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Ion chromatography determination of chloride and sulphate in cement

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Abstract

The contents of chlorine and sulphur species in commercial portland cement were determined by a two-step sample preparation procedure. The first step was carried out by means of sodium carbonate and peroxide fusion, followed by a second step of electrodialytic neutralisation of the resulting solution. The chloride and sulphate contents were then determined by ion chromatography. The accuracy of the method was checked by analysing a certified standard reference material (SRM). Relative standard deviations were 0.56% and 1.35% for sulphur and chloride determination, respectively.

Keywords: Chloride; Sulfate, Characterization; Cement

The presence of chlorides and sulphates in the process of the formation of clinker minerals usually results in the appearance of compounds that are undesirable. It is therefore of great importance to accurately determine the contents of chloride and sulphate in either raw materials or, even more important, in cement clinker.

Chlorine and sulphur species in cement and similar inorganic materials can be analysed by using ion chromatography only after their conversion into chloride and sulphate, respectively. One method of achieving this is the oxidative decomposition of such materials, e.g., sodium peroxide fusion in Parr oxygen bomb or sodium carbonate fusion in Pt-crucible with the addition of some sodium peroxide. Both methods, however, yield quite complicated matrices (highly alkaline in the case of peroxide fusion, and alkaline- and carbonate-rich in the case of carbonate fusion), thus rendering direct ion chromatography impossible. This problem diminished considerably after the introduction of Donnan dialysis as a sample pretreatment step [1–4]. The results on the determination of some anions in alkaline-based samples with Donnan dialysis were published [1].

In our work, the sample preparation step consisted of electrodialytic neutralisation, a process whereby cations from the dialysed sample were exchanged with hydronium ions from the donor solution (electrolysed water). In this way the alkaline sample was neutralised, whereas in the case of carbonate-rich samples, CO_2 and water were formed. The formation of CO_2 required its additional separation which was performed by using double-phase separator.

Applying previously mentioned sample preparation methods, real samples and standard reference material were analysed.

1. Methods

1.1. Reagents

All reagents were of analytical reagent grade. Stock standard solutions of inorganic anions (Cl^-, SO_4^{2-}) were prepared by dissolving the appropriate amounts of their sodium salts in water purified with a Milli-Q system (Millipore, Malsheim, France).

1.2. Instrumentation

All chromatographic measurements were performed with a Dionex 4000i chromatographic system and separation column AS4A-SC (Dionex, Sunnyvale, CA, USA) (4 mm). For the neutralisation of alkaline samples, the electrodialysis system was used [1]. In the case of carbonate-rich samples, double-phase separator was added to the electrodialysis system. Fig. 1 shows the scheme of the system for the removal of the hydroxide, hydrogen carbonate, and/or carbonate from the sample.

1.3. Analytical procedure

Two different sample preparation methods were compared: (1) Sodium peroxide fusion in Parr oxygen bomb: 200 mg of a sample was decomposed with 7 g of Na_2O_2 ac-

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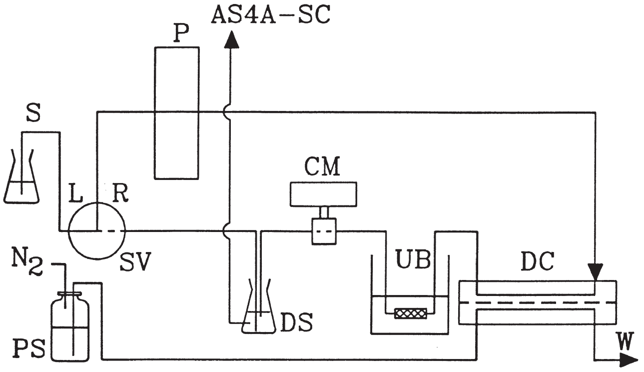

Fig. 1. Scheme of the electrodialysis system for the neutralisation of the alkaline samples. Abbreviations: S, sample; P, peristaltic pump; PS, pneumatic Milli-Q water delivery system; N_2, purging gas; SV, selecting valve; DC, electrodialytic cell; UB, ultrasonic bath with CO_2 separator; CM, conductivity meter; DS, dialysed sample; AS4A-SC, analytical system; W, waste.

cording to the standard procedure for organic material decomposition [5]; and (2) sodium carbonate fusion in Pt-crucible: 1 g of Na_2CO_3 was melted in Pt-crucible. A mixture of 1 g sample and 2 g Na_2CO_3 and 0.2 g Na_2O_2 was added into the cooled Pt-crucible. The mixture in the crucible was covered with an additional 1 g of Na_2CO_3. The mixture was heated (at the melting temperature) for an additional 5 min and cooled.

After the decomposition, the reaction mixture was dissolved in 250 mL of 18 MΩcm water. An aliquot (50 mL) was filtered through the membrane filter with pore size of 0.45 μm. The whole dialytic system was rinsed with the filtered sample. In valve position “LOAD,” approximately 5 mL of sample was collected into the volumetric flask. In valve position “RECYCLE”, the sample from the volumetric flask was dialysed until the conductivity reached the lowest and stable value (Fig. 1). To ensure quantitative elimination of dissolved CO_2 (in the case of carbonate fusion decomposition), the dialysed sample was transferred into and kept in an ultrasonic bath for about 15 min. The concentrations of individual anions in the dialysed samples

Table 1
Analytical results of the determination of sulphur in standard reference material (SRM 2704 Buffalo River Sediment)

		Determined value (%S)	
Sample	Certified value (%S)	Peroxide fusion in Parr oxygen bomb	Carbonate fusion in Pt-crucible
SRM 2704 Buffalo River Sediment	0.397 ± 0.004	0.428 ± 0.021	0.397 ± 0.016

Table 2
Comparison of two different decomposition methods for the determination of sulphur and chlorine in cement

	Determined value (%S)		Determined value (%C1)	
Sample	Peroxide fusion in Parr oxygen bomb	Carbonate fusion in Pt-crucible	Peroxide fusion in Parr oxygen bomb*	Carbonate fusion in Pt-crucible
C1	0.07	0.07	—	0.02
C2	0.08	0.07	—	0.02
C3	0.10	0.10	—	0.04
C4	0.89	0.92	—	0.47
C5	0.28	0.24	—	0.47

* Quantification not possible because of matrix effects.

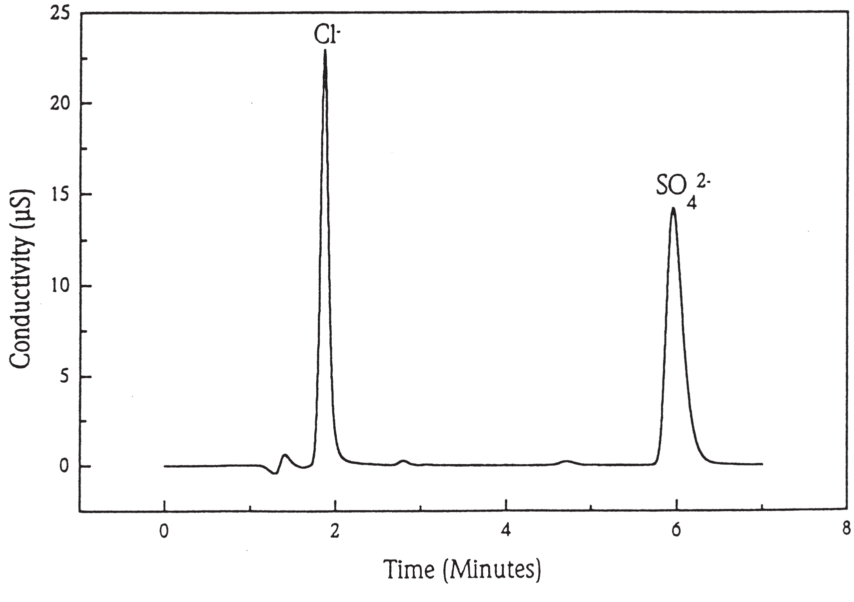

Fig. 2. Chromatogram of sample (mass, 1 g; final volume of the sample solution, 250 mL) decomposed with carbonate fusion in Pt-crucible and neutralised in electrodialytic cell.

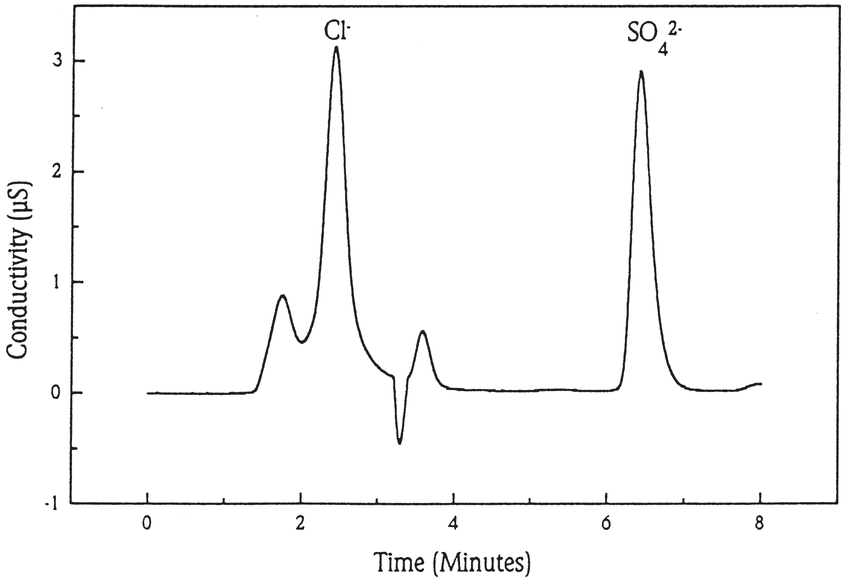

Fig. 3. Chromatogram of sample (mass, 0.2 g; final volume of the sample solution, 250 mL) decomposed with peroxide fusion in Parr oxygen bomb and neutralised in the electrodialytic cell.

were determined by ion chromatography using the standard addition method.

2. Results

The accuracy of two different decomposition methods in combination with ion chromatography (IC) determination of some sulphur was checked using standard reference material SRM 2704 Buffalo River Sediment. The certified value for sulphur in the SRM 2704 was 0.397% (standard deviation, 0.004%). The determined value for the decomposition method in Parr oxygen bomb was 0.428% (standard deviation, 0.021%); and the value for the decomposition method in Pt-crucible 0.397% S (standard deviation, 0.016%). Both procedures yield satisfactory results for sulphur (Table 1), but sodium carbonate decomposition gave evidently better results with slightly lower standard deviation.

The results obtained with two different decomposition methods for sulphur and chlorine in real samples of cement are given in Table 2. In the case of chlorine determination, the sodium carbonate decomposition method was found to be more useful (Fig. 2) because, in the case of peroxide fusion (Fig. 3), some matrix effects remained even after the electrodialytic neutralisation. The calculated relative standard deviation obtained by carbonate fusion in Pt-crucible was 0.56% for sulphur and 1.35% for chlorine ($n = 7$).

3. Conclusions

Based on the results obtained in our work, the following conclusions can be made:

1. The decomposition process results in a strongly alkaline solution in the case of both decomposition procedures. In the case of sodium carbonate fusion decomposition, carbonate-rich sample occurs also, that results in additional interferences during IC determination of anions. Electrodialysis was found to be the most successful sample neutralisation procedure with simultaneous elimination of dissolved carbonate species without further sample contamination.
2. Sodium carbonate fusion method was found to be superior to sodium peroxide decomposition method when chlorine has to be determined, because in the peroxide fusion method some matrix effects remained even after electrodialytic neutralisation. Sulphur can be determined by IC after both decomposition procedures. Sodium carbonate fusion in Pt-crucible again resulted in slightly better results compared to those obtained after sodium peroxide decomposition.
3. The accuracy of two different decomposition methods was checked using a standard reference material (SRM 2704). Both decomposition methods yielded satisfactory results for sulphur.
4. Relative standard deviation of the results obtained by carbonate fusion in Pt-crucible was 0.56% for sulphur and 1.35% for chloride.

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