Renato Zanella,
Ednei G. Primel,
Ayrton F. Martins

Departamento de Química,
Universidade Federal de Santa
Maria, 97105–900 Santa Maria
– RS, Brazil

Determination of chloride and sulfate in pore solutions of concrete by ion chromatography

Key Words: Chloride; Sulfate; Ion chromatography; Pore solution of concrete

Ms received: July 27, 2000; accepted: January 28, 2001

1 Introduction

It has long been recognized that chloride and sulfate ions can induce corrosion of steel in reinforced concrete [1, 2]. Chloride and sulfate ions can exist as a result of aggregate contamination. However, they can also penetrate into the concrete from the outer environment [3, 4]. The presence of sulfate has some influence on the chloride binding capacity of cement and the pore solution chemistry [5, 6]. When sulfate is present in substantial quantities it can decrease the amount of bound chloride, and thereby increase corrosion of the steel [7]. Methods usually employed for determining chloride in pore solution involve the use of titration against silver nitrate [5], potentiometric titration using a chloride ion selective electrode [6, 8–10], X-ray fluorescence [11], static mercury drop polarography [12], spectrophotometry [13], and measurement on a pre-calibrated chloride analyzer [7, 14]. The determination of sulfate can be performed by gravimetry [5], by XRF [15], by ICP [16], and, indirectly, by AAS [17]. Many of these methods require extensive sample preparation procedures prior to the final determination steps and a relative large volume of sample. In the last decade, ion chromatography (IC) has become one of the most frequently used techniques for the simultaneous determination of anions. However, no reference was found to the determination by IC of chloride and sulfate in pore solutions of concrete. In this work, the suitability of a IC method was investigated to determine chloride and sulfate in pore solutions of concrete.

2 Experimental

2.1 Chemicals and reagents

All chemicals were of analytical-reagent grade and all eluent and standard solutions were prepared using water purified with a Milli-Q system (18 MΩ cm; Millipore, Bedford, MA, USA). Stock standard solutions of chloride and sulfate (10^{-2} mol L^{-1} each) were prepared by dissolving the appropriate amounts of their sodium salts (Merck, Germany).

2.2 Instrumentation

The analysis was performed with a Shimadzu Model LC-10AD liquid chromatograph (Kyoto, Japan) equipped with a CDD-6A conductivity detector connected to a C-R6A integrator for data acquisition. The column was a CA A14 (250 × 4 mm ID) from Sykam (Gilching, Germany). An ASRS-I (Dionex, Sunnyvale, CA, USA) suppressor module operated in the chemical suppression mode (sulfuric acid 20 mmol L^{-1}; flow rate = 3.0 mL min^{-1}) was used. The eluent was 9.0 mmol L^{-1} sodium carbonate at a flowrate of 1.2 mL min^{-1}. The injection volume was 20 μL and each sample was injected three times. The signal values were obtained by peak height. The quantification of chloride and sulfate was performed with external standards using multiple points.

2.3 Sampling and sample preparation

The pore solution samples were obtained by using a pore solution extractor as described in Barneyback and Diamond [17] and then centrifuged at 6000 rpm for 10 min. Immediately prior to IC analysis, the resulting solutions were filtered through a PTFE membrane (0.45 μm) filtration tip. Four different samples were analyzed.

3 Results and discussion

3.1 Ion chromatographic analysis

The calibration curves were obtained with a series of five standard solutions between 0.05 and 1.0 mmol L^{-1}, and corresponds to: $y = 0.041 + 85.786x$ ($r^2 = 0.9993$) for chloride, and $y = 0.112 + 73.268x$ ($r^2 = 0.9972$) for sulfate. Where y = peak height, in mm, x = concentration, in mmol L^{-1}, and r^2 = determination coefficient. Chloride and sul-

---

Correspondence: Prof. Renato Zanella, Departamento de Química, Universidade Federal de Santa Maria, 97105–900 Santa Maria – RS, Brazil.
E-mail: rzanella@base.ufsm.br
Fax: +55 55220 8031

1615-9306/2001/0303–0230$17.50+.50/0

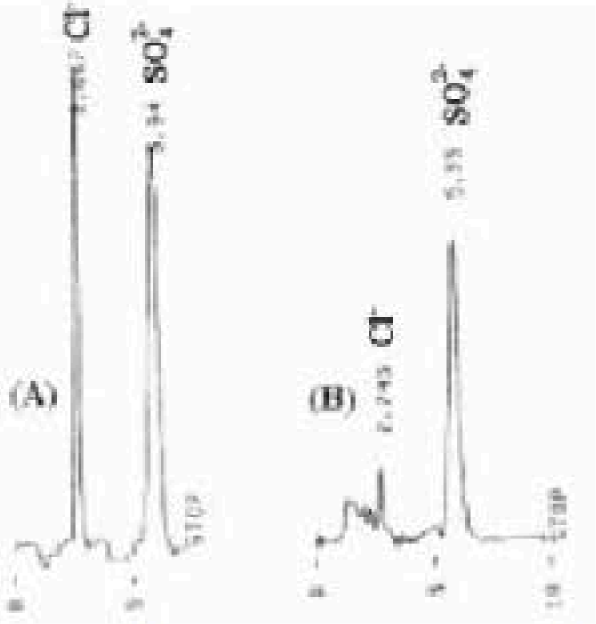

Figure 1. Typical chromatograms from a standard solution (chloride and sulfate, 0.5 mmol L^{-1} each) (**A**) and from a real sample (**B**) obtained by IC. Chromatographic conditions as reported in Section 2.2.

fate showed retention times of 2.7 and 5.9 min, respectively. The limits of detection were obtained according to the IUPAC [18] and corresponds to 0.01 and 0.02 mmol L^{-1} for chloride and sulfate, respectively. The RSD ($n = 10$) of a solution containing 0.1 mmol L^{-1} of chloride and 0.5 mmol L^{-1} of sulfate were 1.8 and 1.3%, respectively. Typical IC chromatograms are shown in **Figure 1**.

3.2 Determination of chloride and sulfate in pore solution of concrete

The determination of chloride and sulfate in different samples yielded results (**Table 1**) in good agreement with those obtained by potentiometric titration [9] and gravimetric [5] methods, respectively. The good agreement between the methods revealed the accuracy of IC for this analysis. Mean average content in the investigated samples varied from 0.09 to 0.16 mmol L^{-1} for chloride and from 0.55 to 0.84 mmol L^{-1} for sulfate.

Table 1. Determination (mean ± RSD) of chloride and sulfate in pore solutions of various concrete matrices by IC.

Sample	Chloride (mmol L^{-1})	Sulfate (mmol L^{-1})
A	0.14 ± 5.2	0.73 ± 6.8
B	0.09 ± 8.3	0.55 ± 7.2
C	0.16 ± 4.9	0.84 ± 4.1
D	0.16 ± 8.6	0.72 ± 7.5

4 Conclusions

It can be concluded that the proposed procedure is satisfactory for the simultaneous determination of chloride and sulfate in pore solutions of concrete. The advantages of this method lie in its simplicity and its sensitivity. Determinations at concentration levels of 0.1 mmol L^{-1} for chloride and 0.5 mmol L^{-1} for sulfate can be achieved within an average RSD of 1.8 and 1.3%, respectively. The results denote the great potential of the procedure for the determination of chloride and sulfate in pore solution of concrete, since only a little sample volume and a very simple preparation of sample are required.

Acknowledgments

The authors are indebted to CNPq, Brazil, for financial support to the laboratory and for a scholarship.

References

[1] C.L. Page, P. Lambert, P.R.W. Vassie, *Mater. Struct.* **1991**, *24*, 243.

[2] G.K. Glass, N.R. Buenfeld, *Corr. Sci.* **2000**, *42*, 329.

[3] S. Bonnet, B. Perrin, *Mater. Struct.* **1999**, *32*, 492.

[4] P. Sandberg, *Cem. Concr. Res.* **1999**, *29*, 473.

[5] C.L. Page, O. Vennesland, *Mater. Struct.* **1983**, *16*, 19.

[6] Y. Xu, *Cem. Concr. Res.* **1997**, *27*, 1841.

[7] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, *Cem. Concr. Comp.* **1998**, *20*, 263.

[8] M.N. Haque, O.A. Kayyali, *Cem. Concr. Res.* **1995**, *25*, 542.

[9] G.K. Glass, Y. Wang, N.R. Buenfeld, *Cem. Concr. Res.* **1996**, *26*, 1443.

[10] T.D. Marcotte, C.M. Hansson, B.B. Hope, *Cem. Concr. Res.* **1999**, *29*, 1555.

[11] M. Castellote, C. Andrade, C. Alonso, *Cem. Concr. Res.* **1999**, *29*, 1799.

[12] F.R. Foulkes, P. McGrath, *Cem. Concr. Res.* **1999**, *29*, 873.

[13] N.J. Coleman, C.L. Page, *Cem. Concr. Res.* **1997**, *27*, 147.

[14] C.P. Atkins, J.D. Scantlebury, P.J. Nedwell, S.P. Blatch, *Cem. Concr. Res.* **1996**, *26*, 319.

[15] E. Proverbio, F. Carassiti, *Cem. Concr. Res.* **1997**, *27*, 1213.

[16] L. Divet, R. Randriambololona, *Cem. Concr. Res.* **1998**, *28*, 357.

[17] R.S.Jr. Barneyback, S. Diamond, *Cem. Concr. Res.* **1981**, *11*, 279.

[18] J.D. Winefordner, G.L. Long, *Anal. Chem.* **1983**, *55*, 712A.

Short Communication