

Simultaneous Determination of Alkaline Earth Metal Ions by a Conventional High Performance Liquid Chromatographic System

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Abstract □ A simultaneous determination method of alkaline earth metals was attempted with the conventional high performance liquid chromatographic system. Four cations, namely, magnesium, calcium, strontium and barium ion, were injected directly as aqueous solution into an eluent containing copper chloride solution and were successfully separated and determined on a separating column (Zipax SCX, 4, 6 mm i.d. \times 25 cm length, Du Pont, USA) by using a variable wavelength UV detector. The linear calibration curves were obtained in the range from 1.0×10^{-4} M to 5.0×10^{-4} M and the correlation coefficient of the calibration curve for each metal was in the range of 0.9952–0.9996. The proposed method was applied to the determination of magnesium and calcium in tap water.

Alkaline earth metals were determined with the conventional high performance liquid chromatographic system.

Keyword □ Simultaneous determination, Alkaline earth metal, Indirect photometric chromatography, Light-absorbing eluent, Copper chloride, Conventional HPLC.

The separation and determination of alkaline earth metals have been of great interest in analytical chemistry, because these metals exist widely in nature and play momentous roles in the field of biology.

Atomic absorption spectrophotometry (AAS) must be a useful and sensitive analytical method of these metals, but are not available for their simultaneous determination. AAS is only usable for the individual metal.

Ion chromatography (IC) which was developed by H. Small *et al.* (1) in 1975, has been applied successfully for the analysis of inorganic cations as well as the determination of inorganic anions. Alkaline earth metal ions were separated on a cation-exchange column of low capacity without a suppressor column and detected with a conductivity detector (2-4). However, many defects which are belonged in IC, are the expensiveness of apparatus, the complexity of IC instrumentation, the periodic regeneration of suppressor column and the decline of detective sensitivity on the non-suppressor system. A liquid chromatographic-spectrophotometric system which was introduced by M. Zenki (5), developed to separate alkaline earth metals.

In 1982, indirect photometric chromatography (IPC) (6, 7) was designed by H. Small *et al.* The key-point of this method is that the use of light-absorbing eluent which has a dual role, namely, selectively displacing the sample ions from the separating column and revealing the sample ions in the eluent. The light-absorbing ion enables sample ions to appear as troughs in the baseline absorbance as transparent sample ions substitute for the light-absorbing displacing ions.

Although the specially supplied resin had been used on IPC method, we (8, 9) tried to utilize a simple, convenient apparatus and a common ion-exchange resin which were available for conventional high performance liquid chromatographic (HPLC) system for the microanalysis of cations and anions, individually. The results that are not inferior to efficiency of IC method were obtained by our method. In this paper, the simultaneous determination of alkaline earth metal ions was attempted and this method was applied to the analysis of tap water.

EXPERIMENTAL METHODS

Apparatus and Reagent

The HPLC system was consisted of an eluent

reservoir, a pump (Jasco TRIROTAR-III), a sample injector, a separating column (4, 6 mm i.d. \times 25 cm length stainless steel), a photometric detector (Jasco UVIDEK-100-III), a recorder (Jasco RC-225) and an integrator (Shimadzu C-R1A CHROMATOPAC) for the calculation of trough-area.

A Hitachi 170-10 AAS for alkaline earth metals were used in the practical tap water analysis.

A Zipax SCX (Du Pont, USA) resin whose average particle size was about 30 μ m was slurry-packed into a stainless steel column. The resin was conditioned with a sufficient amount of eluent solution before use. All chemicals in this work were of the analytical reagent grade. All standard solution of the cations were prepared by direct weighing and dilution of the chlorides. Eluent was made in distilled-deionized water and filtered through a 0,40 μ m membrane filter before use. Distilled-deionized water was used throughout.

HPLC Conditions

Typical HPLC conditions giving the best compromise between efficiency, speed and sensitivity of separation were: eluent, $1,0 \times 10^{-2}$ M copper chloride; flow rate, 1,0 ml/min; column temperature, ambient; detector, a variable ultraviolet monitor at a wavelength of 230 nm with range of 0,04 Aups; sample volume, 100 μ l. A typical chromatogram of alkaline earth metal ions under

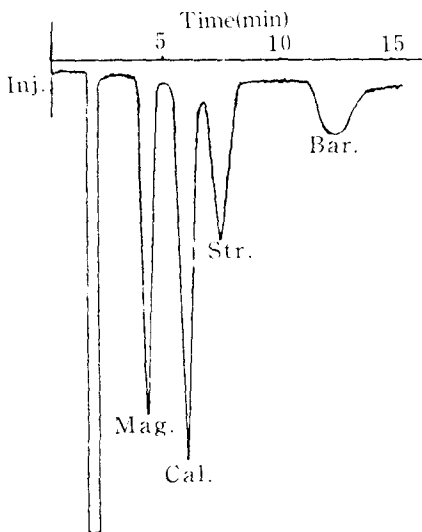


Fig.1. Typical chromatogram of alkaline earth metal ions.

Experimental conditions are same to those of experimental section.

Sample: 100 μ l mixture containing $5,0 \times 10^{-4}$ M of each ion.

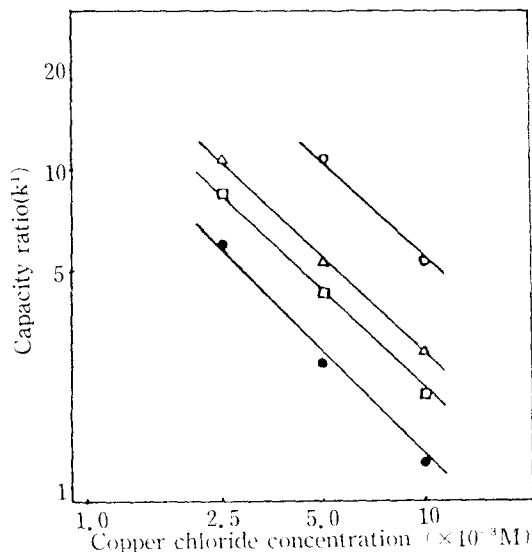


Fig.2. Comparison of capacity ratio on various eluent concentration.

Other experimental conditions are same to those of experimental section.

Ba(\circ), Sr(Δ), Ca(\square), Mg(\bullet).

the above-mentioned HPLC conditions is shown in Fig.1. Four cations could be determined with 15 min.

RESULTS AND DISCUSSION

Effect of Resin and Column-length

The elution time of ion, generally, becomes too late when the ion-exchange capacity is voluminous. Therefore, the Zipax SCX, a low-capacity exchanger (about 0,1 meq/g) was selected in this work. All other resin experimented which were commercially available couldn't be used because of their high ion-exchange capacity. Being incomplete on the 12 cm length column, the separation of calcium and strontium was enough to analyze on the 25 cm length column. The size of the column used in this work was 4,6 mm i.d. \times 25 cm length.

Effect of Eluent Concentration

The relationship between the eluent concentration and the capacity ratio of each ion is shown in Fig.2 and the effect of eluent concentration on the slopes is parallel. The increase of the concentration of copper chloride results in the reduction of capacity ratio, but a lowering of the sensitivity. In case of high concentration, above $1,0 \times 10^{-2}$ M, magnesium was duplicated in initial eluent trough. The broadening of barium-trough appeared in low concentration, below $5,0 \times 10^{-3}$ M. The eluent conce

Table I. Effect of column temperature.

Temperature (°C)	Capacity ratio		Resolution function
	Calcium	Strontium	
20	2.2	3.0	1.8
60	2.0	2.5	1.1

Other experimental conditions are same to those of experimental section

stration was decided to be 1.0×10^{-2} M copper chloride with acceptable resolution and retention time.

Influence of Column Temperature and Flow-rate

Generally speaking, an ascent of column temperature in HPLC increases the resolution efficiency of interest substance and sharpens the elution peak. Of course, the capacity ratios became also smaller and the trough-depth were improved in our experiment, but it became insufficient to separate calcium and strontium according to the rise of temperature, and the baseline on the chromatogram was unstable. Table I shows the effect of column temperature in this method.

Elution time also quickened according to the fastness of flow-rate, however, it was not enough to be dropped off in efficiency of resolution of calcium and strontium ions. The resolution function was 1.02 in case that flow-rate was 2.0 ml/min. Therefore, it is sufficient for this cations to be determined within 10 min in spite of some fluctuation of trough-depth.

Selection of Detection Wavelength

The absorption maximum and molar absorptivity (ϵ) in ultraviolet spectrum of eluent, copper chloride solution, was 211 nm ($\epsilon = 1.0 \times 10^3$). Even though the sharp troughs appeared at below

Table II. Regression equations of calibration curves for alkaline earth metal ions.

Ion	Regression equation	Correlation coefficient
Magnesium	$y = 0.1368x$	0.9989
Calcium	$y = 0.1448x$	0.9996
Strontium	$y = 0.0669x$	0.9987
Barium	$y = 0.0375x$	0.9952

Experimental conditions are same to those of experimental section except the detector range, 0.02 Afs. Range of sample concentration; 0.5×10^{-4} ~ 5.0×10^{-4} M of each ion. Y: peak height (cm) \times ; metal concentration

Table III. Detection limits of interest ions.

Ion	Detection limit (ppb, S/N=2.5)
Magnesium	73
Calcium	80
Strontium	430
Barium	137*

These data were determined under experimental conditions similar to typical those except detection wavelength, 235 nm and detector range, 0.005 Afs. * ppm

225 nm, this chromatogram was unstable, variable the settled baseline were obtained, however, trough-depth was reduced remarkably. The adequate, selected wavelength in our work was 230 nm.

Calibration Curve and Detection Limit

The linear calibration curves of four cations were gained in the range from 1.0×10^{-4} M to 5.0×10^{-4} M with either of the trough-depth or trough-area method under the typical HPLC conditions except detector range, 0.02 Afs. All the working curves obtained showed good straight line. Regression lines obtained and values or correlation coefficient are summarized in Table II.

Detection limits for four cations, determined under the typical HPLC conditions except the detection wavelength, 235 nm and detector range, 0.005 Afs, are given in Table III. It was calculated as 2.5 times short-term noise. All interest ions except barium were detected in 0.1 ppm level under the simultaneous determination.

Interference Metal Ions and Their Elimination

Divalent metal ions, namely, cadmium, zinc, manganese, nickel and cobalt ion, have similar

Table IV. Recovery % of the three cations from composite sample.

Ion	Taken (μ g)	Found (μ g)	Recovery (%)
Magnesium	0.48	0.46 ± 0.012	95.83
Calcium	0.80	0.78 ± 0.025	97.50
Strontium	1.76	1.68 ± 0.067	95.45

Coexistent ions(mg): Cd(II) 0.45, Zn(II) 0.26, Mn(II) 0.22, Ni(II) 0.23 and Co(II) 0.24

Experimental conditions are the same as those of experimental section except the detector range, 0.02 Afs.

Table V. Determination of interest ions in tap water.

Ion	unit; ppm		
	Proposed method	AAS method	EDTA-titration
Magnesium	7.4±0.09	7.8±0.03	7.5±0.01
Calcium	19.5±0.14	18.9±0.02	19.3±0.02

retention time to that of magnesium at room temperature. It was within the realms of possibility to separate magnesium and each ion in case of the climbing of column temperature or the retardation of the flow-rate. However, if the concentration of other ion would be leveled with one-fifth of magnesium ion, the presence of disturbing ion couldn't be acknowledged in the chromatogram. Data were shown in Table IV. Some of organic materials should be eliminated with pretreatment in practical work, because they interfere the stabilization of baseline on chromatogram.

Application

For the availability of this method, the determination of tap water (containing spring water) was attempted with this present method, AAS method and EDTA titration method. The results obtained were summarized in Table V. Data indicate that concentrations determined by present method were in good agreement with those from other analysis method.

CONCLUSION

This present method permitted the simultaneous determination of 0, 1 ppm levels of alkaline earth metal ions in aquatic sample without receiving serious interference from foreign ions. This method is suitable for a routine analysis owing to its simplicity and accuracy, and doesn't require so expensive apparatus and special skillfulness.

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