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Analysis of difficult samples by capillary zone electrophoresis I. Simultaneous separation of detrimental anions in concrete digested with concentrated nitric acid

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Abstract

The analysis of detrimental anions (chloride and sulfate) in concrete digested with concentrated nitric acid is extremely difficult due to the high acidity, ionic strength and nitrate background of the digest. Employing capillary zone electrophoresis, chloride and sulfate in a diluted digest were separated simultaneously with full resolution in less than 6 min. An electrolyte comprising 10 mM lithium nitrate, 1 mM thiocyanate and 0.8% (v/v) 1-butanol at pH 6 was used. The development of this electrolyte and the analytical performance are discussed. © 1998 Elsevier Science B.V.

Keywords: Concrete; Buffer composition; Chloride; Sulfate; Inorganic anions

1. Introduction

The analysis of chloride and sulfate in concrete is important as these anions can have deleterious effects on concrete and concrete structures. These anions must therefore be kept at low levels [≤0.02% (m/m) for chloride and ≤0.5% (m/m) for sulfate] in concrete. For porous reinforced concrete structures, chloride can catalyse the corrosion of iron. Sulfate reacts with $Ca(OH)_2$ and calcium aluminate in the concrete to form products that cause an increase in volume, which results in the cracking of the concrete [1]. The standard methods of analysis for the two anions in concrete are a Volhard titration for chloride and a gravimetric determination for sulfate as $BaSO_4$

[2]. The Volhard method is limited by the use of costly silver and the presence of interfering species that oxidise the thiocyanate titrant. For the gravimetric method, nitrate and iron give high and low results, respectively, by interfering in the precipitation of $BaSO_4$ [3]. Errors can also arise from occlusion and adsorption effects. A further major limitation of both methods is the long time of analysis.

Dissolution of concrete with HNO_3 [2] yields a digest that is difficult to analyse due to the resultant high acidity (pH~2), ionic strength, nitrate background; and concomitant metal ions (e.g. Fe^{3+}) that can complex the sulfate and chloride [4]. In addition, the normal levels of chloride and sulfate in concrete are rather low for the standard methods to be applied easily. For these reasons a more sensitive and rapid method to which the difficult matrix of the sample can be amenable is desirable. Capillary zone electro-

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phoresis (CZE) is fast, sensitive, can separate both anions simultaneously, and has been used to analyse acid-digested concrete [1]. However, only sulfate was detected and the separation time was >10 min [1]. The aim of this study was to develop an improved CZE method for the rapid, simultaneous separation of chloride and sulfate in concrete digested with concentrated HNO_3.

2. Experimental

2.1. Instrumental

A Quanta 4000 CE system (Waters, Milford, MA, USA) interfaced with Maxima 820 software was used for all separations. Unless noted, the separation voltage was −20 kV, data was acquired at 20 Hz and the sampling was performed hydrostatically (10 cm for 30 s). Separations were carried out in a polyamide-coated fused-silica capillary (75 μm I.D., 52 cm effective length, 60 cm total length). Indirect UV detection was applied at the anodic side. Milli-Q (Millipore, Bedford, MA, USA) water was used throughout.

2.2. Reagents

Except where noted, the following chemicals were analytical reagent-grade sodium salts, sourced from Ajax Chemicals (Sydney, Australia) and dried (100°C overnight): sulfate (Rhône-Poulenc, Manchester, UK), chloride (BDH, Victoria, Australia), nitrate, lithium nitrate·$3H_2O$ (undried, BDH, Poole, UK), concentrated HNO_3, thiocyanate (undried, GPR, Hopkin & Williams, UK) and $Fe(NO_3)_3$·$9H_2O$ (undried, Feinbiochemica, Heidelberg, NY, USA).

2.3. Procedure

2.3.1. Capillary conditioning
Prior to separation with each background electrolyte (BGE), the capillary was conditioned according to procedure 6 in Ref. [5], except that the water blank was separated in triplicate under the running conditions for 1 min. This procedure yielded stable migration times [5].

2.3.2. Preparation of sample and standards
A comminuted concrete sample was prepared according to British Standard 1881 [2]. The sample (5.0032 g) was dispersed in water (25 ml) and concentrated HNO_3 (1 ml) added. Hot water (50 ml) was added and the mixture heated without boiling for ≥15 min, filtered (Whatman 541 pre-washed with hot water), cooled and diluted to 100 ml. From this solution, a 10% (v/v) dilution was made. External standards (2.5–150 μg ml^{-1}) were made from 1000 μg ml^{-1} stock solutions of chloride and sulfate, respectively. Standard additions of 2–40 μg ml^{-1} of chloride and 10–40 μg ml^{-1} of sulfate were made to a 10% (v/v) diluted digest.

3. Results and discussion

3.1. Background electrolyte composition

In CZE, the inclusion of cationic surfactants in the BGE alters the electroosmotic flow and allows for short migration times for anions when reversed polarity of the separation voltage is used. However, the system peak from the surfactant counter-ion can cause severe interferences when high ionic strength samples are separated. For example, the bromide system peak from the widely used teradecyltrimethylammonium bromide can increase in size and swamp chloride and sulfate. For this reason, no surfactant was added to the BGE developed in this work.

To determine chloride and sulfate rapidly and simultaneously, indirect UV detection using a suitable UV-absorbing co-ion (or probe) is usually employed. Chromate is the probe used most commonly for the separation of anions but is unsuitable because it gives an indirect response for all anions and, in the particular sample under consideration, the large peak due to nitrate swamps both the chloride and sulfate peaks [1]. Thiocyanate has been used for the analysis of concrete [1] by CZE but does not permit the detection of chloride. As the digest has a high nitrate content, nitrate was chosen as the probe and was used at a concentration similar to that present in the sample matrix so that there would be little or no detector response to the nitrate in the samples. When a sodium nitrate BGE without added
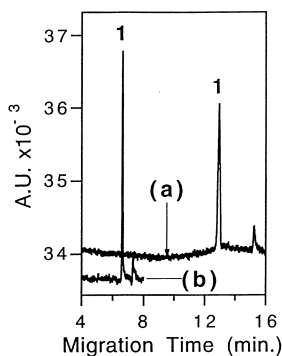
Fig. 1. Comparison of separation using nitrate salts of sodium (a) and lithium (b) as probe counter-ions. Electrolyte: apart from the difference in counter-ion, both separations used electrolytes with 10 mM nitrate at pH 6. Conditions: the sampling time was 10 s, the separation voltage −20 kV, the time constant 1 s, the detection wavelength 214 nm, and the data acquisition rate 20 Hz. The peaks were made to appear positive by reversing the detector leads. Key: 1, chloride (18 µg ml^{-1} in 0.05% (v/v) HNO$_3$).

surfactant was used and a separation voltage of −20 kV was applied, separation times of over 10 min were recorded (Fig. 1a). In contrast lithium nitrate under identical conditions gave separation times below 10 min and a higher detection sensitivity (Fig. 1b). Another advantage of lithium as the BGE counter-ion is that it is less conducting than sodium, so the separation voltage can be increased to lower the separation time.

The resolution between chloride and sulfate improved with increasing concentration of nitrate in the BGE. However, this was at the expense of longer separation times and decreased detection sensitivity (Fig. 2). To keep the separation time short and to
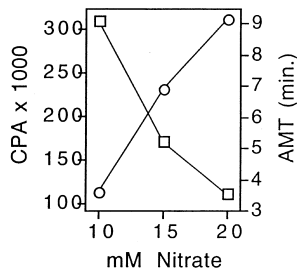

Fig. 2. Effect of lithium nitrate concentration on the peak area response (□) and migration time (○). Conditions: the separation voltage was −21 kV. The model anion was chloride (18 µg ml^{-1} in 0.05% (v/v) HNO$_3$). Other conditions were as in Fig. 1. Key: CPA, corrected peak area; AMT, absolute migration time.

also give the best match with the nitrate levels in the diluted sample matrix, 10 mM lithium nitrate was chosen as the optimal BGE concentration.

Concrete normally contains ~0.003% Fe(III) which can form complexes with both sulfate (particularly at pH ~2 [4]) and chloride and is therefore likely to cause a decrease in the detection response for these species. This is simulated in Fig. 3. Sulfate was omitted from the simulation as the separations were performed at pH 6 where iron–sulfate complex does not form [4]. In order to minimise this interference, approaches to mask this Fe(III) were investigated, and so that the total analysis time would be minimised, on-capillary complexation was used. It was found that addition of 1 mM thiocyanate to the BGE caused complete release of chloride from 0.0003% Fe(III). Thiocyanate was chosen because the FeSCN^{2+} formed would migrate to the cathode and would not interfere with the analyte anions. Migration times were stabilised by the addition of 0.8% (v/v) 1-butanol [6,7] to the BGE.

3.2. Analysis of acid-digested concrete

Based on the above observations, a BGE comprising 10 mM lithium nitrate, 1 mM thiocyanate and 0.8% (v/v) 1-butanol at pH 6 was constituted. The pH was maintained at <7 to prevent precipitation of
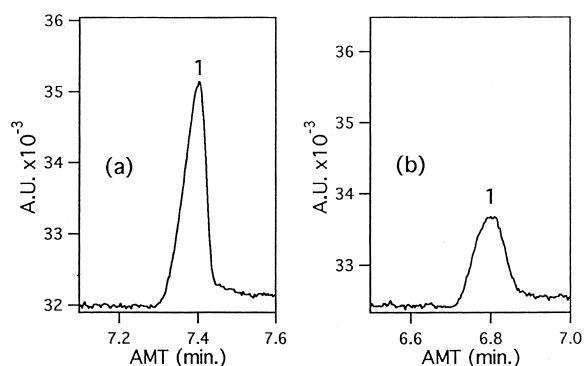

Fig. 3. Effect of iron(III) on the response of chloride. Conditions: electrolyte contained 10 mM lithium nitrate at pH 6. The separation voltage was −21 kV. Data were acquired at 214 nm using a rate of 5 Hz. Key: AMT, absolute migration time; (a) 18 µg ml^{-1} chloride in 0.05% (v/v) HNO$_3$; (b) as in (a) but spiked with >0.0003% of Fe(III); 1, chloride.
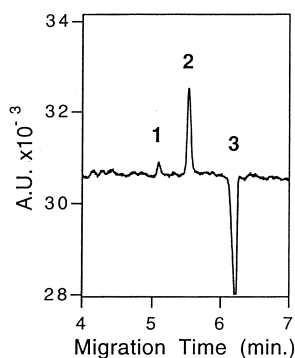
Fig. 4. Separation of 10% (v/v) diluted HNO_3-digested concrete. Electrolyte: 10 mM lithium nitrate, 1 mM thiocyanate and 0.8% (v/v) 1-butanol at pH 6. Conditions: as in Fig. 1 except that the voltage was −21 kV and the data acquisition rate was 5 Hz. Key: 1, chloride; 2, sulfate; 3, thiocyanate (ligand).

iron hydroxide, which could cause capillary blockage. Fig. 4 shows the separation of chloride and sulfate in a diluted concrete digest using this BGE and a separation voltage of −21 kV. The peaks were identified by co-injection. The negative system peak due to the thiocyanate in the BGE can be used as a reference marker.

Several advantages apparent from Fig. 4 are that both anions were separated with baseline resolution,

there was no interference from a surfactant system peak, and the separation time was short. In contrast to the standard methods, the method developed here represents significant savings in analysis time. It should also be noted that the BGE used in Fig. 4 was found to be stable for over 3 days, which is an advantage over BGEs that need to be prepared freshly each day.

3.3. Analytical performance

The analytical performance characteristics of the separation in Fig. 4 are summarised in Table 1. For sulfate, comparisons have been made with previous work [1]. An acidified mixture containing disparate levels of chloride (10 µg ml^{-1}) and sulfate (150 µg ml^{-1}) was analysed to determine the precision (as %R.S.D.) of absolute migration time (AMT) and peak area. Precision of AMT for chloride (2.4%) and sulfate (2.5%) compared well with those published for real samples, i.e. 2–14% [1,8]. Precision of corrected peak areas (i.e. peak area×velocity of anion) for chloride (2.9%) and sulfate (2.5%) also compared well with those (1.2–2.3%) published for inorganic anions in general [9] and for sulfate in concrete (1.7%) [1]. On the other hand, precision for corrected peak heights for chloride (4.3%) and

Table 1
Analytical performance characteristics

Feature	Chloride (n) A	Sulfate (n)	
		A	B
Precision (% RSD)[a]			
Migration time (min)	2.4 (10)	2.5 (10)	1.7 (5)
Corrected peak area (µV cm)	2.9 (7)	2.5 (8)	3.6 (5)
Corrected peak height (µV)	4.3 (7)	4.5 (9)	—
Absolute migration time (min)	5.2	5.8	>10
Linear calibration range			
External standards (µg ml^{-1})	2.5–150	2.5–150	10–100
Standard addition (µg ml^{-1})	0–40	0–40	0–40
External standard linearity (r^2)	0.998	0.997	0.996
Recovery (%)	103[b] (3)	108[b] (3)	102[c] (2)
Limit of detection (µg ml^{-1})	1 (3)	4 (3)	4 (2)
Amount detected (% m/m)	0.02	0.4	0.5

Key: n=number of readings; A, this work; B, from Ref. [1].
[a]For A for a mixture with 10 µg ml^{-1} fluoride, 150 µg ml^{-1} sulfate and 0.1% (v/v) HNO_3, whereas for B, for the diluted sample.
[b]Calculated from 10% (v/v) diluted sample spiked with 10 µg ml^{-1} each of chloride and sulfate.
[c]Calculated from 10% (v/v) diluted sample spiked with 40 µg ml^{-1} of sulfate; limit of detection, calculated at $3 \times S/N$ ratio using the 10% (v/v) diluted sample for chloride in A and B, and the 10 µg ml^{-1} standard for sulfate in A; r^2, linear correlation coefficient; and m/m, mass/mass dry basis.

sulfate (4.5%) were inferior to previously published values, e.g. 3% [10]. Despite the use of a proven protocol to condition the capillary [5] and the inclusion of 1-butanol in the BGE [6,7] to stabilise the migration time, the AMTs of chloride and sulfate were found to show a trend similar to that reported previously [11,12]. That is, there was a relatively large change in AMT for these anions when the BGE vial was replenished. This effect was minimised when corrected peak areas [13,14] were used for quantification.

The calibration curves using corrected areas for sulfate (a) and chloride (b) are shown in Fig. 5. The concentration range covering the maximum standard addition concentration are contrasted. The curves for sulfate using external standards and standard additions were linear and had similar slopes (Fig. 5a). In contrast, the curves for chloride, although linear, had
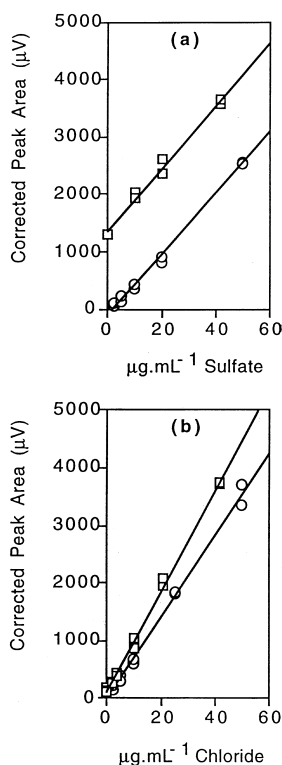
dissimilar slopes (Fig. 5b). This suggested that under the conditions used, there was some matrix interference. For this reason, standard addition is recommended for the quantification of chloride.

The recoveries obtained for 10 μg ml^{-1} standard additions were 108% for sulfate and 103% for chloride. The limits of detection (LODs) for chloride and sulfate were adequate for the 10% (v/v) diluted sample in which a chloride content of >10 μg ml^{-1} and a sulfate content of ≥ 50 μg ml^{-1} would have caused concern. The LOD for sulfate matched that (4 μg ml^{-1}) published for concrete analysed by CZE [1].

4. Conclusion

A BGE comprising 10 mM lithium nitrate, 1 mM thiocyanate and 0.8% (v/v) 1-butanol at pH 6 was developed to simultaneously and rapidly separate chloride and sulfate in nitric acid-digested concrete using CZE. For the analysis of both anions in concrete, the method developed here offers significant savings in analysis time compared to the standard methods. The analytical performance was more than adequate for the application. To account for variability in AMT, corrected peak areas were used for quantification. Standard addition is recommended for the quantification of chloride in these samples.

Fig. 5. Comparison of the calibration curves for sulfate (a) and chloride (b). Key: □, standard addition; ○, external standards. For (a), the slopes were 55 and 53 μV ml μg^{-1} for standard addition and external standards, respectively. Likewise, for (b), the slopes were 88 and 71 μV ml μg^{-1}, respectively.

References

[1] A.H. Harakuwe, P.R. Haddad, R. Thomas, Anal. Proc. Incl. Anal. Commun. 32 (1995) 493.
[2] British Standards Institution, BSI 1881 (Part 6), BSI, Milton Keynes, UK, 1971, p. 26.
[3] American Public Health Association, Standard Methods for the Examination of Water and Wastewater, APHA/AWWA/WPCF, Washington, DC, 1985.
[4] J. Kragten, Atlas of Metal-Ligand Equilibria in Aqueous Solution, Ellis Horwood, Chicester, 1978, p. 338.

[5] A.H. Harakuwe, P.R. Haddad, Anal. Commun. 33 (1996) 103.

[6] N.J. Benz, J.S. Fritz, J. Chromatogr. A 671 (1994) 437.

[7] A.H. Harakuwe, P.R. Haddad, J. Chromatogr. A 734 (1996) 416.

[8] B.F. Kenney, J. Chromatogr. 546 (1991) 423.

[9] W.R. Jones, P. Jandik, Am. Lab. June (1990) 51.

[10] K.D. Altria, C.F. Simpson, Chromatographia 24 (1987) 527.

[11] J.A. Lux, H.-F. Yin, G. Schomburg, Chromatographia 30 (1990) 7.

[12] B. Gassner, W. Friedl, E. Kenndler, J. Chromatogr. A 680 (1994) 25.

[13] P.R. Haddad, A.H. Harakuwe, W. Buchberger, J. Chromatogr. A 706 (1995) 571.

[14] G. Bondoux, P. Jandik, W.R. Jones, J. Chromatogr. 602 (1992) 79.