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Short communication

Cation analysis on a new poly(butadiene–maleic acid)-based column

Markus W. Läubli*, Barbara Kampus

Metrohm Ltd., CH-9101 Herisau, Switzerland

Abstract

The use of poly(butadiene–maleic acid)-coated silica for the determination of monovalent and divalent cations is well accepted in ion chromatography. The new Metrosep Cation 1-2 column based on this type of material extends the use of such materials to a broad range of amines due to its improved stability against organic solvents. Sample preparation was performed by diluting the sample in eluent or at least millimolar nitric acid.

1. Introduction

Since its introduction in 1989 by Schomburg [1] the poly(butadiene–maleic acid)-coated silica found a wide range of applications in ion chromatography (IC) [2,3]. This material showed a relatively poor stability against organic solvents. The use of eluents containing more than 5% organic solvents led to a loss of capacity and resolution within a short time. Therefore, the use of eluents containing such organics has been limited. The new Metrosep Cation 1-2 column (Metrohm, Herisau, Switzerland) is based on the same type of ion exchanger, but with much improved stability against organics. This improvement could be reached by using a different manufacturing procedure. This type of material may be washed with pure acetone without any change in separation performance. Due to the carboxylic groups alcohols should be avoided as eluent modifiers. Therefore, the direct determination of different basic components (amines, ethanolamines, etc.) is possible by using eluents with organic modifier.

2. Experimental

All measurements were performed on an IC instrument comprising a 709 IC pump, 690 ion chromatograph (both Metrohm). Data acquisition took place on a 714 IC Metrodata integration system (Metrohm). All chemicals used were purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany) and used without further purification.

Eluents were prepared with freshly deionized water and the respective amounts of components as mentioned in the figure legends. Eluents were degassed for about 2 min under vacuum.

Sample solutions were prepared in 2 mmol/l nitric acid or eluent except in case of the pH dependence measurements.

* Corresponding author.

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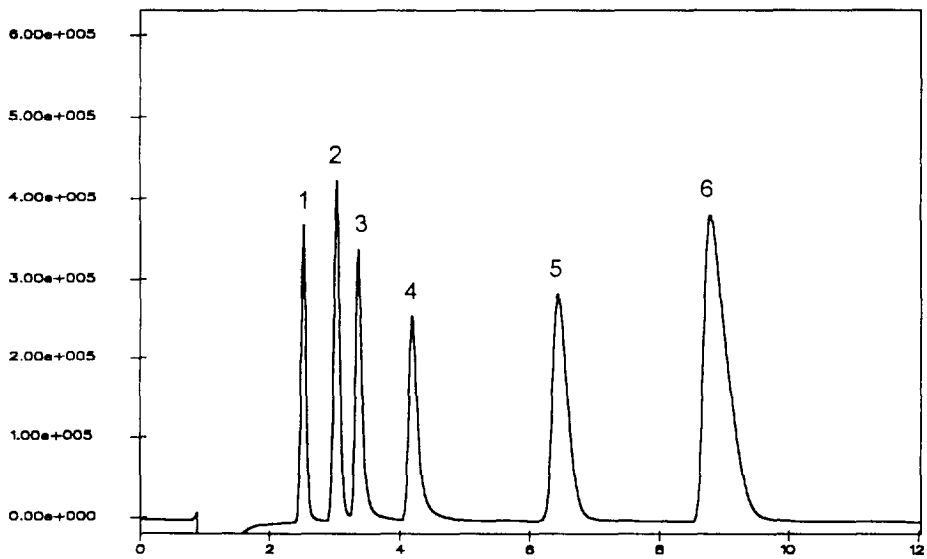

Fig. 1. Determination of alkali and alkaline earth metal cations. Eluent: 4 mmol/l tartaric acid–1 mmol/l dipicolinic acid. Peaks: 1 = lithium (1 ppm); 2 = sodium (5 ppm); 3 = ammonium (5 ppm); 4 = potassium (10 ppm); 5 = calcium (10 ppm); 6 = magnesium (10 ppm).

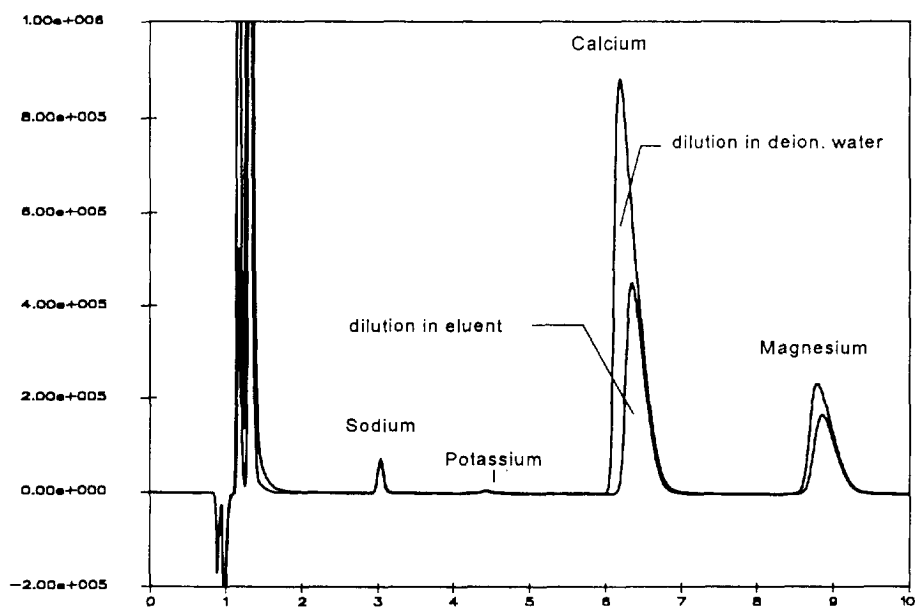

Fig. 2. Influence of sample acidification of drinking water. Drinking water was 1:10 diluted with deionized water or eluent, respectively. Eluent: 4 mmol/l tartaric acid–1 mmol/l dipicolinic acid.

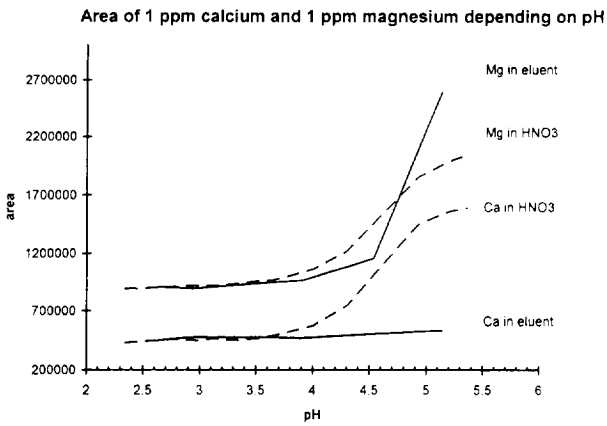

Fig. 3. Influence of sample pH on peak area and height. Ca^{2+} and Mg^{2+} in HNO_3: the standard solutions were prepared in the appropriate concentration of HNO_3 to reach the respective pH value. Ca^{2+} and Mg^{2+} in eluent: the standard solutions were prepared in eluent and adjusted to the respective pH with 2 *M* NaOH.

3. Results and discussion

3.1. Alkali and alkaline earth metal

The Metrosep Cation 1-2 column is packed with a weak cation exchanger that was based on spherical silica gel coated with poly(butadiene–maleic) acid groups. The main application is the determination of alkali and alkaline earth metal within a single isocratic run.

Fig. 1 presents the separation of lithium, sodium, ammonium, potassium, calcium and magnesium within 10 min, using 4 mmol/l tartaric acid–1 mmol/l dipicolinic acid as eluent.

Dipicolinic acid acts as complexing agent for heavy metals and calcium. As a result, the heavy metals are eluted with the front peak and calcium is moved in front of the magnesium peak thus improving the separation of the divalent cations.

3.2. Sample pretreatment

Cation analysis requires a correct sample pretreatment to get reproducible results. Fig. 2 presents two injections of drinking water diluted with either deionized water or eluent. The area of the divalent cation depends on the sample pH.

As Fig. 2 shows, the calcium peak is 2.3 and the magnesium peak 1.5 times larger than the peaks of the acidified sample.

Reproducible results were obtained when stan-

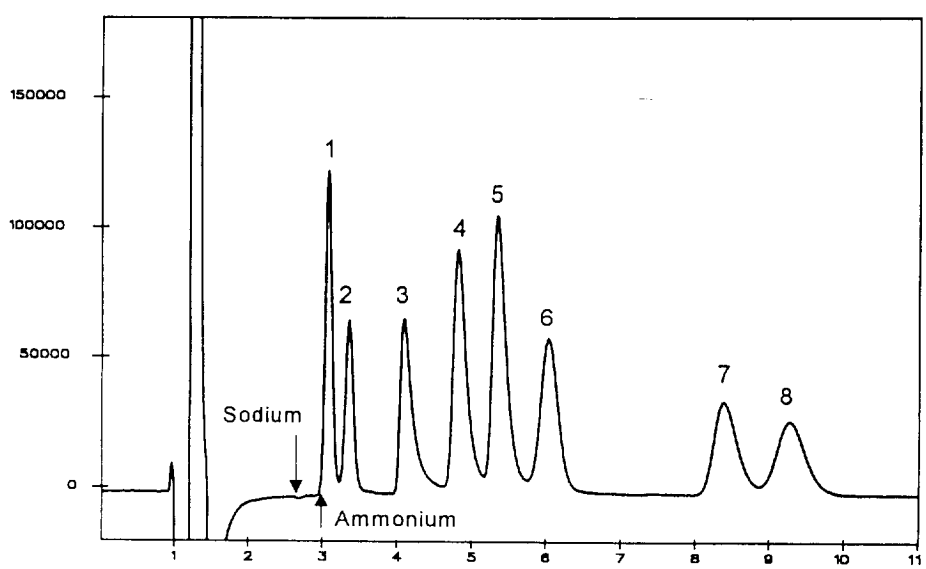

Fig. 4. Separation of organic amino compounds. Eluent: 8 mmol/l tartaric acid–10% acetone. Peaks: 1 = ethanolamine (5 ppm); 2 = diethanolamine (5 ppm); 3 = dimethylamine (5 ppm); 4 = diethylamine (10 ppm); 5 = trimethylamine (10 ppm); 6 = cyclohexylamine (10 ppm); 7 = triethylamine (10 ppm); 8 = dibutylamine (10 ppm).

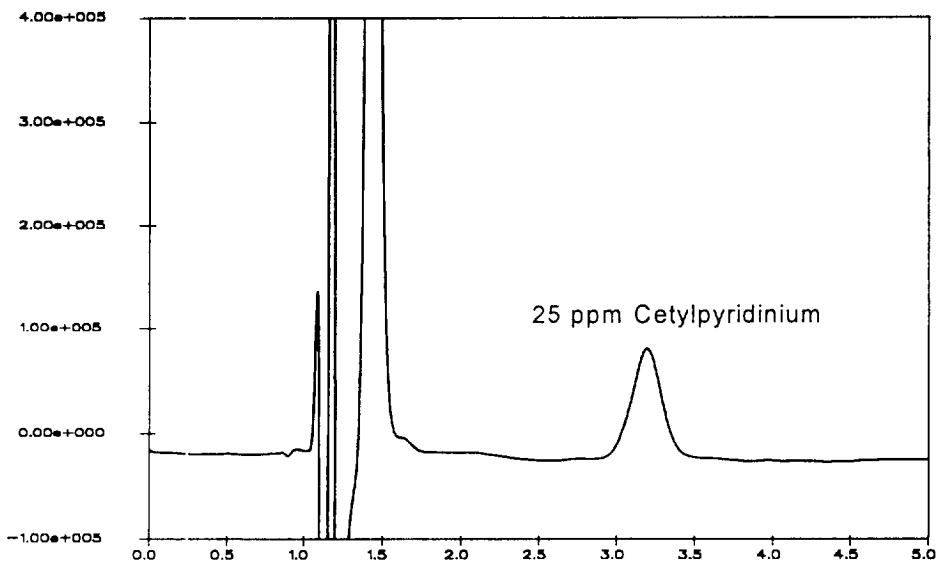

Fig. 5. Determination of cetylpyridinium chloride in throat tablets. Eluent: 10 mmol/l tartaric acid–1 mmol/l dipicolinic acid–2 mmol/l HNO_3–60% acetone.

dard and sample were prepared in eluent or nitric acid; thereby the pH should reach a value between 2.5 and 3.5 (see Fig. 3).

The influence of this pretreatment on area and height of the monovalent cations is very small. The reason for this pH dependence is not yet clear and has to be investigated further. The same effect can be recognized on other types of cation exchangers (e.g. silica-based strong acid cation exchangers) [4].

3.3. Organic modifiers

The Metrosep Cation 1-2 column can be used with a variety of eluents; especially the wide range of organic modifier concentrations makes it possible to analyse organic amines by direct conductivity detection.

Fig. 4 presents the separation of ethanolamines, alkylamines and cyclohexylamine.

Fig. 5 presents the determination of cetylpyridinium chloride (hexadecylpyridinium chloride) in throat tablets. After dissolving the tablet in eluent followed by filtration (0.25 μm), the solution could be injected directly without further sample preparation.

Under these conditions, the component can be analyzed without interference of other organic compounds.

References

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[2] M.W. Läubli, in P.A. Williams (Editor), *Recent Development in Ion Exchange*, 1990, pp. 31–39.
[3] L.M. Nair, R. Saari-Nordhaus and J.M. Anderson, Jr., *J. Chromatogr.*, 640 (1993) 41–48.
[4] M.W. Läubli, unpublished results.