Identification of compounds in real samples was performed by comparing the relative migration times of unknown peaks with those obtained from the injection of a standard mixture. The relative migration time was calculated as the ratio between the migration time of the analyte peak and the migration time of the internal standard (molybdate) peak.

Quantification was performed using the corrected peak area ratios, that is to say the ratios between the corrected peak areas of analytes and the corrected peak area of internal standard (molybdate). Corrected peak area is defined as the peak area divided by the migration time. Molybdate was chosen as internal standard because it cannot in any cases be present in real samples, it possesses an adequate electrophoretic mobility not interfering with the concerned analytes and it has been already used for this purpose [20].

3. Results and discussion

3.1. BGE composition

First, the influence of TMA concentration was studied within the range 5–15 mM by adjusting the pH of the BGE to 8.7 with diethanolamine and 10 mM was found to be optimal. Indeed, lower concentrations are unfavorable because of the increasing peak broadening due to electrodispersion and higher concentrations generate non-detector noise originating from Joule heat production [26]. For the rest of the study, because diethanolamine absorbs too much carbonate which leads to a very broad system peak in the electropherogram, diethanolamine was replaced by Tris(hydroxymethyl)aminomethane (Tris) that shows higher buffering capacity. The pH was optimized and electropherograms illustrating this study are presented in Fig. 1. When pH increases, the selectivities between fluoride and formate (analytes 11 and 12) and between acetate and glycolate (analytes 16 and 17) increase. In addition, the phosphate peak (analyte 14) become more and more efficient because the pH of BGE move away from the pKa of the couple

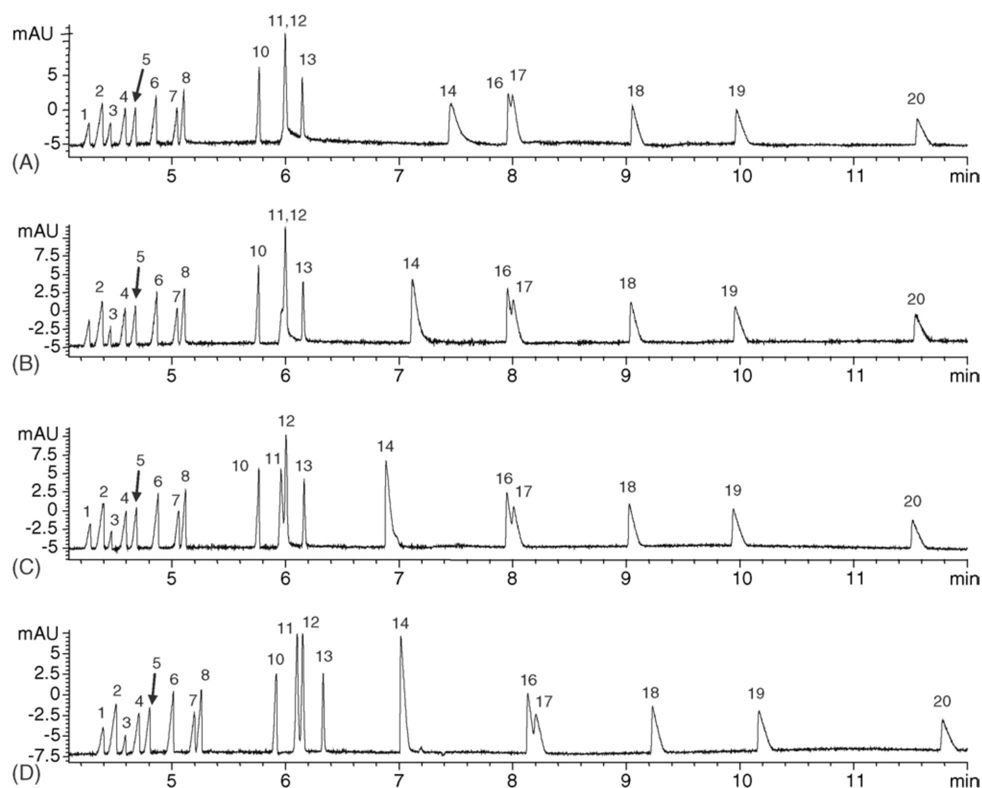

Fig. 1. Influence of pH and Tris concentration on the separation. BGE: 10 mM trimellitic acid, adjusted with Tris, at different pH. Capillary: standard capillary, $L = 82$ cm, $l = 73.6$ cm, I.D. = 50 μm. *Conditions*: $V = -30$ kV, $T = 25$ °C, (A) pH 7.30, $i = -14.6$ μA; (B) pH 7.75, $i = -14.6$ μA μA; (C) pH 8.34, $i = -14.4$ μA; (D) pH 9.00, $i = -13.3$ μA. Injection: standard mixture 10 mg/L, hydrodynamic 50 mbar, 30 s. Peaks: (1) bromide, (2) chloride, (3) thiosulfate, (4) nitrite, (5) nitrate, (6) sulfate, (7) thiocyanate, (8) oxalate, (10) malonate, (11) fluoride, (12) formate, (13) tartrate, (14) phosphate, (16) acetate, (17) glycolate, (18) propionate, (19) butyrate, (20) cyclohexanoate.

$H_2PO_4^-/HPO_4^{2-}$ (p*K*a = 7.2). The more satisfactory pH regarding to the best quality of separation was found to be 9.0 and this value corresponds to a Tris concentration of 200 mM. Acidic pH would have been more interesting in order to control the selectivity for organic acids, but only neutral to basic pH were studied (7.3–9.0) in accordance with Tris concentration, because lean diethanolamine samples are very basic (pH 10–11).

Under pH 9.0 conditions (Fig. 1D), the resolution between acetate and glycolate is too poor for accurate quantification (Rs = 0.96). Fung et al. showed that addition of 0.01% of polyvinyl alcohol (PVA) in BGE results in an improvement of the separation between fluoride and formate [27]. The same approach was implemented with the hope to improve the resolution between glycolate and acetate. Fig. 2 shows that the resolution between acetate and glycolate is increased by a factor 1.5 when 0.1% of PVA is added to the BGE. Calculations demonstrated that this improvement of resolution was not only due to the reduction of the electroosmotic mobility, but to date, no reasonable explanation has been found.

In conclusion, the use of a BGE containing 10 mM trimellitic acid, 200 mM Tris, pH 9.0 and 0.1% PVA results in a satisfactory separation of all 20 anionic analytes.

3.2. Quantitative analysis

3.2.1. Study of the stability of standard mixtures and matrix effect

Some precautions have to be taken when the quantitative analysis deals with analytes such as nitrite, sulfate and thiosulfate. Indeed, nitrite is known to rapidly degrades in aqueous solutions [7]. In addition, oxysulphur species are also concerned by degradation problems in aqueous solutions [28]. The study of stability of standard mixtures was therefore implemented by comparing the variations of responses (corrected peak area ratios between analytes and internal standard), versus time, for 20 mg/L standard mixtures prepared in distilled water and in 1% diethanolamine. After 2 days, thiosulfate in distilled water was considerably degraded. After 7 days, thiosulfate disappeared completely and a significant increase of sulfate concentration was recorded. On the other hand, no degradation or increase of an analyte concentration was observed when standard mixture was prepared in 1% diethanolamine. Moreover, the response of standards prepared in 1% diethanolamine shows a better day-to-day repeatability than the response of standards prepared in distilled water. To date, no fully satisfactory explanation, except the basic pH, was found in order to understand why 1% diethanolamine allows the preservation of some anions. Sullivan and al. studied

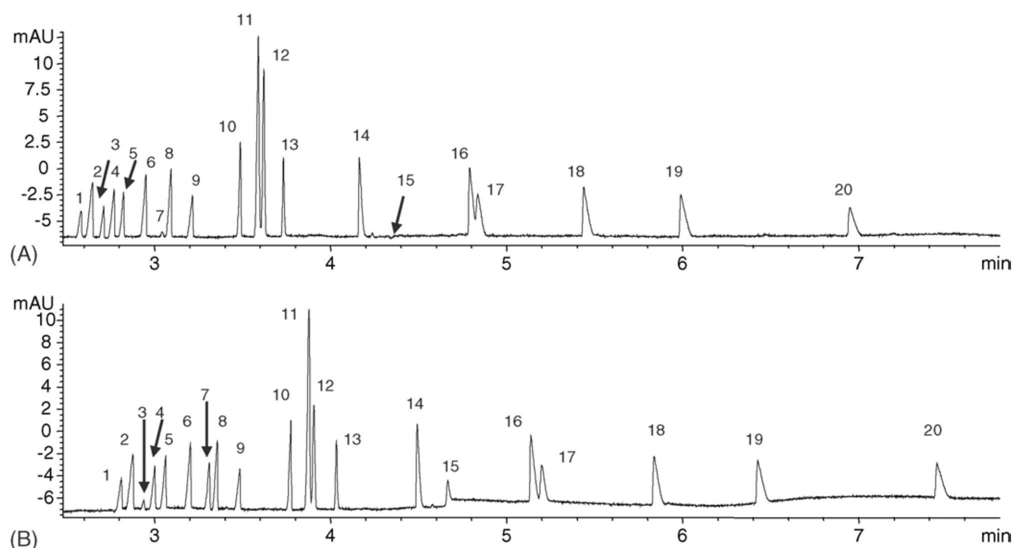

Fig. 2. Effect of the addition of 0.1% PVA in the BGE on the resolution between acetate and glycolate. BGE: 10 mM trimellitic acid, 200 mM Tris, pH 9.0 without PVA (A), and with 0.1% PVA (B). Capillary: standard capillary, L = 64.5 cm, l = 56 cm, I.D. = 50 μm. *Conditions*: V = −30 kV, i = −20 μA, T = 25 °C. Injection: standard mixture 30 mg/L, hydrodynamic 50 mbar, 5 s. Peaks: (1) bromide, (2) chloride, (3) thiosulfate, (4) nitrite, (5) nitrate, (6) sulfate, (7) thiocyanate (8) oxalate, (9) molybdate (internal standard), (10) malonate, (11) fluoride, (12) formate, (13) tartrate, (14) phosphate, (15) carbonate, (16) acetate, (17) glycolate, (18) propionate, (19) butyrate, (20) cyclohexanoate.

the stabilization over the course of a day, of standard mixtures of oxysulphur species with 10 mM sodium hydroxide [28]. The expected effect on nitrite has not been highlighted, but its decomposition in acidic conditions is well known [7].

As mentioned in the introduction, diethanolamine solutions contain 30% of diethanolamine. Compared to standard mixtures prepared in 1% diethanolamine, this high concentration may induce different electrical fields in both sample zones, leading to a significant matrix effect [29]. In order to study this point, the responses of the analytes dissolved at 20 mg/L in 1% diethanolamine and 30% diethanolamine are compared. For all analytes, diethanolamine concentration does not influence their response. Consequently, inorganic anions and organic acids in scrubber solutions containing 30% diethanolamine can be quantitatively determined from calibrations performed with standard mixtures containing 1% diethanolamine. It is important to note that the presence of 30% diethanolamine in the sample zone makes the migration times for all anions increased by 20%, but identification is still correct.

In conclusion, standard mixtures must be prepared in 1% diethanolamine in order to preserve thiosulfate and sulfate, and to improve the day-to-day repeatability. The use of 1% diethanolamine is preferred to the use of 30% diethanolamine because the developed method can also be used to determine anions in refinery wastewaters, which do not contain diethanolamine (results not shown).

3.2.2. Analytical performances

All results concerning analytical performances are presented in Table 1. Thirty injections of standard mixtures at different analyte concentrations were successively performed and precision [measured as relative standard deviation, RSD] of relative migration times ranged from 0.11 to 0.70%. These excellent RSD values allow the unambiguous identification of analytes in real sample by comparing their relative migration times with those obtained from the injection of a standard mixture.

Limits of detection (LOD) were defined as the analyte concentrations corresponding to a signal equal to three times the background noise (S/N = 3). For an injection volume of 0.5% of the effective capillary volume, LOD were found to range from 0.5 to 1 mg/L. Limits of quantification (LOQ) were measured in a simplified way inspired from the Eurachem approach [30], i.e. as the analyte concentration for which the %RSD of the corrected areas ratios reached 10% (in this case, the S/N ratios were approximately equal to 6). LOQ were found to range from 1 to 2 mg/L. These LOD and LOQ are not very impressive but they are adequate for the application.

Calibration curves using corrected peak areas ratios were plotted with three replicates for each level of concentration (1, 2, 5, 10, 20 and 30 mg/L). They were linear, included the intercept for most of all (except for bromide), and correlation coefficients ranged from 0.9948 to 1.0000. The uncertainties on the centroid of each calibration curve were also examined and they ranged from 1.2 to 8.1%, except for bromide (16.6%). On top of bringing a good information on the quality of the linear regression used, this parameter gives an idea of the uncertainties on the determination of each analyte in samples [31].

3.2.3. Recovery study

In order to evaluate the accuracy of the method, a recovery study was performed in a diethanolamine solution sample coming from a refinery. The preliminary injections showed very high concentrations of the concerned analytes. Diethanolamine solution was then diluted by a factor 100 in order to be in the linear range and then divided into two aliquots: the first one was directly analyzed (Fig. 3B), the second one was analyzed after spiking with 5 mg/L of each analyte (Fig. 3C). Quantification of each analyte in each aliquot was carried out from calibration

Table 1
Analytical performances of the method

Analytes	Relative migration time, RSD ($n = 30$) (%)	LOD (mg/L)	LOQ (mg/L)	Correlation coefficient (r^2)	Uncertainty on the centroid, X_m (%)
Bromide	0.11	1	2	0.9948	16.6
Chloride	0.29	1	2	0.9997	3.7
Thiosulfate	0.08	1	2	0.9998	3.1
Nitrite	0.21	1	2	0.9993	6.1
Nitrate	0.23	1	2	0.9998	3.1
Sulfate	0.32	1	2	0.9994	5.5
Thiocyanate	0.22	1	2	0.9997	3.7
Oxalate	0.31	1	2	0.9999	2.7
Malonate	0.22	1	2	0.9999	1.7
Fluoride	0.22	0.5	1	1.0000	1.2
Formiate	0.16	1	2	0.9998	3.3
Tartrate	0.14	1	2	0.9999	2.2
Phosphate	0.13	1	2	0.9999	2.8
Acetate	0.13	1	2	0.9999	2.4
Glycolate	0.25	1	2	0.9988	8.1
Propionate	0.30	1	2	0.9999	1.7
Butyrate	0.43	1	2	0.9999	2.8
Cyclohexanoate	0.70	1	2	0.9996	4.5

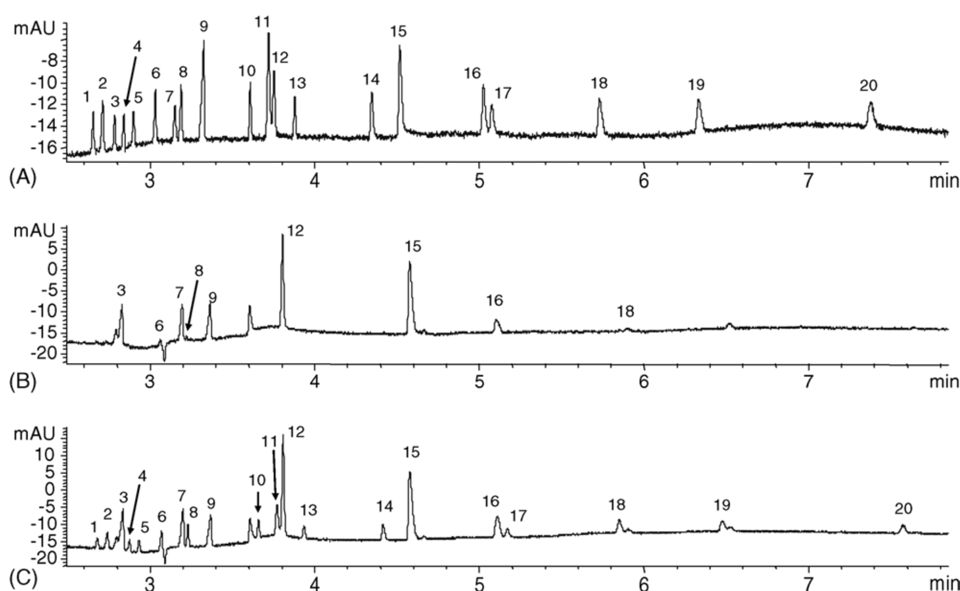

Fig. 3. Electropherograms of the 5 mg/L standard mixture (A), the initial diethanolamine solution sample (B), and the diethanolamine solution spiked with 5 mg/L of each anion (C). BGE: 10 mM trimellitic acid, 200 mM Tris, pH 9.0, 0.1% PVA. Capillary: extended path length capillary (Agilent Technologies), $L = 64.5$ cm, $l = 56$ cm, I.D. = 50 μm. *Conditions*: $V = -30$ kV, $i = -20$ μA, $T = 25$ °C. Injection: hydrodynamic 50 mbar, 5 s. Peaks: (1) bromide, (2) chloride, (3) thiosulfate, (4) nitrite, (5) nitrate, (6) sulfate, (7) thiocyanate, (8) oxalate, (9) molybdate (internal standard), (10) malonate, (11) fluoride, (12) formate, (13) tartrate, (14) phosphate, (15) carbonate, (16) acetate, (17) glycolate, (18) propionate, (19) butyrate, (20) cyclohexanoate.

curves constructed by injection (three replicates) of standard mixtures at 2, 5, 10, 20 and 30 mg/L in 1% diethanolamine. Fig. 3A shows an example of electropherogram obtained for the injection of the standard mixture at 5 mg/L. The recovery of each analyte was calculated as the difference between the concentration determined in each aliquot divided by the spiked concentration. Except for bromide, all recovery values ranged from 90 to 110%, which was greatly satisfactory. The problem encountered for bromide determination arises from the use of the bromide form of hexadimethrine for electroosmotic flow reversal. Indeed, this bias is function of the rinsing step during the coating procedure. Optimization of the rinsing step and anion exchange experiments to transform the bromide form of hexadimethrine into the hydroxide form are still in progress.

4. Conclusion

A new CE procedure was developed for the simultaneous determination of numerous inorganic anions and organic acids. BGE is composed of 10 mM trimellitic acid as a probe, 200 mM Tris as a buffer to adjust the pH at 9.0 and 0.1% PVA as an additive to improve the resolution between acetate and glycolate.

The electroosmotic flow is reversed by using hexadimethrine bromide as a semi-permanent positively charged coating, making the BGE free of additive.

The reliability of the method developed was established by very good calibration linearity, excellent relative migration time repeatability, potential matrix effect study and satisfactory recovery tests. Despite the high LOD and LOQ obtained, the analytical performances were adequate for the application. The method was successfully applied for the determination of numerous anions in diethanolamine solutions. In summary, CE was shown to provide a quick, powerful, economic and reliable method for the simultaneous determination of both inorganic anions and organic acids in diethanolamine solution samples.

Acknowledgement

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