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ION CHROMATOGRAPHIC DETERMINATION OF Mg^{2+} AND Ca^{2+} IONS

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Хилле АЛЛЕМАНН, Яан ПЕНЧУК. ИОНОХРОМАТОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАГНИЙ- И КАЛЬЦИЙ-ИОНОВ

Ion chromatography (IC) is a very powerful, effective and selective method for the determination of cations [1]. For this purpose the single and dual-column methods are used [1–3]. The best results are achieved by the single-column method with a conductivity detector [1, 3].

The aim of the present work was the use of the single-column method with a conductivity detector for the determination of Mg^{2+} and Ca^{2+} ions. The column was packed with lightly sulphonated polymer to achieve a low cation exchange capacity. The eluent used was a mixture of ethylenediamine (EDA) and hydrochloric acid which produces an eluting ethylenediammonium cation. The cation exchange mechanism was described by the following equation:

$$2M^{y+}R_y + yE^{z+} \rightleftarrows yE^{2+}R_2 + 2M^{y+}$$

where M^{y+} represents the sample metal ion, E^{2+} represents the eluent (EDA) cation, R is the solid exchanger, and the subscript on R represents the number of exchange sites of the resin.

Experimental

The chromatographic instrument was equipped with a HPP5001 high pressure pump, injector with 10 µl sample loop, separator column (3×150 mm) packed with KATIEKS-S sorbent (ECOS, Estonia) with 10 µm particle size, JD-1 conductivity detector, and TZ-4620 recorder. It maintained an eluent flow rate of 1.5 ml/min and operated at a chart speed of 1.5 cm/min.

Aqueous solutions of eluents were made of EDA, redistilled to remove moisture, and hydrochloric acid, using bidistillate. All the reagents used were of analytical grade. Mg^{2+} and Ca^{2+} standard solutions were made of $MgSO_4 \cdot 7H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$, respectively, using bidistillate. The concentration of cations in stock solutions was determined titrimetrically.

Results and Discussion

EDA concentration was varied from 4.0 to 5.0 mM to investigate the relationship between the retention times of the cations and EDA concentration, on the one hand, and between the separation criteria and EDA concentration, on the other hand. The concentration of hydrochloric acid, 8.0 mM, was constant. The results obtained indicate (Table 1) that the

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optimum concentration of EDA, which gives the highest peaks, is 4.2 mM. The average conductivity of eluent was 220 μS and the cell constant of detector at 20 °C was 7 cm^{-1}. The chromatogram of Ca and Mg ions is presented in Fig. 1.

Table 2 shows that the best (minimal) retention time for the cations is

Table 1

The relationship between the heights of peaks (mm) of Mg^{2+} and Ca^{2+} and EDA concentration (mM). Concentration of ions — 100 mg/l, of HCl — 8.0 mM

EDA concentration, mM	Heights of peaks, mm		EDA concentration, mM	Heights of peaks, mm	
	Mg^{2+}	Ca^{2+}		Mg^{2+}	Ca^{2+}
4.0	100	37	4.6	87	38
4.2	104	46	4.8	79	41
4.4	103	42	5.0	79	32

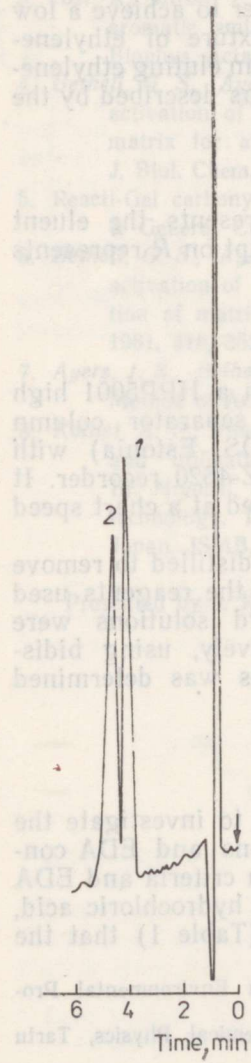

Fig. 1. The chromatogram of Ca and Mg ions. Concentration of ions, 100 mg/l; adjusted retention time of Mg(*1*), 3.8 min, of Ca(*2*), 4.4 min; eluent flow rate, 1.5 ml/min.

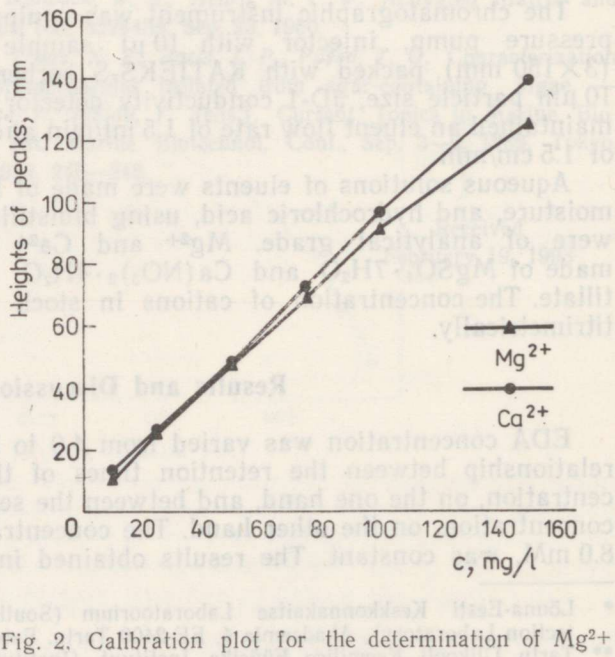

Fig. 2. Calibration plot for the determination of Mg^{2+} and Ca^{2+}.

Adjusted retention times (min) for Mg^{2+} and Ca^{2+} in relation to EDA concentration (mM). Concentration of HCl is constant (8.0 mM); concentration of Mg^{2+}, Ca^{2+} solution, 100 mg/l; $t_0 = 0.5$ min

EDA concentration, mM	Adjusted retention time, t_r', min		Number of theoretical plates N		Separation criteria R
	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	
4.0	4.0	6.4	1 600	910	1.8
4.2	3.9	4.5	1 600	890	1.8
4.4	4.1	4.7	1 700	960	2.0
4.6	4.3	4.9	1 800	1 000	1.8
4.8	4.4	5.1	1 900	1 100	2.0
5.0	4.6	5.2	2 100	1 200	1.9

achieved at the EDA concentration of 4.2 mM. Table 2 represents also the number of theoretical plates N and separation criteria R [4, pp. 11—18; 5, pp. 20—23].

For quantitative analysis it was necessary to determine the linearity of the Mg^{2+} and Ca^{2+} calibration plot. It was found that the peak height of Mg^{2+} and Ca^{2+} is linearly dependent on the ion concentration in the range of 10—100 mg/l (Fig. 2).

Also the reproducibility of the method used was determined at the concentration 50 mg/l [6, pp. 125—127]. For Mg^{2+} the measured average concentration was 48 mg/l (five measurements) and standard deviation of arithmetic mean was 0.59 mg/l. For Ca^{2+} they were 48 mg/l (five measurements) and 0.89 mg/l, respectively.

Conclusions

1. The optimum eluent concentration (4.2 mM) for the determination of Mg^{2+} and Ca^{2+} ions was estimated.
2. The influence of eluent concentration on the peak heights and retention times of Mg^{2+} and Ca^{2+} was studied.
3. The linear part of the Mg^{2+} and Ca^{2+} calibration plot from 10 to 100 mg/l was observed.
4. The reproducibility of the present method for Mg^{2+} and Ca^{2+} ions was calculated.

REFERENCES

1. *Sevenich, G. J., Fritz, J. S.* Addition of complexing agents in ion chromatography for separation of polyvalent metal ions. — Anal. Chem., 1983, **55**, 12—16.
2. *Small, H., Stevens, T. S., Bauman, W. C.* Novel ion exchange chromatographic method using conductimetric detection. — Anal. Chem., 1975, **47**, 1801—1809.
3. *Fritz, J. S., Gjerde, D. T., Becker, R. M.* Cation chromatography with a conductivity detector. — Anal. Chem., 1980, **52**, 1519—1522.
4. *Шпигун О. А., Золотов Ю. А.* Ионная хроматография и ее применение в анализе вод. Изд-во МГУ, Москва, 1990.
5. *Дейла З., Мацека К., Янака Я.* Жидкостная колоночная хроматография. Под ред. В. Г. Березкина. Мир, Москва, 1978.
6. *Васильев В. П.* Аналитическая химия, I. Гравиметрический метод анализа. Высшая школа, Москва, 1989.

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