

Note

Simultaneous determination of sodium, ammonium, potassium, rubidium, caesium, magnesium and calcium ions by a conventional high-performance liquid chromatographic system with a common ion-exchange column

MOTOICHI MIYAZAKI*, KAZUICHI HAYAKAWA and SEUNG-GI CHOI*

Faculty of Pharmaceutical Sciences, Kanazawa University, 13-1, Takara-machi, Kanazawa, 920 (Japan)

(First received February 24th, 1984; revised manuscript received January 2nd, 1985)

Although ion chromatography (IC)¹ has been widely developed in the field of analyses of inorganic ions, simultaneous analyses have not been achieved for ammonium, alkali and alkaline-earth ions. Different conditions involving use of either two analytical columns or two eluent systems were required for this purpose². Meanwhile, indirect photometric chromatography (IPC)³ seems to offer very interesting and suggestive information, since it could be performed on a conventional apparatus for high-performance liquid chromatography (HPLC). However, only a few reports have hitherto been published on the determination of inorganic cations. Therefore, the authors have decided to explore the possibility of applying a conventional HPLC system with photometric detection to the determination of inorganic ions, and have found that use of a commercial HPLC apparatus and common ion exchangers of low capacity will suffice for IC⁴. In this paper, the authors have described the simultaneous determination of sodium, ammonium, potassium, rubidium, caesium, magnesium and calcium ions by using the method below proposed.

EXPERIMENTAL

Apparatus and reagent

The HPLC system consisted of a pump (Jasco TRIROTAR-III), a sample injector, a separating column (DuPont Zipax SAX, 25 cm × 4.6 mm I.D.), an ultraviolet (UV) photometric detector (Jasco UVIDEC-100-III) and a recorder (Jasco RC-225).

All the chemicals used were of analytical reagent grade. All cation standard solutions were prepared with sulphates (except potassium and calcium chlorides). The eluent (copper sulphate solution) was prepared in distilled deionized water and filtered through a 0.40- μ m membrane before use.

HPLC conditions

Typical conditions were: eluent, $2.5 \cdot 10^{-3}$ M copper sulphate; flow-rate, 1

* Present address: College of Pharmacy, Kyung Hee University, Seoul, 131, Republic of Korea.

ml/min; column temperature, ambient (21–25°C); detection wavelength, 220 nm (0.04 a.u.f.s.); sample volume, 100 μ l.

RESULTS AND DISCUSSION

The relationship between the eluent concentration and the capacity ratio of each ion is shown in Fig. 1. The increase of eluent concentration results in the reduction of capacity ratio with different slopes for the mono- and divalent ions. Separation of the seven ions was incomplete when the eluent concentration was above $2.5 \cdot 10^{-3}$ M. It was decided to adjust the eluent concentration to $2.5 \cdot 10^{-3}$ M to give acceptable resolution and retention time. The Zipax SCX used in this work was a low-capacity exchanger. All other resins with high ion-exchange capacities could not be used. Moreover, it is generally observed that the elution of large-size ions from a pellicular-type silica-based resin column is faster than from a styrene-divinylbenzene copolymer resin column with the same ion-exchange capacity. These advantages of Zipax SCX should permit the simultaneous determination of the seven ions.

The capacity ratios decreased with increase in either column temperature or flow-rate, but, in both cases, the separation of ammonium ions from potassium ions became worse. The resolution (R_s) was 1.25 under the typical HPLC conditions cited.

The UV absorption maximum of the eluent was at 205 nm. Even though deep troughs were observed at wavelengths below 220 nm, the baseline was unstable with the wide noise level, because the transmittance was less than 10%. At wavelengths above 220 nm, a stable baseline was observed; however, trough depth decreased.

A typical chromatogram obtained under the conditions described above is

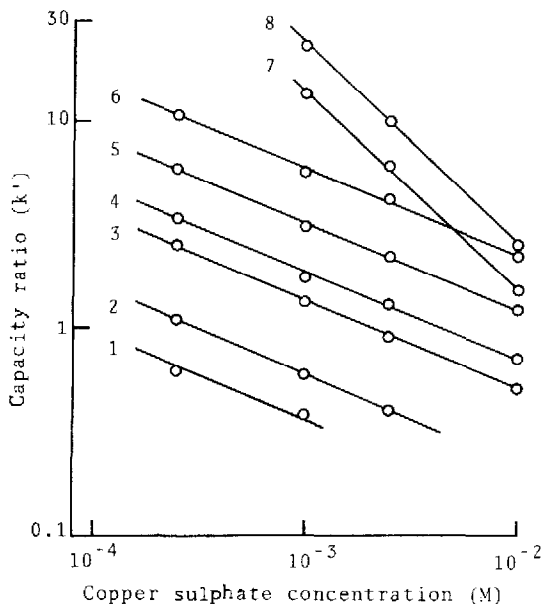


Fig. 1. Relationship between capacity ratio and eluent concentration. The other experimental conditions are the same as in the text. Test cations: 1 = Li⁺; 2 = Na⁺; 3 = NH₄⁺; 5 = Rb⁺; 6 = Cs⁺; 7 = Mg²⁺; 8 = Ca²⁺.

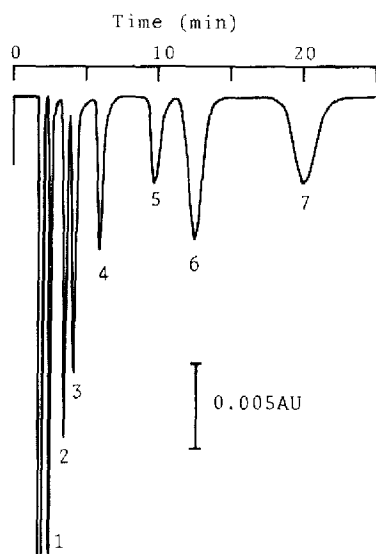


Fig. 2. Chromatogram of seven cations. The experimental conditions are the same as in the text. Test cations (each $4 \cdot 10^{-4} M$): 1 = Na^+ ; 2 = NH_4^+ ; 3 = K^+ ; 4 = Rb^+ ; 5 = Cs^+ ; 6 = Mg^{2+} ; 7 = Ca^{2+} .

shown in Fig. 2. The seven ions were separately determined within 25 min. Linear calibration curves for the seven ions were obtained in the range from $1 \cdot 10^{-5} M$ to $1 \cdot 10^{-2} M$ by either the trough-depth or trough-area method under the typical conditions specified. Detection limits (signal-to-noise ratio, 2.5) were as follows: sodium, 30 ppb; ammonium, 70 ppb; potassium, 300 ppb; magnesium, 90 ppb; and calcium, 300 ppb.

Divalent metal ions, namely, cadmium, zinc, manganese, nickel and cobalt, have retention times similar to that of magnesium at room temperature. It was possible to separate these metal ions from magnesium ion by increasing the column temperature or by decreasing the flow-rate. Some organic compounds that are UV absorbing or ionic may also affect the stability of the baseline. If large amounts of these compounds are present in the sample, they should be eliminated by pretreatment.

To investigate the possibilities of this method, the determination of inorganic cations in tap water (containing spring water) was attempted by the proposed

TABLE I

DETERMINATION OF INTEREST IONS (ppm) IN TAP WATER SAMPLE

Mean value \pm standard deviation ($n = 5$).

Ion	Proposed method	Flame photometry	AAS*	EDTA titration
Sodium	14.3 ± 0.26	14.8 ± 0.05		
Potassium	3.3 ± 0.16	3.4 ± 0.12		
Magnesium	6.4 ± 0.11		6.8 ± 0.04	6.7 ± 0.12
Calcium	17.0 ± 0.08		16.6 ± 0.02	18.0 ± 0.03

* Atomic-absorption spectrophotometry.

method, and the results were compared with those of flame photometry, atomic-absorption spectrophotometry and titration with ethylenediaminetetraacetate. Sodium, potassium, magnesium and calcium ions were determined in the sample. The results summarized in Table I indicate that the concentrations as determined by the proposed method were in good agreement with those of the other analytical methods cited above.

REFERENCES

- 1 H. Small, T. S. Stevens and W. C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 2 J. S. Fritz, D. T. Gjerdc and C. Pohlandt, *Ion Chromatography*, Huthing, New York, 1982.
- 3 H. Small and T. E. Miller, Jr., *Anal. Chem.*, 54 (1982) 462.
- 4 K. Hayakawa, H. Hiraki and M. Miyazaki, *Bunseki Kagaku (Jap. Anal.)*, 32 (1983) 503.