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ION CHROMATOGRAPHIC METHOD FOR MONITORING SULPHATE IN ICE-CORES

ABSTRACT: GRAGNANI R. & TORCINI S., *Ion chromatographic method for monitoring sulphate in ice-cores.* (IT ISSN 0391-9838, 1997).

Using ion chromatography a method was developed for monitoring sulphate in firn and ice cores. With the present method, the sample was loaded automatically in the column without a loop. The results obtained with the monitoring procedure were compared with those obtained with conventional method.

A practical detection limit of 0,4 $\mu\text{Eq/L}$ of SO_4^- was reached when 2 ml of samples were loaded in the column.

KEY WORDS: Ion Chromatography, Monitoring, Sulphate, Ice cores

RIASSUNTO: GRAGNANI R. & TORCINI S., *Metodo di analisi di cromatografia ionica per il monitoraggio dei solfati nelle carote di ghiaccio.* (IT ISSN 0391-9838, 1997).

Mediante cromatografia ionica è stato messo a punto un metodo per la determinazione in continuo della concentrazione dello ione solfato in carote di ghiaccio. Il caricamento del campione avviene direttamente nella colonna cromatografica senza l'utilizzazione di un loop.

Il metodo permette di raggiungere un «practical detection limit» di 0,4 $\mu\text{Eq/L}$ SO_4^- . I risultati ottenuti con il metodo cromatografico convenzionale sono confrontati con quelli ottenuti mediante il metodo qui proposto.

TERMINI CHIAVE: Cromatografia ionica, Monitoraggio, Solfati, Carote di ghiaccio

INTRODUCTION

Sulphate presence in the Antarctic region is mainly due to marine biogenic activity and sea salt. Crustal and anthropic sources are generally negligible. Volcanic events can produce a significant input of SO_x in the atmosphere that can increase the SO_4^- deposition and give a very well marked signal in the snow in sites both close to and far from eruptions (Hammer, 1977 and 1985, Delmas & alii, 1985, Moor & alii, 1991).

The monitoring of sulphate concentration in ice-core makes it possible to identify volcanic events, which can serve as a chronological marker, and to investigate environmental conditions in the past. With these aims, monitoring of SO_4^- and other chemical parameters of ice-core will be carried out during coring in Antarctica (Epica Project).

Turbidimetric and Thorin methods were considered before choosing the ion chromatographic method for sulphate monitoring. The detection limit of 25 $\mu\text{Eq/L}$ as SO_4^- , obtained with the first method, is too high compared to the concentration of 0,5-5 $\mu\text{Eq/L}$ of sulphate generally found in antarctic ice.

With the second method the detection limit corresponds to for the concentration of sulphate found in ice cores (Gjessing, 1984), but the procedure is rather complex for continuous analyses because metal ions have to be removed by a catio-exchange resin.

ANALYTICAL METHOD

Ion chromatography is a suitable method for trace element and compound determination. With the new generation instrument (Dionex DX 500) it is possible to reach an SO_4^- detection limit 4-5 times lower than that obtained by instrumentation available at the moment in our laboratories (Dionex 2020 i). Analysis is generally carried out injecting the sample into the chromatographic system by means of a loop. By this procedure a discontinuous analysis is obtained. The method proposed consists in an automatic loading of the sample directly in the column with the aim of producing a continuous monitoring of SO_4^- along an ice core.

When a single channel system is used, the sample frequency is one every two minutes and loading time is one minute. In the present work, 2 ml of sample were directly loaded with a gradient pump in the chromatographic column in a minute.

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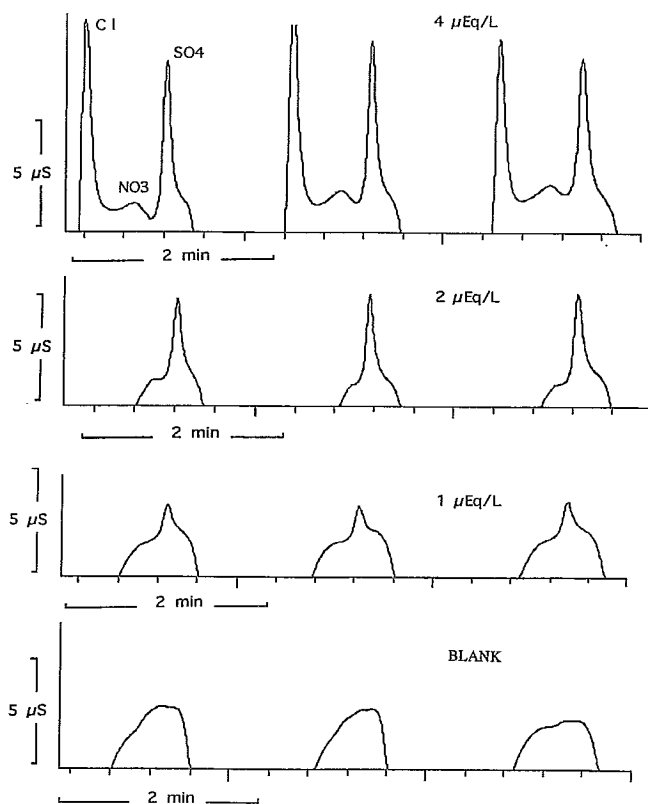


FIG. 1 - Chromatograms for different SO_4^{2-} standard concentrations.

For the double channel system, which requires a double pump, a conductivity detector and a AS-5 column, the sampling is performed continuously by switching from one channel to the other.

Analyses were performed by ion chromatography (mod 2020i Dionex) with a gradient pump module, a 4 MM Anion Self-Regenerating Suppressor and a controller module (Src-1). An advanced computer interface (Aci) was in series with a 486 Uni-bit PC. The separation column used was from Dionex (AS-5) and carbonate - bicarbonate solution (8.8 -11.2 mM respectively) was used as eluent in the analyses.

RESULTS AND DISCUSSION

Using the instrumentation described above a practical detection limit of $0.4 \mu\text{Eq L}^{-1}$ of SO_4^{2-} is reached when 2 ml of sample are loaded in one minute. This is enough to produce a continuous record when ice cores are analysed. The volume and the flow of the sample can be changed to improve the detection limit. The analysis is performed in one minute; since loading time is 1 minute, we have an analytical response every two minutes.

When a bichannel instrument is used in order to alternate both loading and analyses, a continuous monitoring is performed.

In fig. 1 chromatograms for different SO_4^{2-} concentrations are shown, while reproducible data and coefficients

of variation relative to different determinations of sulphate are shown in tab. 1. The Rsd is between 6 and 14 %.

TABLE 1 - Reproducibility for analyses of standard solutions

SO_4^{2-} = $\mu\text{Eq/L}$	Number of samples	Mean Units of Area	RSD %
0.4	4	3.55×10^3	11.3
0.8	8	6.20×10^3	11.6
1	13	6.47×10^3	14.6
2	20	1.93×10^4	14.9
4	34	3.96×10^4	9.0
8	24	8.36×10^4	8.3
16	8	1.59×10^5	6.0
24	8	2.34×10^5	9.2

In fig. 2 the results obtained in samples from Campbell Glacier (Antarctica $74^\circ 15' \text{ S} - 164^\circ 04' \text{ E}$) with the conventional method are compared with those obtained with the monitoring procedure. The highly significant correlation coefficient ($r = 0,985$) and the good coefficient of the regression line ($R_{lc} = 1.116$) confirm the validity of the method for monitoring SO_4^{2-} concentration method in ice cores.

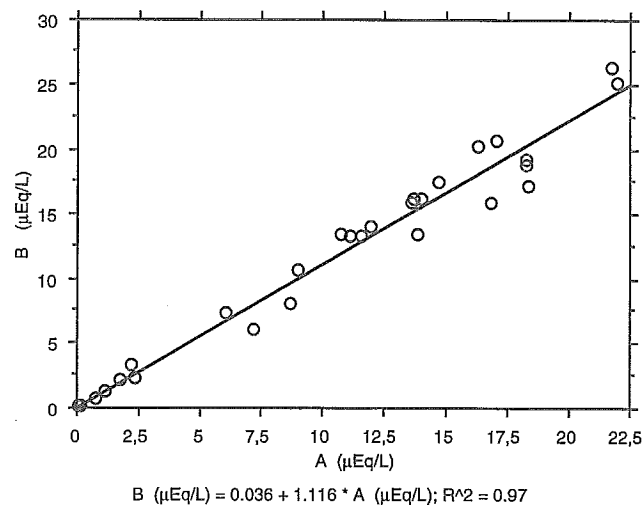


FIG. 2 - Scatter diagram between the results performed by conventional ion chromatography and by the present method. Samples from Campbell Glacier (Antarctica $74^\circ 15' \text{ S} - 164^\circ 04' \text{ E}$). A: SO_4^{2-} concentration by monitoring. B: SO_4^{2-} concentration by conventional ion chromatography.

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