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Capillary electrophoretic determination of degradation products of nitrilotriacetic acid used as a complexing agent in a desulphuration process

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Abstract

Capillary electrophoresis (CE) was assessed for the determination of the expected degradation products of nitrilotriacetic acid (NTA), viz., imiodiacetic acid (IDA), dimethyliminoacetic acid (DMIA), N-methylglycine (NMG), glycine (GLY), acetate, formate and ammonium, in solutions containing iron(III)–NTA complexes which were used for the desulphuration of industrial gases. Owing to the wide range of absolute mobilities and acidic constants of these analytes, the analytical requirements were best met with three different sets of operating conditions, all carried out with indirect absorbance detection. The more mobile ions (formate, acetate and NTA) were obtained without interference with other process-relevant anions using a buffer of pH 6 and an electroosmotic flow modifier under reversed polarity. Using normal polarity and no modifier, the less anionic species (GLY, NMG, DMIA) were determined at pH 9.5, while the major degradation product, IDA, was best determined at pH 7. Ammonium can be detected in the last two cases. The cumbersome presence of iron (III) ions was avoided by either precipitation (potassium hydroxide) or complexation (ethylenediaminetetraacetic acid). Special attention was paid to method validation. The analyses were fast (<6 min) and exhibited low relative standard deviations for migration times (<0.1%) and peak areas (<5%). The methods were applied to monitor the process of desulphuration. The results are well correlated with those obtained by ion chromatography (IC), but CE appeared simpler and more versatile and cost effective.

1. Introduction

A number of processes intended to eliminate gaseous hydrogen sulphide (H_2S) from industrial smokes are based on the washing of the gases with aqueous solutions containing an oxidizing agent capable of converting hydrogen sulphide into sulphur, but also amenable to subsequent regeneration through oxidation. In some of these processes, iron(III) was selected to meet these conditions. The chemical reactions involved are

$$H_2S + 2\ Fe^{3+} \rightarrow S + 2\ Fe^{2+} + 2H^+$$

$$2\ Fe^{2+} + 2H^+ + 1/2\ O_2 \rightarrow 2\ Fe^{3+} + H_2O$$

the balance of which is

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$$H_2S + 1/2\ O_2 \rightarrow S + H_2O$$

However, as written, this reaction scheme could only be implemented in acidic media, which would greatly restrict its interest for a desulphuration process. To delay the precipitation of both iron(III) hydroxide and iron(II) sulphide to neutral or even slightly basic media, a chelating agent of Fe(III) and Fe(II) should be added to the desulphuration bath. A still more appropriate additive should also slightly lower the redox potential of the Fe(III)–Fe(II) system, so as to make easier thermodynamically and kinetically the reoxidation of Fe(II) by air. This last point implies that the stability constant of the Fe(III) chelate should be higher than that of the Fe(II) chelate. Candidate additives are nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and hydroxyethylenediaminetriacetic acid (HEDTA), the most cost effective being NTA. On the other hand, these chelating agents undergo slow degradation under the effect of the alternate formation of iron(III) and iron(II) chelates, leading to a series of known or unknown products, the chelating power of which is less and less pronounced. Eventually, NTA degradation limits the lifetime of the desulphuration solution, as it results in losses of Fe(III) by precipitation.

Addition of some organic or inorganic compounds has been shown to slow the degradation rate. The proper understanding of the degradation schemes and degradation kinetics and of the inhibitory effect of some additives and ultimately the effective monitoring of industrial units require the complete determination of the species involved in such solutions. The classical methods of analysis such as potentiometry, titrimetry, spectrophotometry, determination of nitrogen, sulphur and total organic carbon and chemical oxygen demand provide only partial information and are not suited for monitoring industrial units. Ion chromatographic (IC) techniques have been implemented for this task, but are not entirely satisfactory, insofar as they fail to allow the easy identification and determination of all the components involved. They also require the use of several expensive columns.

The purpose of this work was to assess capillary electrophoresis (CE) as an alternative method for desulphuration solution monitoring. The most attractive features of this technique are its separation selectivity, different from that of IC as a result of the different separation principles, its short analysis times, flexibility, ease of implementation, automation capability and low running costs. In this paper, we describe the CE methods that were developed to determine NTA and its degradation products in the presence of iron ions, hydrogen sulphide and the resulting oxidation products. A method allowing the rapid monitoring of total iron ions was also developed. Validation aspects were especially emphasized. Experiments were conducted at two different sites (referred to as laboratories A and B) by different authors of this paper and the consistency of the results was examined.

2. Experimental

2.1. Apparatus

CE was performed with a Quanta 4000 capillary electrophoresis system (Waters, Milford, MA, USA) equipped with either a positive or a negative high-voltage power supply. Fused-silica capillaries of effective length 58 or 60 cm and 50 or 75 μm I.D. were used. The window for on-column detection was created by burning off a small section (0.5 cm) of the polyimide coating. Both indirect and direct UV detection were performed with a mercury lamp and 254- or 185-nm optical filters. The samples were introduced into the capillary using the gravity injection device provided with the instrument with the capillary inlet raised 10 cm above the outlet for 10, 20 or 30 s. The separation voltage was set at 20 or 30 kV depending on the kind of separation. In some cases the direction of the electroosmotic flow was reversed using OFM BT Anion reagent (Waters). Data processing was performed with a Waters Model 820 data station.

All solutions, electrolytes and standards were prepared using 18 MΩ water generated by a

Milli-Q laboratory water–purification system (Millipore, Milford, MA, USA).

2.2. Standards

Nitrilotriacetic acid disodium salt (NTA), iminodiacetic acid (IDA), N,N-dimethylglycine (DMIA) and N-methylglycine (NMG) were obtained from Sigma (St. Louis, MO, USA), glycine (GLY) from Merck (Darmstadt, Germany) and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) from Prolabo (Paris, France). In laboratory A a standard solution in water was prepared containing the analytes NTA, IDA, GLY, NMG, DMIA, formate, acetate, malonate, sulphate, carbonate, two important process-relevant but confidential components and a 1:2 metal–ligand complex of Fe^{3+}–EDTA. The concentration of each ion in this solution was 1 mmol/l. For all species of interest separate standard solutions each at a concentration of 1 mmol/l were also prepared.

In laboratory B, working standard solutions were prepared by diluting stock standard solutions of NTA (500 ppm), IDA (800 ppm) and GLY (1000 ppm) to various concentrations to cover the required linearity ranges. For peak identification, working standard solutions of sulphate, formate, acetate and two confidential ions were prepared from stock standard solutions of concentration 1000 ppm.

2.3. Sample preparation

The samples obtained from the desulphuration process contain the important components iron(III), at an expected concentration 0.05 mol/l, and NTA as complexing agent, at an expected concentration of 0.1 mol/l. The process also requires the utilization of a buffer (pH 7) and other additives. The accurate composition of the desulphuration mixture cannot be given in this paper on the grounds of confidentiality. The samples were recovered at run times in the process up to 384 h. They were all filtered through a 0.22-μm membrane either before or after dilution.

A difficulty arising from the presence of iron(III) ions in the desulphuration solutions was circumvented either by precipitation (laboratory B) or by complexation (laboratory A). Iron(III) was completely precipitated by addition of 1.2 ml of 1 mol/l potassium hydroxide solution per millilitre of undiluted sample. After precipitation the samples were diluted 1:100 and filtered through a 0.22-μm membrane. The second approach was total complexation of iron(III) in the solution by addition of 10 μl of 0.1 mol/l EDTA solution to 10 μl of filtered sample. Finally, the samples were diluted 1:100, 1:40 or 1:10, depending on the nature and concentration of the ion of interest.

2.4. Electrolytes

The carrier electrolyte for the determination of IDA was prepared from 8 mmol/l *p*-anisic acid and 33 mmol/l Bis-Tris [bis(2-hydroxyethyl)iminotris(hydroxymethyl)methane]. The pH obtained was 7.0. For the separation of GLY, NMG and DMIA a carrier electrolyte containing 10 mmol/l *p*-anisic acid and 63 mmol/l ammediol (2-amino-2-methyl-1,3-propanediol) at pH 9.5 was used. The determination of iron was carried out with an electrolyte prepared from 20 mmol/l boric acid and 0.1 mmol/l EDTA. The pH was adjusted to 9.2 with 1 mol/l NaOH.

For the separation of sulphate, oxalate, formate, NTA and IDA, a carrier electrolyte was made up with 20 mmol/l benzoic acid. The reversal of the electroosmotic flow was obtained by adding OFM BT Anion solution to the electrolyte (dilution factor 1:40). The pH was finally adjusted to 6 with LiOH. After preparation, all electrolytes were filtered (0.45 μm) and degassed in an ultrasonic bath for 20 min or with a vacuum pump for 5 min.

3. Results and discussion

Basically, the desulphuration solution contains the active species iron(III) and nitrilotriacetate, the accompanying ions being sulphate and sodium, but with ageing it is liable to include degradation products of NTA, viz, IDA, GLY,

NMG, DMIA, formate acetate and ammonium. By analogy with the mechanism described by Matsuda and Nagai [1], it can be assumed that the degradation of NTA into IDA and GLY follows an oxidation process; however, the experimental conditions in the desulphuration process are not identical with those mentioned in Ref. [1]. Fig. 1 shows the degradation scheme of NTA into IDA and GLY. NTA loses two electrons per molecule in the first step with formation of IDA. In the second step, glycine is produced from IDA [1]. Carr et al. [2] reported the oxidation of NTA to IDA, GLY and ammonium and the disproportionation of NTA into methyliminodiacetic acid (MIDA) and dimethyliminodiacetic acid (DMIA) and their further degradation to N-methylglycine (NMG), dimethylamine and methylamine (Fig. 2). As this disproportionation seems slower and less probable, the main degradation products of NTA are probably IDA, GLY and ammonium.

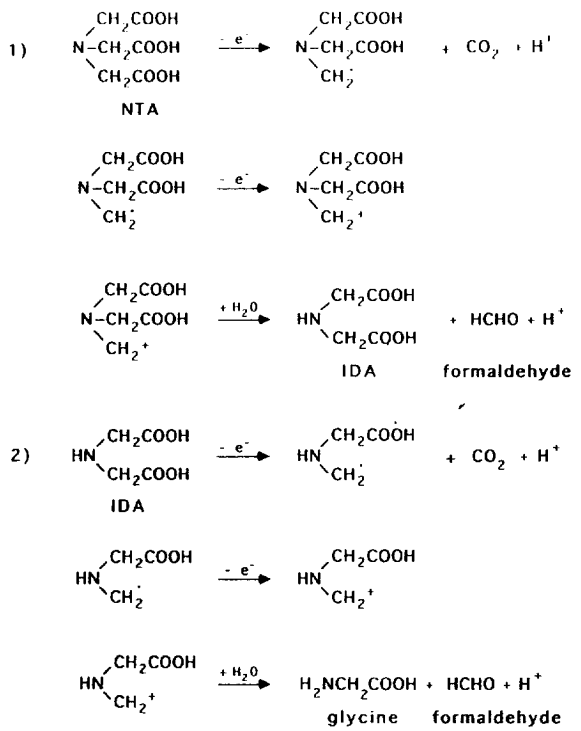

Fig. 1. Degradation scheme of NTA into IDA and GLY according to Ref. [1].

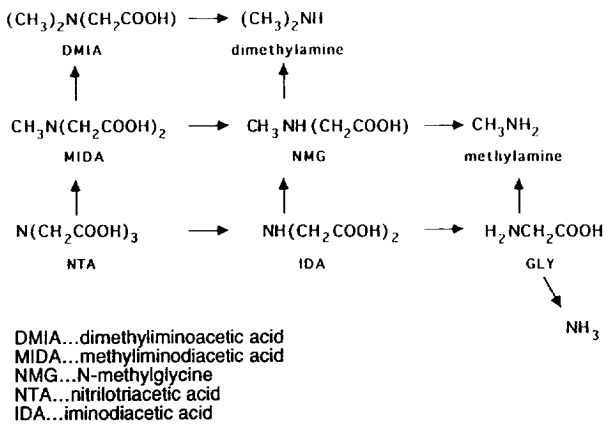

Fig. 2. Overall oxidation scheme of NTA according to Ref. [2].

3.1. Interference elimination of iron(III)

The cumbersome interferences produced by iron(III) ions present in the desulphuration solutions with the other process-relevant ions were avoided through two different methods of sample preparation: either a full complexation of iron(III) with EDTA (laboratory A) or total precipitation of iron(III) by the addition of potassium hydroxide (laboratory B). It has been observed that the Fe(III)–EDTA complex produces a narrow peak which does not hinder the determination of the species of interest.

3.2. Overall separation strategy

The large differences in absolute mobilities and acidic constants of all the analytes of interest made it difficult to find a single set of analytical conditions for the entire process monitoring that fulfilled the demands on resolution, speed and sensitivity. This problem was circumvented using different, more specifically optimized carrier electrolytes. The more mobile ions (sulphate, oxalate, formate, NTA, acetate, IDA) were best determined using a buffer of pH 6 and an electroosmotic flow modifier under reversed polarity. The separations of the less mobile ions [Fe(III)–EDTA complex, IDA, acetate] and of the amphoteric species (NMG, DMIA and

GLY) were preferably carried out without an electroosmotic flow modifier and under normal polarity with a buffer pH of ca. 7–8 for the former and ca. 9–10 for the latter.

3.3. Separation of the less mobile anionic process–relevant species

Several carrier electrolytes were tried in laboratory A to find the optimum analytical conditions for the determination of IDA. The use of carrier electrolyte containing 8 mmol/l *p*-anisic acid as UV-absorbing species and 33 mmol/l Bis-Tris as buffer (pH 7.0) turned out to be the method of choice. A very good separation of the Fe(III)–EDTA complex, IDA, free EDTA, acetate, a confidential anion, NTA and formate, in that order, was obtained by injecting a standard mixture containing all the species of interest. Oxalate and the other major anions of the desulphuration solution, having electrophoretic mobilities higher than the electroosmotic mobility, cannot be detected in this way, which is perceived here as an advantage. This is particularly the case for sulphate, the high concentration of which has no reason to vary during the process. The peak of formate is asymmetric, owing to the large difference in electrophoretic mobilities between the analyte and the UV-absorbing background ion. The less negatively charged species NMG, DMIA and GLY are not detectable under these conditions and will be considered later. The application of this method to a desulphuration solution sampled 24 h after the start of the process is shown in Fig. 3. All peaks were identified by injecting the components of the standard solution separately. Formate ion was not detected in the solutions sampled early during the process.

Before introducing the sample into the capillary, iron(III) was completely bound to EDTA as a result of strong complexation. From the stability constants found in the literature [3], it is inferred that the prevailing complex formed under these conditions is anionic, with a 1:2 stoichiometric metal-to-ligand ratio. On varying the amount of EDTA added to the samples, it was ascertained that iron(III) remained fully

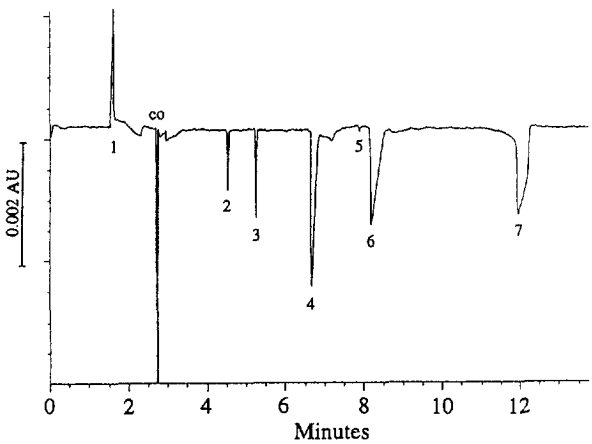

Fig. 3. Electropherogram of a desulphuration solution sampled after 24 h of process run time. Fused-silica capillary, 58 cm × 50 μm I.D. (effective length 50.5 cm); electrolyte, 8 mmol/l *p*-anisic acid–33 mmol/l Bis-Tris (pH 7.0); separation voltage, +30 kV; indirect UV detection at 254 nm; gravity injection for 10 s; sample filtered, diluted 1:100 with water and made up to 1 mmol/l EDTA. Peaks: 1 = sodium; eo = electroosmosis; 2 = Fe(III)–EDTA complex; 3 = IDA; 4 = EDTA; 5 = acetate; 6 = confidential; 7 = NTA.

complexed during the whole migration inside the capillary. The peaks of the complex and free form of EDTA in excess show no interference with IDA and other process-relevant components (Fig. 3). Apart from that, the deformation of the last peak corresponding to NTA does not seem to be fully explained by the mobility difference between NTA and anisate. As a consequence, this method was not retained for the determination of NTA.

Special attention was paid to method validation. To avoid any matrix discrepancy between the standard solutions used for calibration and the real solutions, the initial solution, in which no IDA had been detected, was spiked with four different concentrations of IDA. This method results in a similar matrix for the standard and the unknown solutions and hence in similar electrophoretic behaviours. Fig. 4 shows the calibration graph obtained with four different solutions of known concentration of IDA and how it was utilized for the determination of IDA in the desulphuration solutions. The plot of time-

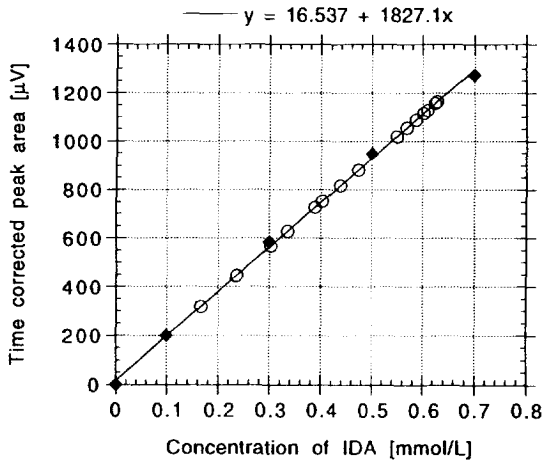

Fig. 4. Calibration graph of time-corrected peak areas as a function of the concentration of IDA added to the initial desulphuration solution. ◆ = Calibration points; ○ = points corresponding to the unknown samples of desulphuration positioned after their measured corrected peak areas. For operating conditions, see Fig. 3.

corrected peak areas versus concentration passes through the origin and is linear with a correlation coefficient of 0.9993.

As shown in Table 1, this method developed in laboratory A allows the determination of IDA with good relative standard deviations (R.S.D.) ($n = 3$) for migration times ($\leq 0.2\%$) and peak areas ($\leq 2\%$).

3.4. Separations of the more mobile anionic process relevant species

A different approach was investigated in laboratory B for monitoring the more mobile compounds involved in the desulphuration solutions, i.e., sulphate, oxalate, formate, NTA, IDA and two confidential ions. An electrolyte composed of lithium benzoate adjusted to pH 6.0, in which benzoate acts both as a chromophore for indirect absorbance detection and as a buffering species,

Table 1
Concentration of IDA as a function of sampling time during the desulphuration process, as determined by two different electrophoretic methods in laboratories A and B, and R.S.D. ($n = 3$) for migration times and peak areas

Process run time (h)	Laboratory A			Laboratory B	
	Concentration of IDA (mmol/l)	R.S.D. for migration times (%)	R.S.D. for peak areas (%)	Concentration of IDA (mmol/l)	R.S.D. for peak areas (%)
0	0.0	–	–	0.0	–
24	23.5	0.2	5.3	22.8	7.6
48	40.3	0.0	2.2	36.5	5.5
72	56.9	0.1	0.5	56.3	4.5
96	60.0	0.5	1.1	60.6	0.7
120	61.0	0.1	0.1	62.4	1.3
144	62.8	0.1	0.9	55.3	1.8
168	62.4	0.2	1.8	58.6	3.0
192	58.7	0.1	3.2	58.3	3.4
216	54.9	0.2	0.5	61.7	2.4
240	47.4	0.0	0.4	47.0	1.6
264	44.0	0.1	1.2	–	–
288	38.9	0.5	0.8	37.4	6.2
312	33.5	0.1	1.0	37.4	3.5
336	30.2	0.1	0.8	35.6	5.0
360	23.6	0.1	1.1	25.1	14.4
384	16.6	0.0	4.4	17.2	–

Electrolytes: laboratory A, anisate–Bis-Tris (pH 7.0); laboratory B, lithium benzoate–OFM BT Anion electroosmotic flow modifier (pH 6.0). See text for further explanations.

was developed. As some of these analytes are amenable to having their effective mobility greater than the electroosmotic mobility, it was highly desirable to reverse the natural cationic electroosmotic flow by adding OFM BT Anion reagent to the electrolyte. These conditions allowed a satisfactory separation of the aforementioned process-relevant ions. Fig. 5 shows the electropherogram of the desulphuration solution sampled after 72 h of process run time. A key advantage of this method for kinetics monitoring of the degradation products of the desulphuration solution is its speed. The degradation of NTA into IDA was followed quantitatively through the determination of both NTA and IDA. The results obtained by this method are given in Table 1. The repeatability ($n = 3$) was mainly less than 5% for the corrected peak areas. In Fig. 6, the calibration graph obtained with seven different concentrations of NTA is plotted. The calculated linear correlation coefficient was 0.9995, which represents excellent linearity. Fig. 7 enables one to compare the results obtained for IDA by the methods developed in laboratories A and B and to obtain further insight into the level of confidence of the electrophoretic techniques. It clearly appears that both methods lead to identical results and they are both suitable for monitoring IDA in the desulphuration process.

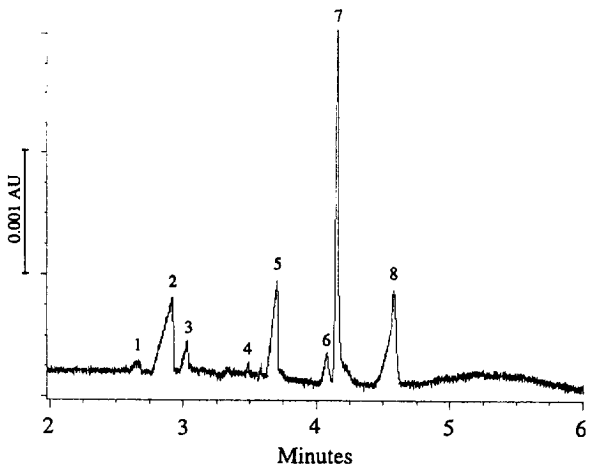

Fig. 5. Electropherogram of a desulphuration solution sampled after 72 h of process run time. Fused-silica capillary, 60 cm × 75 μm I.D. (effective length 52.5 cm); electrolyte, 20 mmol/l benzoic acid–OFM BT Anion (dilution factor 1:40), adjusted to pH 6.0 with LiOH; separation voltage, −20 kV; indirect UV detection at 254 nm; gravity injection for 30 s; iron removed by alkaline precipitation; sample diluted 1:100 with water and filtered. Peaks: 1 = confidential; 2 = sulphate; 3 = oxalate; 4 = formate; 5 = NTA; 6 = acetate; 7 = confidential; 8 = IDA.

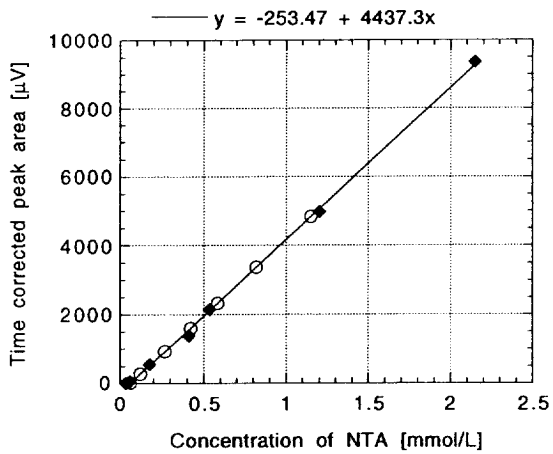

Fig. 6. Calibration graph of time-corrected peak areas as a function of the concentration of NTA. ◆ = Calibration points; ○ = points corresponding to the unknown samples of desulphuration positioned after their measured corrected peak areas. For operating conditions, see Fig. 5.

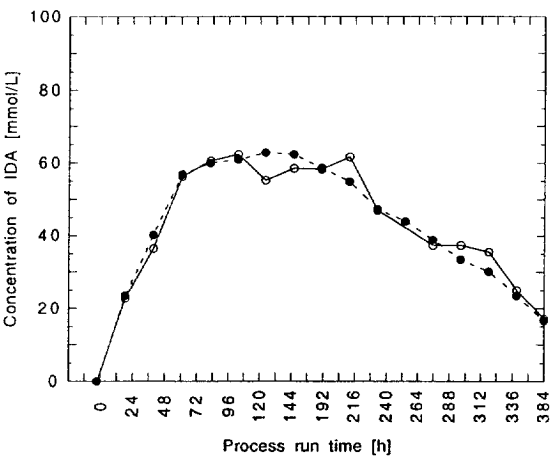

Fig. 7. Comparison of the results for IDA determinations in the desulphuration solutions obtained in laboratories A and B with two different methods. For operating conditions, see Table 1 and text.

3.5. Separations of the amphoteric process relevant species

According to Carr et al. [2], GLY, NMG and DMIA are theoretically possible amphoteric degradation products of NTA. The acid–base dissociation constants found in the literature [4] are 9.78 for GLY, 10.12 for NMG and 9.80 for DMIA. A more appropriate electrolyte with a higher pH value in the vicinity of the pK_1 values of the analyte was therefore sought in laboratory A. Using the anisate–Bis-Tris carrier electrolyte of pH 7.0, the three species were not resolved from the signal corresponding to the electroosmotic flow, the pH value being too close to their isoelectric points, located in the range 6.0–6.2. On injecting a standard mixture, the analytes were best separated with respect to one another, the signal of electroosmotic flow and the other process-relevant compounds dealt with above, with an anisate–ammediol electrolyte of pH 9.5 (Fig. 8a). This electrolyte also results in an increase in the electroosmotic flow, which speeds up the separation and provides satisfactory conditions for indirect absorbance detection. Fig. 8b shows the electropherogram of a desulphuration solution sampled near the end of the process, 360 h after its start, exhibiting a peak assigned to GLY. In fact, GLY was detected in every solution sampled beyond 72 h, whereas DMIA and NMG were never found, in agreement with the assumption that the disproportionation of NTA which produces DMIA and NMG is less likely to occur [2].

The quantitative aspects of GLY determination under these conditions were then considered. In order to obtain known solutions of GLY in a matrix as close to the unknown desulphuration solutions as possible, the GLY solutions used for calibration were prepared by supplementing the initial desulphuration solution (in which GLY had not been detected) with four

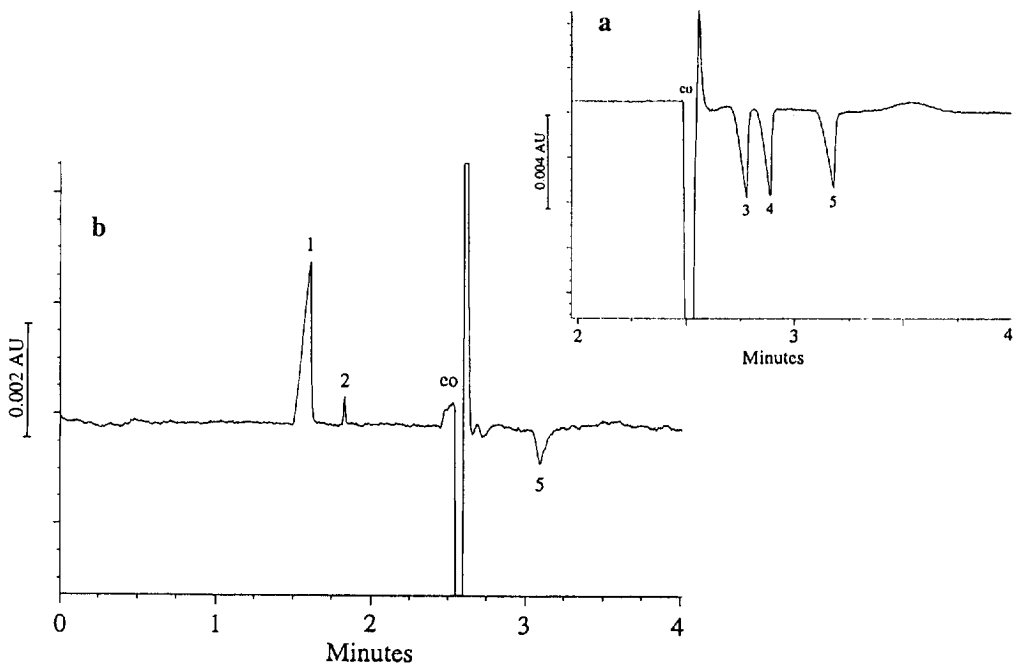

Fig. 8. Electropherograms of (a) a standard mixture of NMG, DMIA and GLY, 1 mmol/l each, and (b) a desulphuration solution sampled after 360 h of process run time. Fused-silica capillary, 58 cm × 50 μm I.D. (effective length 50.5 cm); electrolyte, 10 mmol/l *p*-anisic acid–63 mmol/l ammediol (pH 9.5); separation voltage, +30 kV; indirect UV detection at 254 nm; gravity injection for 20 s; desulphuration sample filtered, diluted 1:40 with water and made up to 2.5 mmol/l EDTA. Peaks: 1 = sodium; 2 = ammonium; eo = electroosmosis; 3 = NMG; 4 = DMIA; 5 = GLY.

different known concentrations of GLY. The method appeared to be well adapted to the determination of GLY, as can be seen from the calibration graph in Fig. 9. This graph is linear with a correlation coefficient of 0.9996.

Using this calibration step, GLY was next determined by laboratory A in all desulphuration process samples, as shown in Fig. 9. For this series, the relative standard deviations ($n = 3$) for migration times and corrected peak areas ranged between 0.0 and 0.2% and between 1.4 and 10%, respectively.

An alternative method for determining GLY was carried out by laboratory B with an electrolyte consisting of 5 mmol/l borax (pH 9.2) and using direct UV detection at 185 nm. With a voltage of 22 kV, the separation was completed in 6 min. The detection sensitivity was lower than that obtained previously with the anisate–ammediol electrolyte but the surface repeatability was correct. Under these conditions, DMIA was not resolved from the neutral species but the method was nevertheless applied in laboratory B for the sake of comparison as it had been established previously that DMIA was absent from all process samples. Fig. 10 shows that the values obtained with the two methods for the determination of GLY are comparable, except for the last ones, which could be explained by degradation of the sample before its processing.

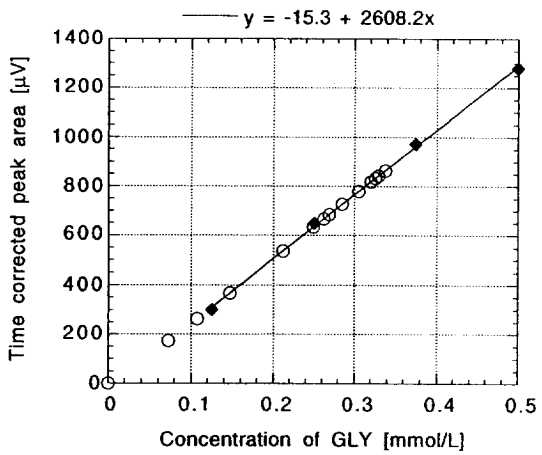

Fig. 9. Calibration graph of time-corrected peak areas as a function of the concentration of GLY added to the initial desulphuration solution. ◆ = Calibration points; ○ = points corresponding to the unknown samples of desulphuration positioned after the measured corrected peak areas. For operating conditions, see Fig. 8.

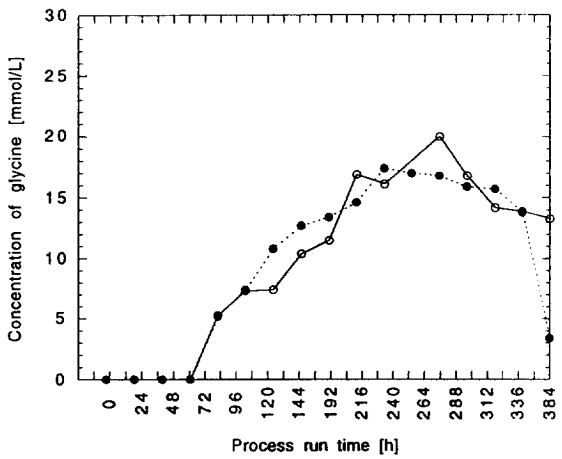

Fig. 10. Comparison of the results of GLY determinations in the desulphuration solutions obtained in laboratories A and B with two different methods. Electrolytes: laboratory A, anisate–ammediol (pH 9.5) (indirect UV detection); laboratory B, borate (pH 9.2) (direct UV detection). See text for further explanations.

3.6. Separations of the cationic process relevant species

One of the unique features of capillary electrophoresis under electroosmotic flow conditions is that it makes possible the simultaneous separation of cationic and anionic species. Further, it is known [5–8] that cationic species can still be detected with acceptable sensitivity in the indirect absorbance mode when an anionic chromophore is used. In effect, with electrolytes of pH 7.0 and 9.5, sodium, originating from both the buffer and additives present in the desulphuration solution and from EDTA used as the disodium salt added to the samples, was detected in all solutions. A second cation identified as ammonium was detected in the solutions sampled beyond 144 h of process run time. However, in this respect, a major benefit of the anisate–ammediol (pH 9.5) carrier electrolyte is that it precludes any interference in case of the

occurrence of potassium. This electrolyte was therefore chosen for the determination of ammonium, the final degradation product of NTA. The analysis can be completed within 2 min. The corresponding electropherogram for the determination of ammonium is presented in Fig. 8b.

As the sodium peak becomes triangular owing to electrophoretic dispersion when too high a concentration is injected, the concentration of EDTA disodium salt added to the samples was lowered to a 1:1 Fe(III)-to-ligand ratio. Under these modified conditions, return to the baseline was always preserved between the peaks of sodium and ammonium, which markedly improved the determination of ammonium. Fig. 11 shows the calibration graph obtained by spiking the initial desulphuration solution with six different concentrations of ammonium. It shows a very good linearity (linear correlation coefficient 0.9990). We next attempted to determine the ammonium concentration in the series of desulphuration samples. The corrected areas of the peaks corresponding to the unknown solutions are reported in Fig. 11. Repeatability was observed, as indicated by the R.S.D. ($n = 3$) of migration times (0.0–0.3%, according to the samples) and corrected peak areas (0.4–15%).

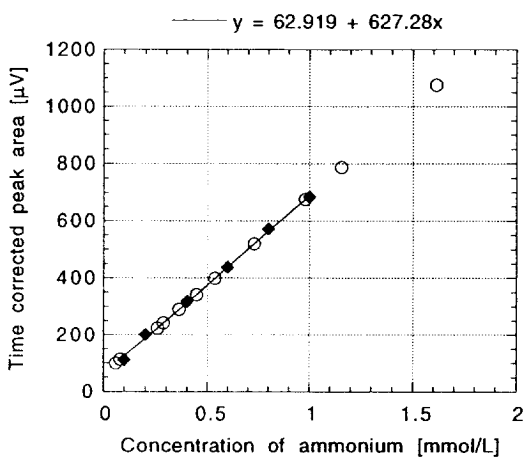

Fig. 11. Calibration graph of time-corrected peak areas as a function of the concentration of ammonium added to the initial desulphuration solution. ◆ = Calibration points; ○ = points corresponding to the unknown samples of desulphuration positioned after the measured corrected peak areas. For operating conditions, see Fig. 8b.

3.7. Monitoring of total iron concentration

As the lifetime of the desulphuration solution was obviously related to keeping iron(III) in the solution, thorough control of the process also required this species to be monitored. Using anisate–Bis-Tris electrolyte (pH 7.0), a narrow peak for the Fe(III)–EDTA complex was obtained with samples supplemented with EDTA in excess with respect to iron(III) (Fig. 3). However, no attempt was made to correlate this signal with iron(III) concentration. A more specific capillary electrophoresis method, using direct UV detection but still based on the fact that Fe(III)–NTA complexes are quantitatively replaced by Fe(III)–EDTA complexes on addition of excess EDTA to the samples, was developed. Dissociation of the complex during its migration inside the capillary into free EDTA and metal ion was totally eliminated by addition of 0.1 mmol/l of EDTA to the electrolyte. Finally, to take advantage of the absorbance of the Fe(III)–EDTA complex near 254 nm, a very transparent buffer, such as borate (pH 9.2), was selected. Fig. 12 shows the electropherogram of

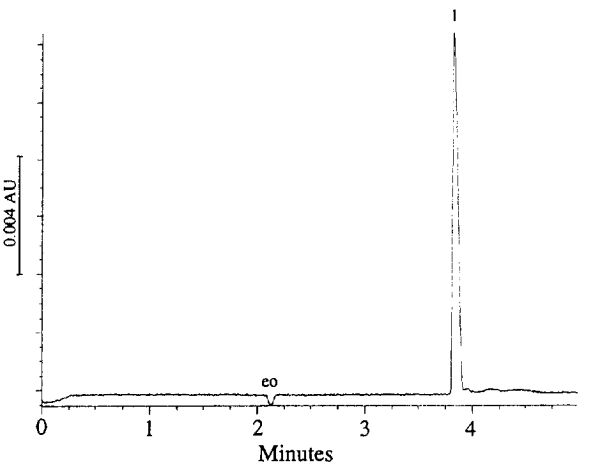

Fig. 12. Electropherogram of a desulphuration solution at zero process run time (initial solution). Fused-silica capillary, 58 cm × 50 µm I.D. (effective length 50.5 cm); electrolyte, 20 mmol/l borate (pH 9.2); separation voltage, +30 kV; direct UV detection at 254 nm; gravity injection for 20 s; sample filtered, diluted 1:10 with water and made up to 50 mmol/l EDTA. Peaks: eo = electroosmosis; 1 = Fe(III)–EDTA complex.

the initial desulphuration solution. A single and symmetrical peak was produced, allowing its easy quantification. It must also be emphasized that under these conditions, Fe(III) and Fe(II) merged into a single peak, presumably because of oxidation of Fe(II) to Fe(III) before or during the electrophoretic process. The method was applied to the determination of total iron in all the solutions sampled during the process. The four calibration points and the points corresponding to the corrected areas measured for the unknown samples are displayed in Fig. 13. The linear correlation coefficient for the calibration points was 0.9991. Finally, the analyses for iron were performed in less than 5 min with R.S.D. ($n = 3$) ranging from 0.0 to 0.2% for the migration times and from 0.1 to 0.9% for the corrected peak areas.

3.8. Overall monitoring of degradation of the desulphuration solution

To gain a deeper insight into the process of degradation of the desulphuration solution, the variations of the concentrations of NTA, IDA, GLY, ammonium and Fe(III) should be considered together. The first panel of Fig. 14 clearly

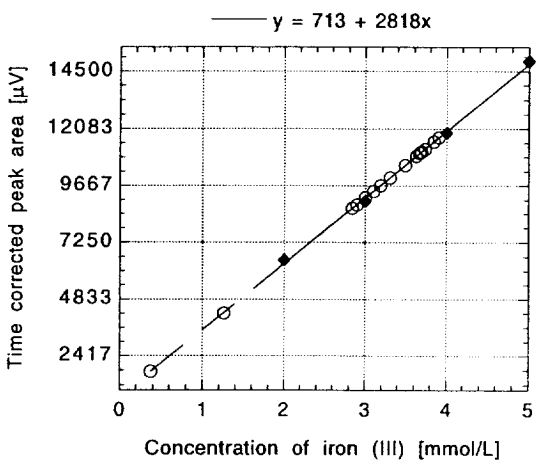

Fig. 13. Calibration graph of time-corrected peak areas as a function of the concentration of iron(III) in the standard solution. ◆ = Calibration points; ○ = points corresponding to the unknown samples of desulphuration positioned after the measured corrected peak areas. For operating conditions, see Fig. 12.

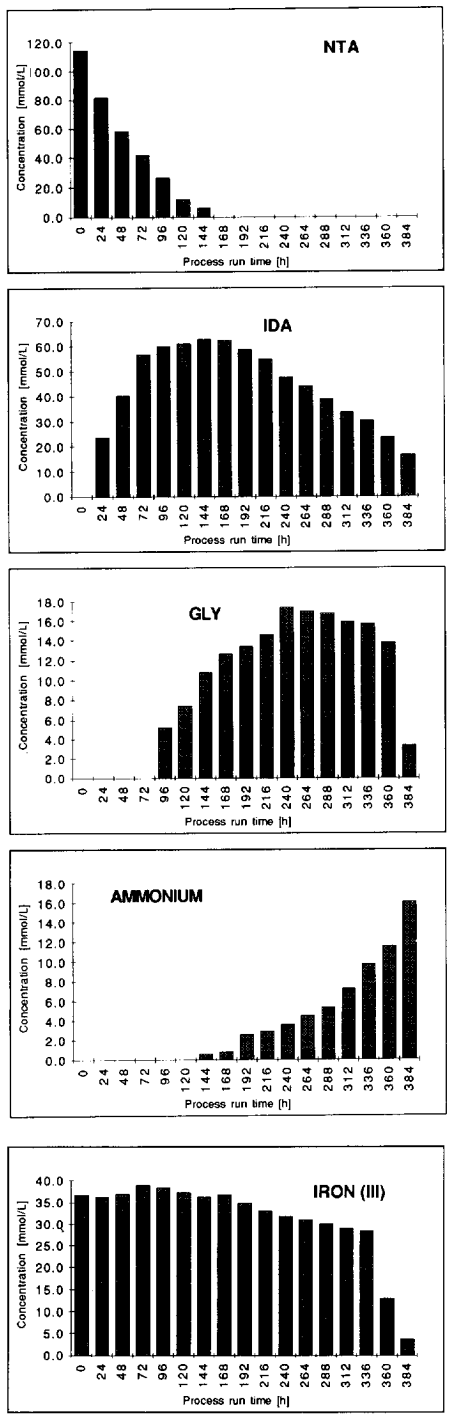

Fig. 14. General outline illustrating the simultaneous variation of the concentrations of NTA, IDA, GLY, ammonium and Fe(III) in the desulphuration solutions as a function of process run time. For further explanations, see text.

illustrates the rapid decomposition of NTA, which totally disappears within 150 h of desulphuration run time. The first step of the degradation leads to IDA, which was detected at a 23 mmol/l concentration level as early as 24 h after the run start. The concentration of IDA increases as long as it is fed by the degradation of NTA, then passes through a maximum as soon as NTA has disappeared and subsequently decreases (Fig. 14, second panel). The following steps of degradation produce GLY and ammonium successively. The degradation of IDA into GLY starts after 96 h of run time, just at the beginning of the period when the concentration of IDA almost reaches a plateau (Fig. 14, third panel). After passing through a maximum, the concentration of GLY decreases in turn at a time corresponding to a larger increase in the concentration of ammonium, appearing as a final degradation product (Fig. 14, fourth panel). Lastly, the results are still corroborated by the variation of Fe(III) concentration (Fig. 14, last panel), which first shows a slow decrease in the concentration of iron(III) as NTA is replaced by IDA and GLY in solution, and in accordance with the order of decreasing stability of the complexes Fe(III)–NTA, Fe(III)–IDA and Fe(III)–GLY [3], [9]. Beyond ca. 350 h of run time the concentration of iron(III) drops drastically, as there is no more complexing agent in the solution.

4. Conclusion

Capillary electrophoresis appears to be a simple, rapid, flexible and cost-effective technique for the quantitative assessment of the various species involved in this desulphuration process. Granted the large differences in absolute mobilities, dissociation constants and charge signs of all the analytes of interest, it was deemed preferable to tailor a few well adapted, distinct methods, rather than a single method, each of them leading to analysis times shorter than 5 min. Special attention was paid throughout this work to quantitative and method validation aspects as they have not often been reported in the past. Very satisfactory repeatabilities were obtained for migration times and peak areas under various electrolyte conditions and with both direct and indirect absorbance modes. As illustrated in Fig. 14, the coherence of the overall results testifies to the confidence that can be placed in these methods. The excellent agreement obtained for the determination of IDA and GLY by different methods and in two different laboratories is also worthy of note. Finally, for the desulphuration process that was the incentive for this study, this set of capillary electrophoresis methods is considered to be very appropriate for fine tuning of the composition of the solution and hence optimizing its lifetime, and subsequently for controlling a scaled-up industrial process.

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