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Determination of aluminium in natural waters by single-column ion chromatography with indirect UV detection

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Abstract

The selective, sensitive and rapid determination of Al was achieved using ion-exchange separation and indirect UV detection. A solution of Ce salt was used as the eluent. The parameters influencing the shape of the Al peak, the selectivity of Al separation and sensitivity of its determination were studied. The separation of Al on chemically modified and on silica gel-based dynamically coated sorbents was achieved. With direction injection the detection limit under the optimum conditions was 50 ng/ml. The time of analysis was about 6 min. The use of a simple preconcentration procedure permitted the detection limit to be decreased. Preconcentration of Al was performed on a complexing sorbent with iminodiacetate functional groups. The technique presented was applied to the determination of Al in natural and tap waters. The technique also provides the determination of alkaline earth metals along with Al.

1. Introduction

The determination of Al and alkali and alkaline earth metal cations is an important part of water quality control during the process of tap water purification. Significant concentrations of Al in tap water can appear because of the contamination of water sources by the waste waters from industrial plants or as a result of water treatment with Al-containing reagents at waterworks. The concentration of Al in natural waters varies from 0.01 to about 250 $\mu\text{g/ml}$, while the concentration of Al in tap water should not exceed 500 $\mu\text{g/ml}$ [1].

A spectrophotometric method is commonly used for the determination of Al in water, but is

time consuming and does not provide sufficient selectivity and sensitivity of analysis [2].

Usually the chromatographic determination of Al involves separation on a cation-exchange column with an eluent containing a complexing agent. Spectrophotometric detection with or without a colour-forming postcolumn reaction is used [3–10].

In this work, Al was determined by ion chromatography (IC) with indirect UV detection. A solution of a non-complexing trivalent Ce salt was used as the eluent. We consider this method to be the simplest and the most rapid for the determination of the cations in question [11,12]. It can be also conventionally used for the determination of alkaline earth metal cations. We attempted to widen the possibilities of the above method, using it for the determination of Al.

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2. Experimental

A Hewlett-Packard Model 1084A liquid chromatograph equipped with a UV detector with a fixed wavelength of 254 nm was used. The stainless-steel separation columns used were 50 × 3 mm I.D. with a surface-sulphonated cation exchanger and 150 × 3 mm I.D. with dynamically coated Separon C₁₈ sorbent (both from Elsiko, Moscow, Russian Federation). The dynamically coated column was prepared by passing a 0.01 mM solution of dodecylbenzenesulphonic acid (flow-rate 1 ml/min) through it for 1 h. A cartridge (30 × 3 mm I.D.) packed with laboratory-made sorbent containing iminodiacetate (IDA) functional groups (exchange capacity 0.1–0.5 mequiv./g) was used for the preconcentration of metal ions. Analytical-reagent-grade Mg, Ca, Sr, Ba, Cr, Ce, Pb, Al and Fe salts and methoxylamine hydrochloride were used for the preparation of eluent and standard solutions. Purified water was obtained using a Milli-Q apparatus (Millipore). Samples of tap and river waters were filtered through a 0.45- μ m filter before injection into the chromatograph.

3. Results and discussion

A sufficiently effective and rapid separation of alkaline earth metals was obtained on both columns with indirect UV detection. Fig. 1 shows the separation of four alkaline earth metal cations with a 1 mM solution of Ce(III) salt as eluent. The time of analysis did not exceed 5–7 min. It should be mentioned that a better selectivity of Ca and Sr separation was observed on the surface-sulphonated cation exchanger.

As the solution of Ce(III) does not possess any complexing ability, the order of elution of cations with this eluent is the same as with an acid-containing eluent. The singly charged cations are eluted first, then doubly charged and finally triply charged cations. This is why a more concentrated solution of Ce(III) is preferably used for the elution of Al, which is a strongly retained cation.

It was found that to obtain a well shaped peak of Al, the pH of eluent should be decreased to <3.

Fig. 2 shows the chromatogram obtained under the above conditions for alkaline earth

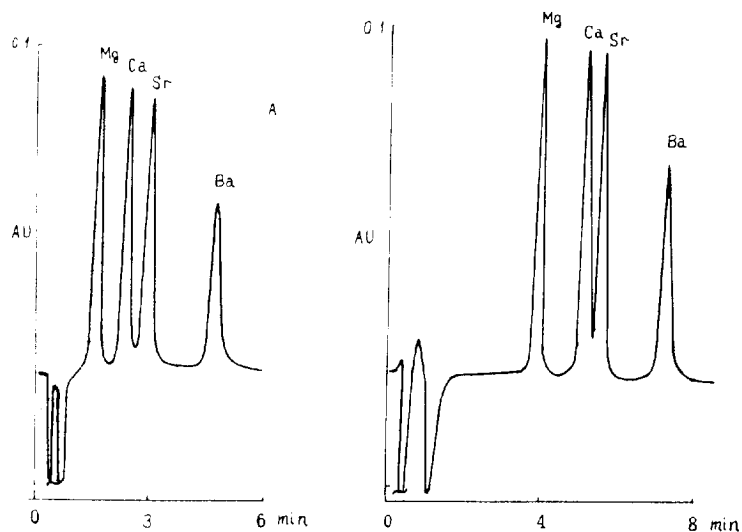


Fig. 1. Separation of alkaline earth metals with indirect UV detection. Column, (A) 50 × 3 mm I.D. with surface-sulphonated sorbent and (B) 150 × 3 mm I.D. with dynamically coated sorbent; eluent, 1 mM Ce(NO₃)₃ (pH 6.2); flow-rate, (A) 1 and (B) 0.8 ml/min; injection volume, 10 μ l; indirect UV detection at 254 nm. Concentrations of cations: Mg = 1.25, Ca = 2, Sr = 3, Ba = 4 μ g/ml.

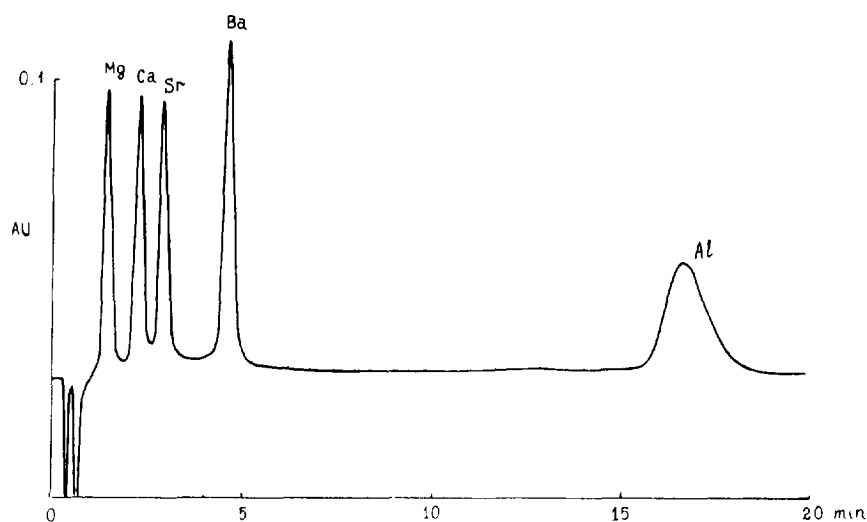


Fig. 2. Separation of alkaline earth metals and Al with indirect UV detection. Column, 50×3 mm I.D. with surface-sulphonated sorbent; eluent, $1 \text{ mM Ce(NO}_3)_3$ – 3 mM HNO_3 (pH 2.5); flow-rate, 1 ml/min . Concentrations of cations: Mg = 1.25 , Ca = 2 , Sr = 3 , Ba = 4 , Al = $5.4 \text{ } \mu\text{g/ml}$.

metal cations along with Al cation. To study the interference of other strongly retained cations on the determination of Al, we investigated the chromatographic behaviour of Ba, Pb, Cr(III) and Fe(III). Being eluted by a neutral eluent (pH 6.2), Al produces a wide peak, the area of which can hardly be calculated. Other strongly retained cations, such as Pb and Cr(III), demonstrate the same behaviour when a neutral eluent is used.

The separations of cations on the surface-sulphonated and the dynamically coated sorbents are presented in Fig. 3. The model mixture analysed contained Ba, Pb, Cr(III) and Fe(III). Fe(III) cation has a long retention time and does not appear on the chromatogram. It can be seen that Cr(III) cation interferes with the determination of Al under these conditions. For qualitative identification of Al and Cr cations when both are present in a sample, a 1 mM solution of methoxylamine hydrochloride and 1 mM nitric acid was added to the cerium(III) nitrate eluent (Fig. 4).

The addition of methoxylamine to the eluent results in a good resolution between Al and Cr. However, the efficiency of their separation is not

sufficient. A decrease in the nitric acid concentration in the eluent leads to an improvement in peak shape. Also, the retention time of Al is strongly decreased. This is demonstrated by the chromatogram in Fig. 5, where Al is eluted earlier than Mg. Cr(III) cation is eluted as an individual peak.

Although not the direct purpose of this study, it should be mentioned that the above chromatographic conditions can be used for the determination of Cr(III) cation and for rapid determination of Mg and Ca in the presence of a large amount of Al. For example, Fig. 6 shows the chromatogram of a technological solution obtained after desorption of Mg and Ca from a natural zeolite ion exchanger. Separation was performed with two different eluents, namely a solution of cerium(III) nitrate with addition of either methoxylamine or nitric acid. It can be seen that when methoxylamine is added to the eluent, the analysis time is five times shorter.

An eluent containing methoxylamine can be used only for a limited number of Al-containing samples, because interference from alkali metal cation peaks and the system peak is possible. This is why for their determination we used

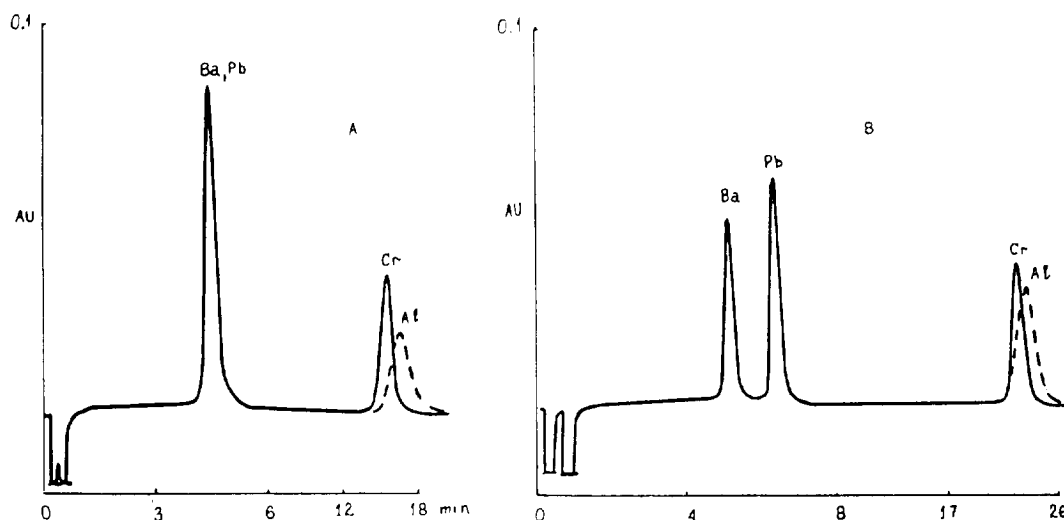


Fig. 3. Separation of Al and the strongly retained cations Ba, Pb and Cr(III). Column, (A) 50×3 mm I.D. with surface-sulphonated sorbent and (B) 150×3 mm I.D. with dynamically coated sorbent; eluent, 1 mM $\text{Ce}(\text{NO}_3)_3$ –3 mM HNO_3 (pH 2.5); indirect UV detection at 254 nm; line recorder rate decreased threefold after (A) 6 and (B) 8 min.

conditions, under which alkali metal cation and system peaks do not interfere with the determination of Al. These chromatographic conditions are as in Fig. 2.

The retention time of Al depends linearly on the concentration of the eluent. More concentrated solutions of cerium(III) nitrate were used as eluent to shorten the analysis time. Thus, 3

mM cerium(III) nitrate solution with a low pH of 2.5 was used for the determination of Al in water. Under these conditions the retention time of Al does not exceed 6 min. As tap and natural water analyses were the object of this work, the presence of noticeable amounts of Cr(III) was not observed and hence its interference was excluded.

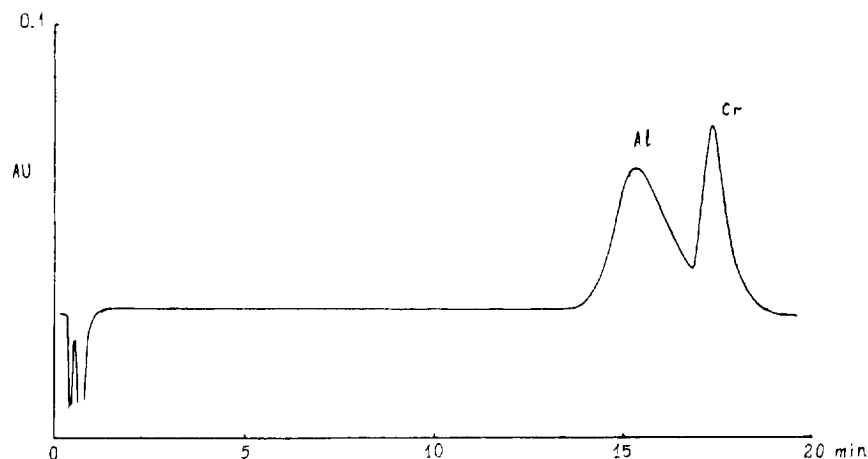


Fig. 4. Separation of Al and Cr(III) cations with a methoxylamine hydrochloride and nitric acid-containing eluent: 1 mM $\text{Ce}(\text{NO}_3)_3$ –1 mM methoxylamine hydrochloride–1 mM HNO_3 (pH 2.9). Other conditions as in Fig. 2.

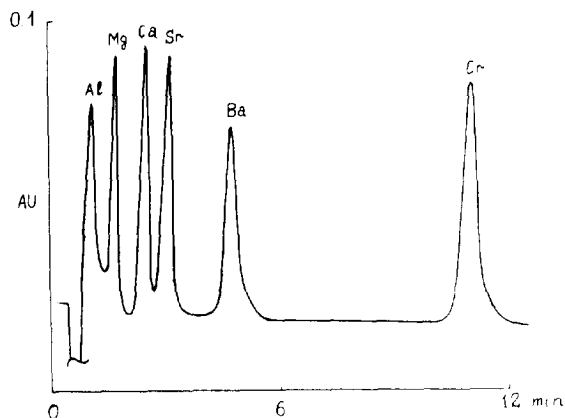


Fig. 5. Separation of cations with a methoxylamine hydrochloride-containing eluent: 1 mM $\text{Ce}(\text{NO}_3)_3$ -1 mM methoxylamine hydrochloride (pH 5.8). Other conditions as in Fig. 2.

A close linear dependence between this peak area and the concentration of Al was observed up to at least 100 $\mu\text{g}/\text{ml}$. The detection limit (calculated for $S/N=3$) obtained for Al, based on a 200- μl injection volume, was 50 ng/ml.

Preliminary sample mineralization was not applied, because the Al cations are not bound into strong complexes in tap water. The water sample was injected directly into the chromatograph. Fig. 7 shows a chromatogram for Moscow

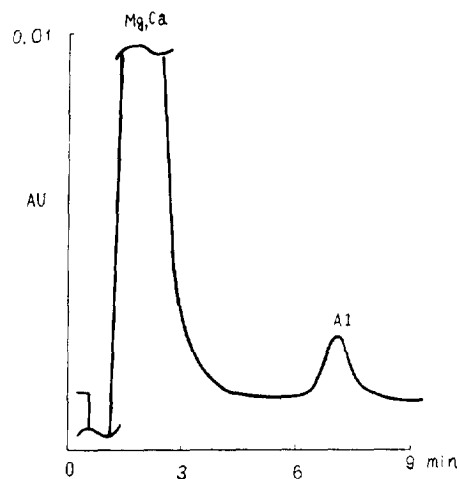


Fig. 7. Determination of Al in tap water by IC with direct sample injection. Column, 50 \times 3 mm I.D. with surface-sulphonated sorbent; eluent, 3 mM $\text{Ce}(\text{NO}_3)_3$ -3 mM HNO_3 (pH 2.5); flow-rate, 1 ml/min; indirect UV detection at 254 nm; attenuation, 2; injection volume, 100 μl .

tap water. After direct injection of 100 μl of sample this water was found to contain 270 ng/ml of Al.

The sensitivity of the determination under these conditions is not high enough for the analysis of waters with trace concentrations of Al. To increase the sensitivity of the method,

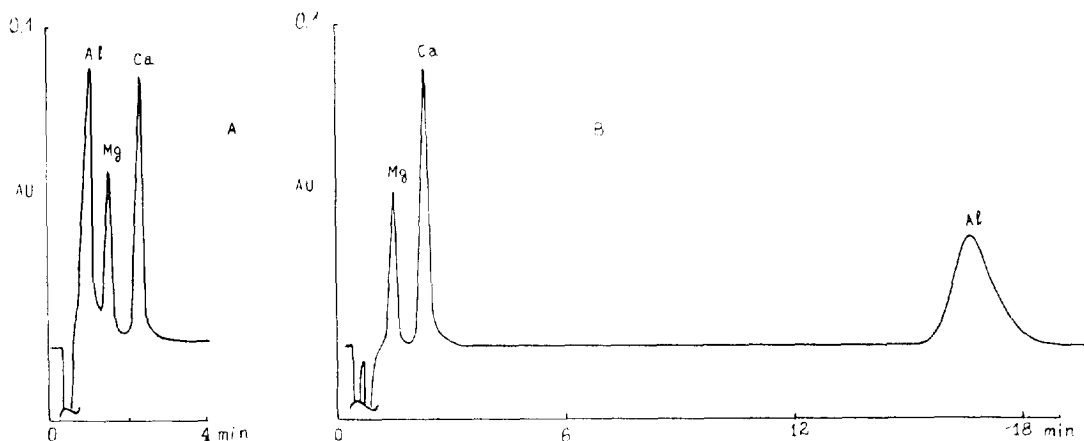


Fig. 6. Determination of Ca and Mg in the presence of Al. Column, 50 \times 3 mm I.D. with surface-sulphonated sorbent; eluent, (A) 1 mM $\text{Ce}(\text{NO}_3)_3$ -1 mM methoxylamine hydrochloride (pH 5.8) and (B) 1 mM $\text{Ce}(\text{NO}_3)_3$ -3 mM HNO_3 (pH 2.5); flow-rate, 1 ml/min; indirect UV detection at 254 nm.

preconcentration was applied. Preconcentration of Al was performed on a 30×4 mm I.D. cartridge packed with IDA sorbent, through which 20 ml of sample were passed. Mg and Ca cations were selectively washed out from the sorbent with 1 M ammonium acetate solution, then Al was washed out with 1 ml of 2 M nitric acid. In this case, the injection volume was only $10 \mu\text{l}$.

A chromatogram for Moskva river water obtained using preconcentration is shown in Fig. 8. The chromatogram shows that the preconcentration procedure permitted the same injection volume to be retained for the determination of Al as for the determination of Ca and Mg, although the concentration of Mg and Ca in river water was two orders of magnitude higher than the Al concentration. It is sufficient to change the attenuation in this case. Preconcentration also permits the concentration of the eluent to be increased and thus the time of analysis for Al to be shortened.

Table 1 gives the results for the determination of Al in Moscow tap water and in Moskva river water. It can be seen that the tap water is noticeably contaminated with Al after treatment at the waterworks.

To control the reliability of this technique, the same sample was analysed by an inductively

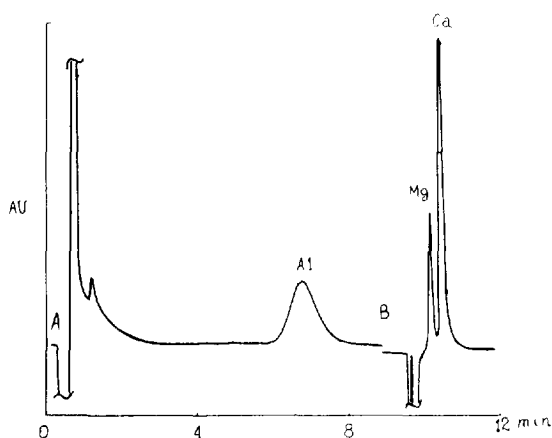


Fig. 8. Determination of Al, Mg and Ca in river water by IC. Eluent, 3 mM $\text{Ce}(\text{NO}_3)_3$ –3 mM HNO_3 (pH 2.5); attenuation, (A) 2 and (B) 6; injection volume, $10 \mu\text{l}$. Other conditions as in Fig. 7.

Table 1

Determination of Al, Mg and Ca in Moskva river water and in Moscow tap water by IC and ICP methods

Element	Concentration (mg/l)			
	River water		Drinking water	
	IC	ICP	IC	ICP
Al	0.08	0.07	0.27	0.28
Mg	15.5	15.1	14.7	15.0
Ca	62.4	61.7	60.2	59.8

coupled plasma (ICP) method. The comparison showed an adequate correlation between the results of the two methods (Table 1).

The suggested technique for the determination of Al with indirect UV detection is characterized by good reproducibility. The efficiency of separation and the retention times of the cations are virtually unchanged even after 300 sample injections.

4. Conclusions

The proposed IC technique for the determination of Al along with alkaline earth metal cations in natural and tap waters, based on a cation-exchange separation with indirect UV detection, has a detection limit of about 50 ng/ml and the Al peak response is linear up to 100 $\mu\text{g}/\text{ml}$. The results correlate well with those obtained by an ICP method. The suggested method provides a rapid, selective and sensitive determination of Al in multi-component mixtures of cations.

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