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Determination of carbonate, inorganic anions and anionic metal complexes by single-column ion chromatography with conductimetric and UV detection

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Abstract

The determination of carbonate ion and some transition metals in the form of their EDTA anionic complexes by single-column ion chromatography (IC) is reported. Determinations were carried out on a column packed with a silica-based sorbent with a tetraalkylammonium base, linked by long hydrocarbon radicals. The simultaneous separation and determination of the anions F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} and SO_4^{2-} and anionic EDTA complexes of Al^{3+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pd^{2+} were achieved. Sodium citrate solution (pH 3.9) was used as the eluent for the determination of carbonate ion and potassium hydrogenphthalate solution (pH 6.5) for the determination of anionic metal-EDTA complexes.

1. Introduction

We used ion chromatography (IC) to determine ionic components in natural, waste and technological waters and some geological materials. However, it is not possible to determine all relevant ions using the traditional IC conditions [1–4]. We have established conditions for the determination of anions that make it possible to determine both inorganic anions and carbonate ion and also anionic complexes of some transition metals simultaneously. The determination was performed by single-column IC with conductimetric and UV detection. The ionic separation was carried out using columns filled with silica-based sorbents with a tetraalkylammonium base linked to their matrix.

2. Experimental

Analyses were carried out with a Hewlett-Packard Model 1084A liquid chromatograph with a UV detector (fixed wavelength of 254 nm) and a conductimetric detector. The separation columns used were 50×3 mm I.D. and 100×3 mm I.D. Dianion-1 and 150×4 mm I.D. Dianion-2 (Elsiko, Russian Federation). Potassium hydrogenphthalate and sodium citrate solutions were used as eluents. The anionic metal-EDTA complexes were obtained by adding equivalent amounts of EDTA disodium salt to metal salt solutions. The loop size was 175 μ l.

3. Results and discussion

Carbonate ion was determined by single-column IC because it is a weak acid anion. Un-

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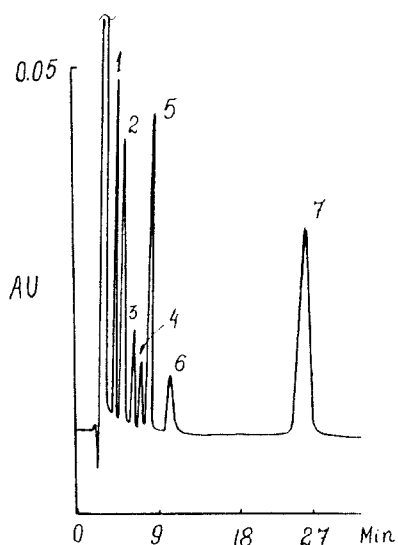


Fig. 1. Chromatogram of inorganic anions. Column: 100×3 mm I.D. Dianion-1; eluent 1 mM potassium hydrogenphthalate (pH 6.6); flow-rate, 1 ml/min; detection, UV at 254 nm. Peaks: 1 = HCO_3^- ; 2 = Cl^- ; 3 = NO_3^- ; 4 = Br^- ; 5 = NO_3^- ; 6 = HPO_4^{2-} ; 7 = SO_4^{2-} .

fortunately, the determination cannot always be carried out with acceptable sensitivity and selectivity. Fig. 1 shows the chromatogram of an inorganic anion mixture including carbonate ion. This separation was performed with the Dianion-1 column with potassium hydrogenphthalate as eluent. It can be seen that the carbonate ion has a short retention time. The carbonate peak can interfere with the peaks of weakly retained macrocomponents of the sample. Particular difficulties arise in the use of this method for the determination of carbonate in brines.

In order to increase the separation selectivity and determination sensitivity, we suggest the use of sodium citrate solution as the eluent. Detection can then be carried out with a conductimetric detector. The advantages of this eluent are that citric acid is hardly adsorbed on the hydrophobic sorbent surface and that the system peak is eliminated. In addition, the retention of carbonate under these conditions is much stronger than that with the phthalate eluent.

We studied the influence of the eluent pH on the carbonate signal and retention time. It was

found that the maximum separation selectivity and sensitivity of determination for carbonate were achieved at pH 4.6.

Figs. 2 and 3 show chromatograms for Moscow drinking water and Lake Baikal water obtained on the Dianion-2 column with sodium citrate (pH 4.6) as eluent. A small amount of sodium hydrogenphthalate was added to the eluent to eliminate the non-linear sorption of nitrate ion. These chromatograms demonstrate the good results achieved. In spite of the low eluent pH, carbonate ion is detected as a positive peak, resulting from the high pressure used: the carbonic acid dissociates under high pressure in the first step to a greater extent than without pressure.

The retention time of carbonate is increased by the use of the citrate eluent and by the possible presence of non-ionic sorption of the carbonic acid on the sorbent. After passing through the column, the pressure of the chromatographic system falls and the degree of

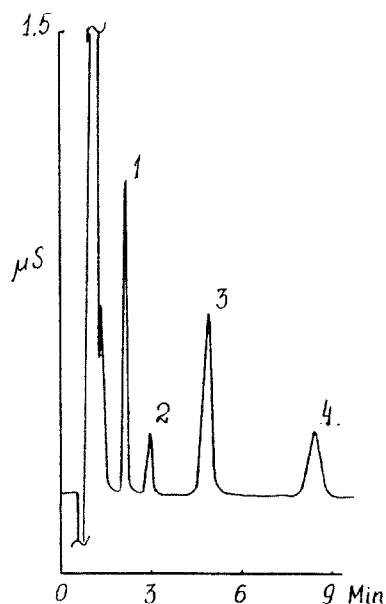


Fig. 2. Determination of carbonate ion and other inorganic anions in Moscow drinking water. Column, 150×4 mm I.D. Dianion-2; eluent, 2 mM citric acid–0.1 mM phthalic acid (pH 4.6); flow-rate, 1 ml/min; detection, conductimetric. Peaks: 1 = Cl^- (4.8 mg/l); 2 = NO_3^- (2.5 mg/l); 3 = HCO_3^- (10 mg/l); 4 = SO_4^{2-} (6.0 mg/l). Sample dilution 1:4.

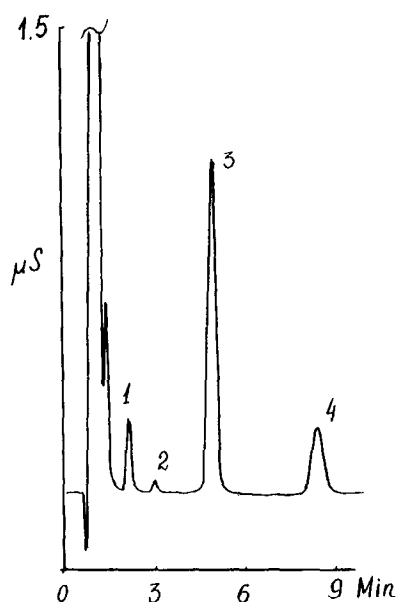


Fig. 3. Determination of carbonate ion and other inorganic anions in the Lake Baikal water. Conditions as in Fig. 2. Peaks: 1 = Cl^- (1.1 mg/l); 2 = NO_3^- (0.4 mg/l); 3 = HCO_3^- (18.5 mg/l); 4 = SO_4^{2-} (6.6 mg/l).

dissociation of the carbonic acid decreases. The conductivity increases because of the ion-exchange equilibrium shift. There is a linear dependence of this signal shift on carbonate concentration in the sample, *i.e.*, the calibration graph is linear over a wide range of injected concentrations (0.05–100 ppm).

The limit of determination of carbonate is 0.005 mg/l. Doubly distilled and degassed water was used to obtain the calibration graph. Doubly distilled water is not applicable without vacuum treatment for the preparation of standard low-carbonate solutions as it contains dissolved CO_2 .

The optimized chromatographic conditions were successfully used in analyses of natural and waste waters, brines and fluid inclusions for their anionic constituents.

The choice of the Dianion-1 separation column for the separation of anions and anionic transition metal complexes was determined by its high separation selectivity of singly and doubly charged inorganic anions (Fig. 1). The phthalate eluent and UV detection are used. As Fig. 1

shows, the most frequently found anions, *viz.*, Cl^- , NO_2^- , NO_3^- and HPO_4^{2-} , are sufficiently separated by this column and are eluted faster than the sulphate ion. The retention time of the EDTA anion is much longer than that of sulphate and nearly twice as long as that of phosphate. Hence the EDTA anion does not hinder the determination of other inorganic anions, *i.e.*, SO_4^{2-} and the earlier eluted HPO_4^{2-} , NO_2^- , NO_3^- and Cl^- .

The choice of the eluent pH value was determined by the following factors: (1) the stability of the silica-based sorbent (pH 2–8), (2) the absence of a system peak in the chromatogram (pH 6) and (3) stability of the anionic metal–EDTA complexes. These conditions are fulfilled in a very restricted pH range (6–8). The selectivity of the separation of anions decreases and the time of analysis increases with increase in pH because of the stronger retention of the EDTA anion. This is why an eluent of pH 6.6 was chosen.

The charge of the above metal anionic complexes is -1 or -2 in the pH range 6–8. The ratio between singly and doubly charged anions may change according to the pH value, *i.e.*, the effective charge of the complex anion can appear fractional. Hence such anionic metal complexes must be eluted between singly and doubly charged anions. In addition, the retention times of the complexes may be affected by other factors that change the sorption properties of these complexes. The presumed retention times of the metal–EDTA anionic complexes were confirmed experimentally. A small change in the pH of the phthalate eluent noticeably influenced the separation selectivity of some anionic complexes and inorganic anions.

The optimum conditions providing the best separation selectivity of both the metal complexes and inorganic anions studied are 1 mM potassium phthalate as eluent at pH 6.35. Fig. 4 shows the chromatogram of a mixture of the inorganic anions and the anionic complexes of some transition metals obtained under these conditions. The absorption characteristics of the metal complexes in the UV range varies, which is why Al^{3+} , Cd^{2+} and Zn^{2+} detection is performed indirectly [5].

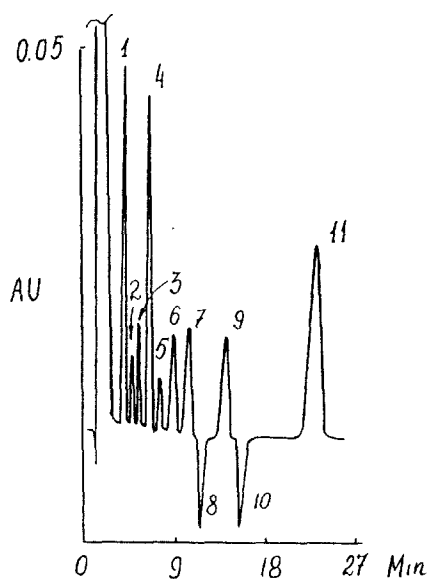


Fig. 4. Chromatogram of a mixture of inorganic anions and some metal EDTA anionic complexes. Column: 100×3 mm I.D. Dianion-1; eluent, 1 mM potassium hydrogenphthalate (pH 6.35); flow-rate, 1.5 ml/min; detection, UV at 254 nm. Peaks: 1 = Cl^- ; 2 = NO_2^- ; 3 = Br^- ; 4 = NO_3^- ; 5 = HPO_4^{2-} ; 6 = Al^{3+} ; 7 = Cd^{2+} ; 8 = Pb^{2+} ; 9 = Zn^{2+} ; 10 = Cu^{2+} ; 11 = SO_4^{2-} .

Cu^{2+} and Pb^{2+} are detected directly as the absorbance of their EDTA complexes at 254 nm

is greater than that of for phthalate ion. The difference in the absorption characteristics of the metal complexes can produce interferences in detection in the determination of combined metals.

The limit of determination of the metals provided by the described technique is 0.01–0.05 ppm. The calibration graphs are linear over a wide range of concentrations (up to 0.05–100 ppm, $n = 5$, $r = 0.999$).

The described technique for the determination of metals was applied to waste and technological waters and proved highly sensitive for the determination of ions in multi-component mixtures.

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