

Short Communication

Electrodialysis pretreatment system for ion chromatography of strongly acidic samples and its application to the determination of magnesium and calcium

Y. OKAMOTO, N. SAKAMOTO, M. YAMAMOTO^a and T. KUMAMARU*

Department of Chemistry, Faculty of Science, Hiroshima University, 1–1–89 Higashisenda-machi, Naka-ku, Hiroshima 730 (Japan)

(First received July 10th, 1990; revised manuscript received October 17th, 1990)

ABSTRACT

A newly developed electrodialysis pretreatment system in combination with a new dual anion-selective membrane tubes was employed to reduce the acidity of a strongly acidic sample solution prior to the ion chromatographic determination of magnesium(II) and calcium(II). By using this system, anions such as sulphate or nitrate were also removed from the sample solution through the membrane. The detection limits were 7.8 and 25 ng/ml and the upper limits of the linear response were 2 $\mu\text{g/ml}$ and 5 $\mu\text{g/ml}$ for magnesium(II) and calcium(II), respectively. Results of the analyses of some strongly acidic solutions are given.

INTRODUCTION

Trace ions in a strongly acidic or basic solution cannot be determined by direct injection into an ion chromatograph equipped with a cation- or anion-exchange separation column and conductivity detector, owing to the high background conductance of the sample in addition to the low capacity of the column. Therefore, the solution should be diluted to alleviate the load of excess ions on the column. However, such a dilution makes analysis difficult if the concentrations of the ions in the original sample are close to the detection limits. Pettersen *et al.* [1] reported a method for reducing high concentrations of sodium and hydroxide ions without dilution for the determination of sulphate and nitrate ions. Their method was based on electrolysis in combination with a sheet of cation-selective membrane. In this preliminary work, a new dual anion-selective membrane tube electrodialysis system

^a Present address: Kure Research Laboratory, Babcock Hitachi KK, 3–36 Takara-machi, Kure, 737, Japan.

was developed and applied, as an example, to the determination of magnesium and calcium ions in strongly acidic solutions by non-suppressed or single-column ion chromatography.

EXPERIMENTAL

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) Model CCPD double-plunger pump, a Tosoh Model IC-Cation column, a Rheodyne (Cotati, CA, U.S.A.) Model 7125 injector with a 100- μ l sample loop and a Tosoh Model CM-8 conductivity detector. The sensitivity of the detector was 0.5 μ S/cm. The mobile phase (pH 5.3) consisted of ethylenediamine (0.25 mmol/l) and tartaric acid (0.25 mmol/l). The flow-rate was 1.0 ml/min.

The electro dialysis system consisted of an electro dialysis cell, a constant-current d.c. electric source (0.9 A), a relative conductivity monitor, a Tokyo Rikakikai (Tokyo, Japan) Model MP-3 two-channel peristaltic pump and an M & S Instruments (Osaka, Japan) Model JR magnetic stirrer. For the electric source and the monitor, the components of a Tosoh Model IE-Labo system were used. The design of the electro dialysis cell, shown in Fig. 1, utilized a Tosoh TASN-85 anion-selective membrane tube (40 cm \times 1.00 mm I.D. \times 2.25 mm O.D.), containing a platinum wire (50 cm \times 0.30 mm O.D.), inserted inside a Tosoh TASN-80 anion-selective membrane tube (30 cm \times 2.75 mm I.D. \times 3.13 mm O.D.). A stainless-steel wire (2 m \times 0.50 mm O.D.) was coiled around the outer membrane tube and held negative with respect to the central conductor. Inlet and outlet liquid connections were made with silicone-rubber tees. Sample solution flowed in the outer channel, whereas anode electrolyte solution (0.1 mol/l sulphuric acid) flowed in the inner channel. Sodium hydroxide solution (0.1 mol/l) was used as the cathode electrolyte solution. Other parts of the system were connected with polytetrafluoroethylene tubing (1.0 mm I.D.).

The electro dialysis procedure was as follows. The sample channel was filled with an aliquot of a strongly acidic sample solution (*ca.* 2.5 ml). The solution was then circulated at a flow-rate of 3.7 ml/min and the anode electrolyte solution was also pumped at the same flow-rate. Subsequently, platinum and stainless-steel wire

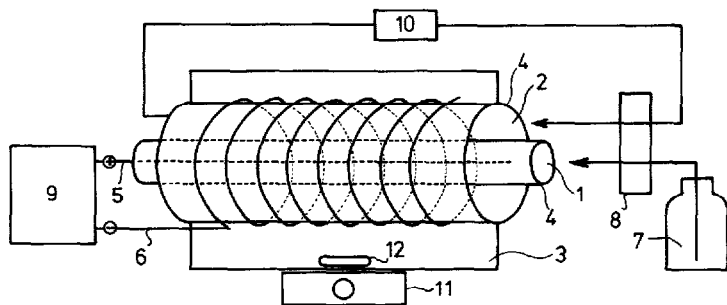


Fig. 1. Schematic diagram of electro dialysis system. 1 = Anode electrolyte solution channel; 2 = sample channel; 3 = cathode electrolyte solution; 4 = anion-selective membrane tube; 5 = anode; 6 = cathode; 7 = anode electrolyte solution; 8 = two-channel peristaltic pump; 9 = electric source; 10 = relative conductivity monitor; 11 = magnetic stirrer; 12 = stirring bar.

electrodes were connected to the source to start the electro dialysis. The relative conductivity was monitored throughout. After the dialysis, the neutralized sample was removed from the apparatus for analysis.

RESULTS AND DISCUSSION

The electro dialysis conditions were optimized using a 0.5 mol/l sulphuric acid test solution spiked with 200 ng/ml of magnesium(II) and 200 ng/ml of calcium(II). During the dialysis, sulphate ions move from the sample solution through the anion-selective membrane into the anode electrolyte solution. At the same time, hydroxide ions move from the cathode electrolyte solution into the sample solution and neutralize the sample. The outer membrane prevents the analyte metal ions from penetrating into the cathode electrolyte solution. The electro dialysis was stopped when the relative conductivity decreased to the level of 10–12%. The time required was at least *ca.* 10 min. Further dialysis should be avoided, because gradual penetration of the analyte ions from the sample to the cathode electrolyte solution was apt to occur.

Using this procedure, the determination of magnesium(II) and calcium(II) in strongly acidic solutions by ion chromatography was achieved without any loss of the analyte ions (Table I). The detection limits were 7.8 and 25 ng/ml and the upper limits of the linear response were 2 and 5 $\mu\text{g/ml}$ for magnesium(II) and calcium(II), respectively.

TABLE I

DETERMINATION OF MAGNESIUM AND CALCIUM IN STRONGLY ACIDIC SOLUTIONS

Sample ^a	Magnesium			Calcium		
	Added (ng/ml)	Found ^{b,c} (ng/ml)	Recovery (%)	Added (ng/ml)	Found ^{b,c} (ng/ml)	Recovery (%)
0.5 mol/l H ₂ SO ₄	0	N.D. ^d	—	0	28 ± 4	—
	100	98 ± 3	98.0	100	132 ± 3	104
	200	200 ± 2	100	200	242 ± 8	107
1.0 mol/l HNO ₃	0	N.D. ^d	—	0	55 ± 2	—
	100	102 ± 2	102	100	146 ± 3	91.0
	200	190 ± 3	95.0	200	244 ± 6	94.5

^a Commercially available acid diluted with deionized water.

^b Retention times: magnesium 6.83 min, calcium 12.9 min.

^c Mean ± average deviation, 3 results.

^d N.D. = Not detected.

The proposed method is applicable to the determination of trace cations in strongly acidic solutions such as an acid-digested sample. Moreover, it can readily be extended to on-line instrumentation and also to the determination of anions in strongly basic solutions by using a similar system with cation-selective membrane tubes, on which our further work is now focusing in progress.

ACKNOWLEDGEMENTS

The authors acknowledge Tosoh for providing the anion-selective membrane tubes. This work was partially supported by a Grant-in-Aid for Scientific Research, No. 02453034, from the Ministry of Education, Science and Culture of Japan.

REFERENCE

- 1 J. M. Pettersen, H. G. Johnsen and W. Lund, *Talanta*, 35 (1988) 245.