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Ion chromatographic determination of beryllium in rock and waste waters with a chelating sorbent and conductimetric detection

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Abstract

The sensitive separation of Be and other alkaline earth metals on a complexing sorbent with iminodiacetate (IDA) functional groups using indirect conductimetric detection is described. The selectivities of the separation of Be and other alkaline earth metals on IDA and surface-sulphonated sorbents were compared. The influence of the nature of the mobile phase complexing agent on the selectivity of the separation between Be and other alkaline earth metals was studied. An eluent containing dipicolinic acid and nitric acid proved to be optimum for the elimination of interferences from transition metals. The detection limit for Be was 10 μg/l. Preconcentration of Be on the complexing IDA sorbent increases the sensitivity of determination. This technique was successfully applied to the analysis of rock and natural water samples.

1. Introduction

Beryllium metal and its compounds are widely involved in present day technologies. Beryllium-containing waste waters from industrial plants and power plants can contaminate natural waters, which may in turn lead to the pollution of tap water. The concentration of Be in natural waters varies from 0.1 to 500 ng/ml. High concentrations of Be are observed in regions with W and Mo deposits. In addition to the pollution of natural waters, there is another source of Be in potable water, namely wetted parts made of copper–nickel alloys. It should be stressed that Be ion is noted for its ecological toxicity. The mechanism of Be toxicity involves the destruction of cellular membranes and decrease in enzyme activity. Also, Be is carcinogenic [1]. All of the above emphasizes the need to develop simple, selective and sensitive techniques for the measurement of Be.

This paper describes a technique for the sensitive determination of Be by ion chromatography (IC).

2. Experimental

Analyses were carried out with a Hewlett-Packard Model 1084A liquid chromatograph using a conductimetric detector. The stainless-steel separation columns used were 50 × 3 mm I.D. packed with a laboratory-prepared surface-sulphonated sorbent and 250 × 3 mm I.D. packed with a laboratory-prepared chelating iminodiacetate (IDA) sorbent. The exchange

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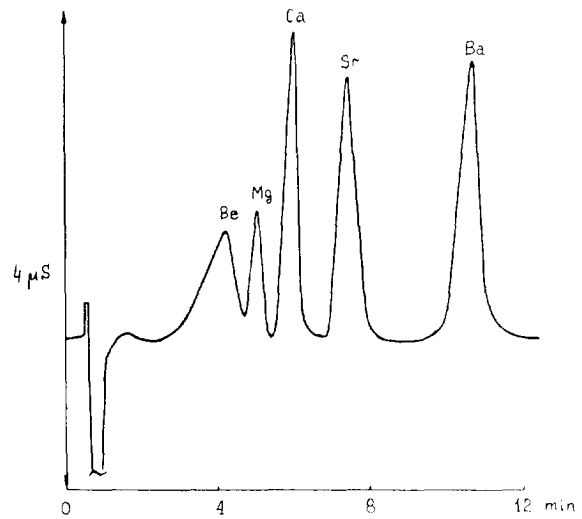

Fig. 1. Separation of alkaline earth metal cations on surface-sulphonated cation exchanger. Column, 50 × 3 mm I.D.; eluent, 2 m*M* ethylenediamine–2 m*M* citric acid–2 m*M* tartaric acid; flow-rate, 1 ml/min; indirect conductimetric detection.

capacity of both sorbents was 0.1–0.5 mequiv./g. An IDA sorbent-packed cartridge (30 × 3 mm I.D.) was used for the preconcentration of metal ions. Analytical-reagent grade chemicals were used for the preparation of eluent and standard solutions. Purified water was obtained from a Milli-Q apparatus (Millipore).

3. Results and discussion

Normally, a surface-sulphonated cation exchanger is used for the IC determination of Be. Detection is carried out with a conductimetric or a spectrophotometric detector after postcolumn reaction [2–5]. Fig. 1 shows an example of the separation of alkaline earth metal cations, including Be on a surface-sulphonated cation-exchanger using conductimetric detection. A mixture of ethylenediamine, tartaric acid and citric acid was used as the eluent. As can be seen, Be is eluted earlier than Mg and Ca on this sorbent. Some transition and heavy metal cations elute before Mg and interfere with the determination of Be. Also, the Be peak is wide and this technique is not sufficiently sensitive.

A more selective and sensitive determination of Be was achieved by using a complexing sorbent, such as a silica gel-based sorbent with IDA functional groups [6–8], for the separation. This sorbent is characterized by a higher selectivity for transition and heavy metal cations and for Be; the higher selectivity is due to the fact that in contrast to other alkaline earth metals, Be forms more stable complexes with the IDA functional groups. Fig. 2 shows the chromatogram of a model mixture of cations, including Be, separated on the IDA sorbent with an eluent

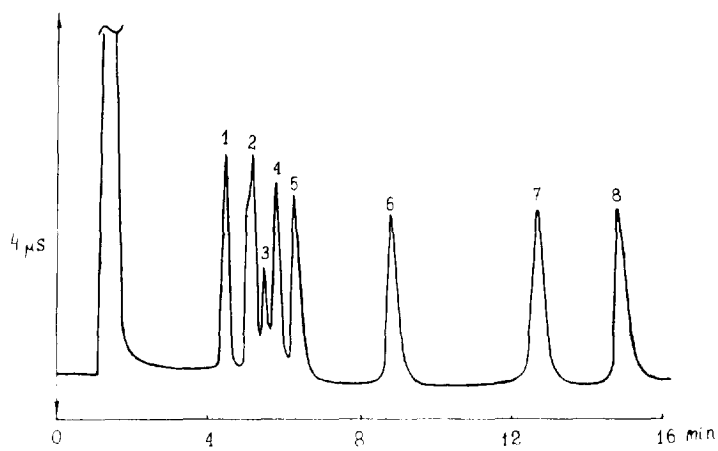

Fig. 2. Separation of alkaline earth, transition and heavy metals on IDA sorbent using non-complexing eluent. Column, 250 × 3 mm I.D.; eluent, 7 m*M* HNO_3; flow-rate, 1 ml/min; indirect conductimetric detection. Peaks: 1 = Mg; 2 = Ca, Sr; 3 = Mn; 4 = Ba; 5 = Be; 6 = Co; 7 = Cd; 8 = Zn.

containing nitric acid, using indirect conductimetric detection. It can be seen that Be is eluted after the other alkaline earth metals; this differs from the order of elution on the surface-sulphonated cation exchanger.

With the IDA stationary phase, Be is fully separated from Mg, Ca, Al and Fe(III), which are the main matrix components of rock and waste water samples.

Beryllium cation is more strongly retained than Mn and Ba cations on the IDA sorbent. Sr and Ca cations have similar retention times under these elution conditions.

The above conditions can be used for determination of Be along with some transition and heavy metals. The long retention times of transition and heavy metals significantly increase the time of analysis. Therefore, to shorten the time of analysis, to increase the separation of Be from other alkaline earth metal cations and to eliminate the interference of transition and heavy metal cations, we used a complexing eluent. A number of organic complexing acids were studied, e.g., citric, tartaric, oxalic and dipicolinic acid. All of these acids are capable of forming coordination complexes with divalent cations.

Dipicolinic acid was found to be the most suitable. This compound forms stable complexes with transition and heavy metal cations and these complexes are not retained on the IDA sorbent. As alkaline earth metals and Be do not form stable complexes with dipicolinic acid, their retention times do not vary significantly from those obtained with the non-complexing mobile phase.

Fig. 3 shows the chromatogram of a model mixture of cations obtained on the IDA sorbent with an eluent containing dipicolinic and nitric acid. Transition and heavy metal cations are eluted before Mg and do not increase the time of analysis. The selectivity for the separation of Be from Ba and transition metal cations is increased.

Under the above conditions, Ca and Sr are well separated on the IDA sorbent and Be is eluted as a narrow, well shaped peak. These chromatographic conditions were found to be the most selective for separating Be from other cations.

A close linear dependence between the peak area and the concentration of the analyte ions over a wide range of concentrations was observed with this technique. The detection limit (calculated for $S/N = 3$) obtained for Be, based on a 175-μl injection volume was 2 ng/ml.

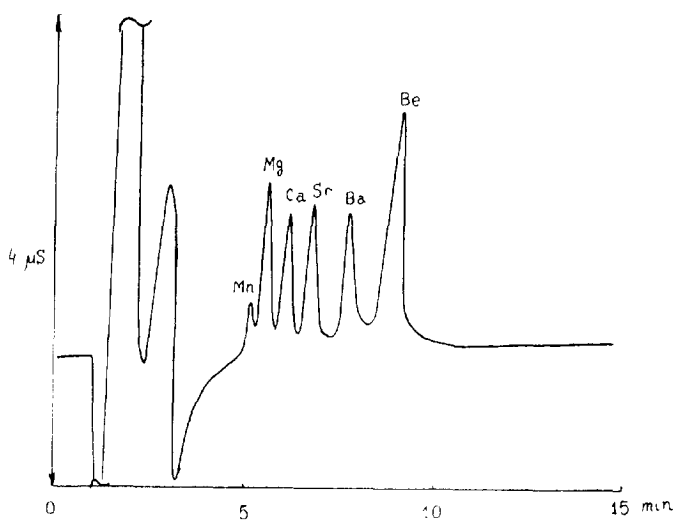

Fig. 3. Separation of cations including Be on IDA sorbent using complexing eluent. Column, 250 × 3 mm I.D.; eluent, 5 m*M* HNO_3–2 m*M* dipicolinic acid; flow-rate, 1 ml/min; indirect conductimetric detection.

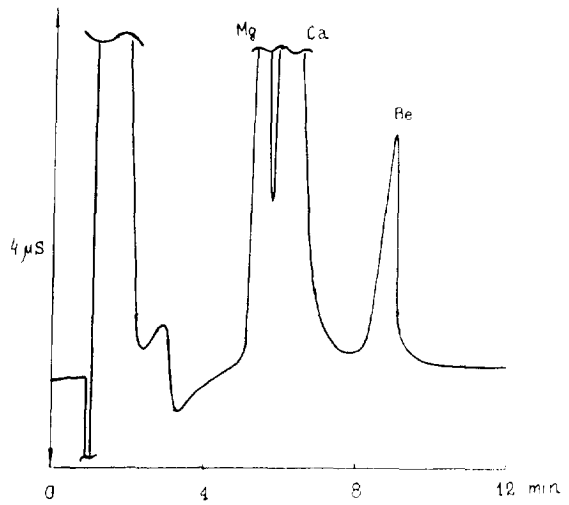

Fig. 4. Determination of Be in a geological sample by IC. Column, 250 × 3 mm I.D. with IDA sorbent; eluent, 5 m*M* HNO_3–2 m*M* dipicolinic acid; flow-rate, 1 ml/min; indirect conductimetric detection.

We analysed a number of rock samples containing Be, and a number of samples with preset contents of Be. Sample preparation involved the dissolution of 1 g of the sample in a mixture of concentrated hydrofluoric and hydrochloric acid, evaporation to dryness, dissolution of the residue in hydrochloric acid and dilution with water [9].

The chromatogram of a rock sample and the chromatographic conditions for the determination of Be are shown in Fig. 4.

The relative standard deviation of the results was <5%, as evidenced from a comparison of the results for model samples with preset Be contents (Table 1).

Table 1
Determination of Be in model samples by IC

Be concentration (μg/ml)	
Present in model sample	Found by IC
0	0
10	9.8
20	20.1
30	29.2

Two samples of the minerals Albit and Muskovit with unknown Be contents were analysed using the same technique. The results of IC and spectrometric analyses of these samples are given in Table 2. As can be seen, the results obtained by the two methods agree closely.

As already mentioned, Be is noted for its high ecological toxicity, and concentrations of Be exceeding 200 ng/l constitute an environmental hazard. The procedure for preconcentration on a cartridge packed with IDA sorbent was used for the determination of Be at this level. The conditions of sorption concentration of Be on this sorbent were studied.

With the help of the preconcentration procedure, the detection limit of Be in waters by the IC method was decreased to 50 ng/l. A 500-ml volume of the sample was preconcentrated for this value.

A number of waste water samples from the Ust'-Kamenogorsk metal plant were analysed using the preconcentration procedure. A 100-ml volume of the sample was passed through the cartridge packed with the IDA sorbent. The main part of the sorbed Mg and Ca was washed out from the cartridge with 20 ml of 0.01 *M* nitric acid. Concentrated Be with the remainder of the sorbed Ca was washed out with a further 2 ml of 1 *M* nitric acid. The pH of the samples was increased to 2.5 before injection into the chromatograph.

Fig. 5 shows the chromatogram of the Be-containing waste water. The concentration of Be in this sample was 1 μg/l. Five out of ten samples analysed contained high concentrations of Be. These data were verified by spectrometric analysis.

Table 2
Determination of Be in geological samples

Sample No.	Be concentration (μg/ml)	
	IC	Spectrometric method
1	13.3	12.1
2	75.1	73.9

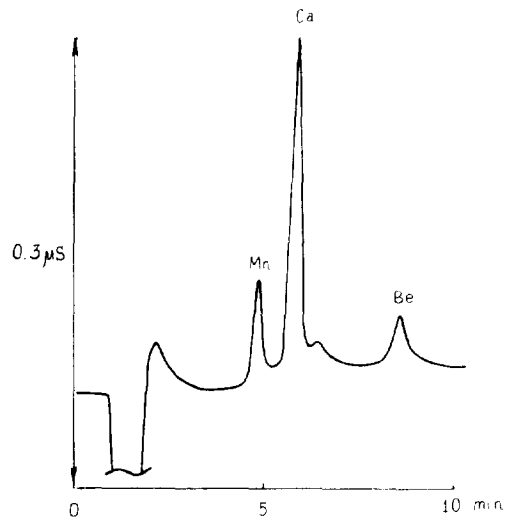

Fig. 5. Determination of Be in waste water by IC. Column, 250 × 3 mm I.D. with IDA sorbent; eluent, 7 m*M* HNO_3–2 m*M* dipicolinic acid; flow-rate, 1 ml/min; indirect conductimetric detection.

4. Conclusions

The feasibility of using IC for the trace determination of Be in rock and natural water samples, based on cation-exchange separation on a complexing sorbent and indirect conductimetric detection, was successfully demonstrated. The method had a detection limit of 2 μg/l and the Be peak response was linear up to at least 100 mg/l.

Satisfactory accuracy was shown. No interferences from alkaline earth, transition and heavy metals were found. The results of the chromatographic method agreed with those obtained by an independent spectrometric method.

The results demonstrate that the IC method using a complexing sorbent provides high selectivity and sensitivity of Be determination and may be employed for the routine determination of Be.

References

[1] H. Noda, K. Saitoh and N. Suzuki, *Chromatographia*, 14 (1981) 189.
[2] M. Betti and S. Cavalli, *J. Chromatogr.*, 538 (1991) 365.
[3] P.K. Dasgupta, *J. Chromatogr. Sci.*, 27 (1989) 422.
[4] B. Kondratjonok and G. Schwedt, *Fresenius' Z. Anal. Chem.*, 337 (1988) 332.
[5] M.L. Litvina, I.N. Voloschik and B.A. Rudenko, *J. Chromatogr.*, 671 (1994) 29.
[6] A. Bonn, S. Reiffenstuhl and J. Jandik, *J. Chromatogr.*, 499 (1990) 669.
[7] P.N. Nesterenko, T.I. Tihomirova, V.N. Fadeeva, I.B. Yuferova and Q.Y. Kukriavtsev, *Zh. Anal. Khim.*, 46 (1991) 1108.
[8] I.N. Voloschik, M.L. Litvina and B.A. Rudenko, *J. Chromatogr.*, 671 (1994) 205.
[9] H. Arginier, *Chim. Anal. (Paris)*, 12 (1960) 600.