

Method of the Simultaneous Determination of Anions and Cations Using a Nanosized Cation Exchanger and On-Column Formation of Anionic Chelates

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Abstract—A method is proposed for the simultaneous determination of anions and cations of chelating metals based on anion chromatography with the chemical suppression of electrical conductivity of the mobile phase. It is distinguished by a high selectivity of the separation of groups of anions and cations. To implement the method, a special treatment of the protecting precolum with a nano-cation exchanger hydrosol solution is carried out and a special mode of operation of the automatic sample introduction device is used. The developed method can be implemented on any ion chromatograph. Examples of rapid analyses of tap and mineral waters for the concentration of inorganic anions, hardness salts, and zinc and copper impurities are given.

Keywords: ion chromatography, nanosized ion exchangers, simultaneous determination of anions and cations

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In analyzing the ionic composition of solutions, information is often required both on anions and on cations: in mineral water, along with the anion composition, it is important to know the concentrations of hardness salts and toxic metals; in environmental monitoring, it is necessary to know not only the concentration of trace elements, but also their degree of their oxidation in the cationic and anionic forms of an element (problem of speciation analysis). Two systems are used to obtain this information in ion chromatography: cationic and anionic. The systems are mutually independent and, in fact, are two ion chromatographs. For the convenience of single sample injection and reducing the cost of equipment, methods for the simultaneous determination of anions and cations are being developed. They use one-column versions with column packings exhibiting both anion-exchange and cation-exchange properties and a mobile phase finely selected both in terms of elution force characteristics, which are dictated by both cation and anion separation, and in terms of detection characteristics [1, 2]. Such a combination of functions has certain disadvantages associated with the lack of a possibility of using the chemical suppression of electrical conductivity, i.e. with a loss of sensitivity, and with the mutual effect of anions and cations, peaks of which are recorded in the same region of the chromatogram. Some authors use a possibility of chemical suppression in the anionic system, introducing a chelating additive into the eluent, but, in this case, the mutual effect of anions and

anionic metal complexes, which reduces the resolution of the method, is still observed [3].

Earlier, we proposed a method for the simultaneous determination of anions and cations based on the bipolarity of separating KanK adsorbents [4–6]. Like its counterparts, the method provides a single sample injection and the reduction of the cost of equipment. The difference and an advantage of the proposed method are in the absence of the mutual effect of the anionic and cationic compositions on the peak resolution and in maintaining the high sensitivity of detection because of the use of the chemical suppression of the electrical conductivity of the eluent. In commercial chromatographs such a method cannot be implemented directly because of the absence of cation exchange capacity in the anion exchange phases used, stopping the cations.

The procedure proposed in this article makes it possible to realize the indicated method in any ion chromatograph. The technical implementation of the simultaneous determination of anions and cations became possible because of the use of a nanosized ion exchanger [7, 8] for the treatment of the guard column installed before the separation column.

EXPERIMENTAL

Reagents. A 4 mM solution of a chelating ligand (CL), EDTA (reagent grade), in water was used. The eluent was prepared from sodium carbonate, a 0.5 M

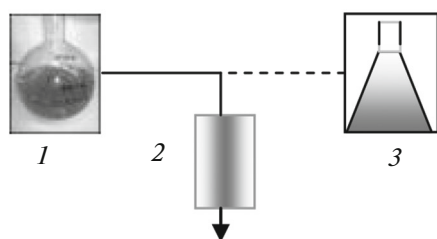


Fig. 1. Precolum processing scheme: (1) NIK hydrosol, (2) guard column from the set for anion analysis, and (3) water–acetonitrile washing solutions.

solution; sodium hydrogen carbonate, a 0.5 M solution; and the CL. The eluent composition was 1 mM NaHCO_3 , 3.2 mM Na_2CO_3 , and 0.001 M CL. A solution for the regeneration of the chemical suppressor was a 0.2 M sulfuric acid. The auxiliary solution for treating the precolum was hydrosol of a NIK-2 nano-cation exchanger in the H-form with the concentration of functional groups 0.038 M, prepared by a special procedure developed at the Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences [8, 9].

To prepare analytes, solutions of anion salts (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , and SO_4^{2-}) with a concentration of 1 g/L in the anion and metal salts (Mg^{2+} , Ca^{2+} , Zn^{2+} , and Cu^{2+}) with a concentration of 1 g/L in the cation prepared from precisely weighed portions were used. The standard mixture contained the following ions, ppm: 2 F^- , 17.7 Cl^- , 15 NO_2^- , 15 Br^- , 20 NO_3^- , 25 HPO_4^{2-} , 50 SO_4^{2-} , 5 Mg^{2+} , 10 Ca^{2+} , 10 Zn^{2+} , and 8 Cu^{2+} .

Equipment. A Metrohm ion chromatograph (Switzerland) of the 883 Basic IC plus brand with a conductometric detector and the chemical suppression of electrical conductivity was used. The analytical system of the chromatograph consisted of an injector with a 20 μL metering loop, a Metrosep A Supp 5 – 150/4.0 separation anion-exchange column with a Metrosep A Supp 4/5 Guard/4.0 precolum, and a node with three miniature MSM suppressing columns, each time incorporating freshly regenerated column into the new experiment. The arrangement and characteristics of the chromatograph are presented on the website of the company [10].

The procedure of precolum special treatment. To implement the method on 883 Basic IC plus ion chromatograph, a node with Metrosep A Supp 4/5 Guard/4.0 precolum was specially treated. The precolum was treated with the aim to impart cation-exchange properties to it by passing 10 mL of a NIK-2 auxiliary solution through it, after which it was thoroughly washed with acetonitrile and water (Fig. 1). After such treatment, all the protective functions of the precolum were restored.

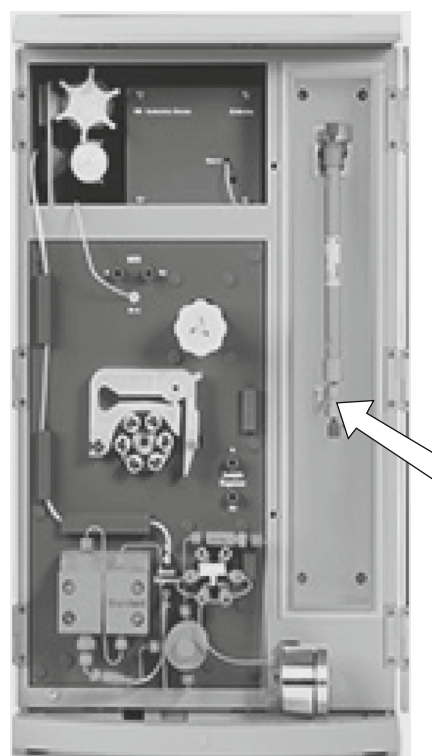


Fig. 2. Chromatograph scheme (the device stopping and accumulating sample cations is shown by the arrow).

RESULTS AND DISCUSSION

The proposed method was applied to the highly selective analysis of the anionic and cationic composition of aqueous solutions in a single sample injection using an anion-exchange ion chromatography system with chemical suppression without sample preparation and in a reasonable time (about 20 min).

The idea of the method [4] is in the separate elution of the sample anions and those cations that form anionic complexes stable under the experimental conditions, created at a certain point in time with the help of the CL dispensed through an injector. For the separate elution of anions and cations, a device was installed immediately after the injector to stop and accumulate sample cations.

In our experiments, a specially prepared precolum (Metrosep A Supp 4/5 Guard/4.0) acted as such a device (Fig. 2). The packing of the precolum with anion-exchange properties was modified in a dynamic mode by passing a solution of a hydrosol of a nano-cation exchanger, which passed through the drainage of the column freely. Negatively charged particles of the nano-cation exchanger were deposited and retained on the positively charged surface of the packing granules due to electrostatic forces.

The CL forming strong anionic complexes with the stopped cations was a solution of EDTA with the concentration 3–5 mM. This solution was introduced into

Table 1. Operating program of automatic units of the chromatograph in the method of the simultaneous determination of cations and anions

No.	Time, min	Device, module	Command: parameter	Comment
1	0.0	Autosampler (AS), needle of AS	Move to: test tube with sample	Test sample
2	0.5	AS, needle of AS	Lower into: working position	Washing of injector with sample
3	1.0	883 Basic IC plus 1 (ion chromatograph, IC), injector of IC	Switch to: position "filling"	Beginning of washing of injector
4	1.0	AS, peristaltic pump (AS PP)	On/Off: On, work speed = 2 (rel. un., 1 rel. un = 0.4 mL/min)	End of washing of injector
5	3.0	AS, AS PP	On/Off: Off	Sample injection
6	3.0	883 Basic IC plus 1 (IC), injector of IC	Switch to: "input" position	Time 0 min on chromatogram
7	3.0	Recorder, chromatogram recording program	Beginning of recording detector data	Washing of AS system with water
8	3.5	AS, needle of AS	Move to: test tube with water	Beginning of washing of AS
9	4.0	AS, needle of AS	Lower into: working position	End of washing of AS
10	4.5	AS, AS PP	On/Off: On, work speed = 2	
11	9.0	AS, AS PP	On/Off: Off	
12	9.0	883 Basic IC plus 1 (IC), injector of IC	Switch to: position "filling"	
13	9.0	AS, needle of AS	Move to: test tube with a solution of chelating ligand (CL = 4 mM Na ₂ EDTA in water)	CL (Na ₂ EDTA – sodium ethylenediamine tetraacetate)
14	9.5	AS, needle of AS	Lower into: working position	
15	9.5	AS, AS PP	On/Off: On, work speed = 2	Beginning of washing of injector
16	11.5	AS, AS PP	On/Off: Off	End of washing of injector
17	11.5	883 Basic IC plus 1 (IC), injector of IC	Switch to: "input" position	Injection of CL. Time on chromatogram: 8.5 min
18	11.5	AS, needle of AS	Move to: test tube with water	Washing of AS system with water
19	12.0	AS, needle of AS	Lower into: working position	
20	12.0	AS, AS PP	On/Off: On, work speed = 2	Beginning of washing of AS
21	17.0	AS, AS PP	On/Off: Off	End of washing of AS

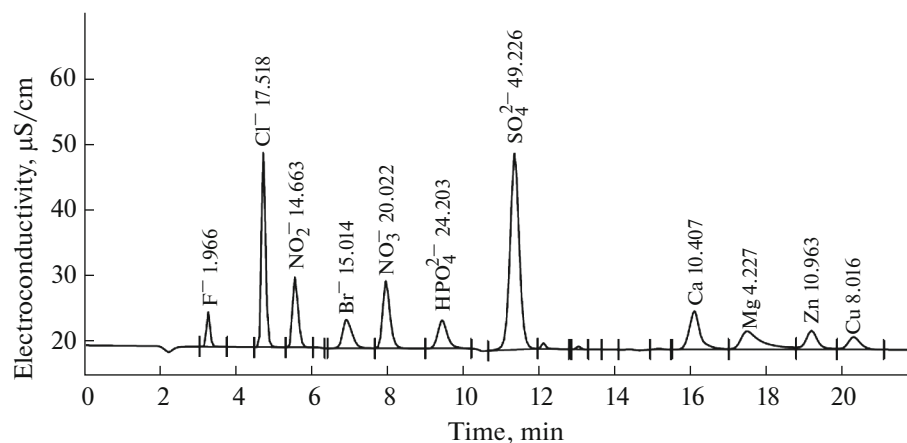


Fig. 3. A chromatogram of a standard solution containing 11 detectable components obtained on the Metrohm 883 Basic IC plus system.

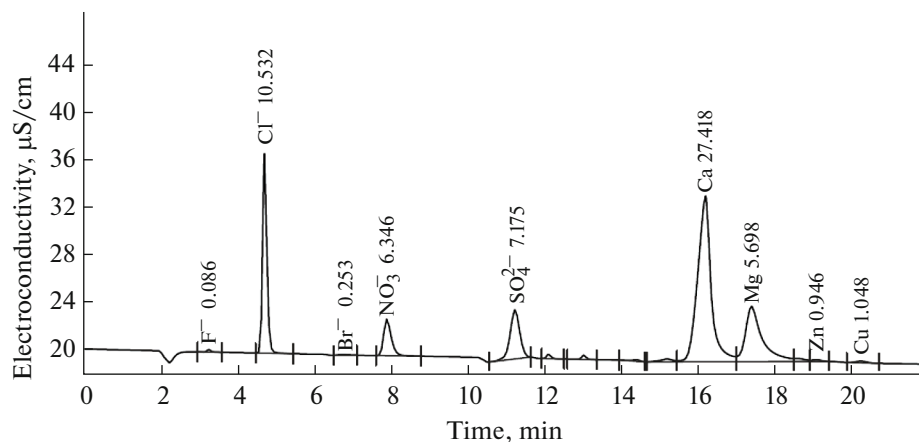


Fig. 4. A chromatogram of mineral water "Lipetsk buvette" (the found values of ion concentrations, ppt, are shown).

the chromatograph system through an injector, which was thoroughly washed with water after the sample. The dosing time was determined by the elution of the last anion, and taking into account the dead time and free space in the chromatogram, to save the analysis time, dosing was carried out 3.5–4 min before the end of the complete separation of the anions. The developed procedure is rather sensitive to the presence of impurities in the eluent forming chelates with the CL; therefore, to mask them, 1/1000 of the CL concentration was added to the eluent.

Of great importance for the reproducibility of the procedure was the automatic sample injection device that was provided with the chromatograph. The program of its work is presented in the Table 1.

In model experiments, a standard solution of seven anions and four cations of a given composition, ppm: 2 F^- , 17.7 Cl^- , 15 NO_2^- , 15 Br^- , 20 NO_3^- , 25 HPO_4^{2-} , 50 SO_4^{2-} , 10 Ca^{2+} , 5 Mg^{2+} , 10 Zn^{2+} , and 8 Cu^{2+} , was used.

In the resulting single chromatogram, first all anions and then cations were eluted. The total analysis time was 21 min (Fig. 3).

The developed method for the simultaneous highly selective determination of anions and cations turned out to be very convenient for the rapid analysis of natural, drinking, and mineral waters. Figures 4 and 5 show chromatograms obtained in the analysis of such samples.

At this stage of development, the proposed method is not free from disadvantages. One can state that the detection of trace components of metals, such as Zn and Cu, in these experiments is still not sufficiently reliable because of the effect of the addition of CL to the eluent. The preliminary purification of the eluent components from chelating impurities and the elimination of the masking CL additive to the eluent will improve the procedure in this aspect.

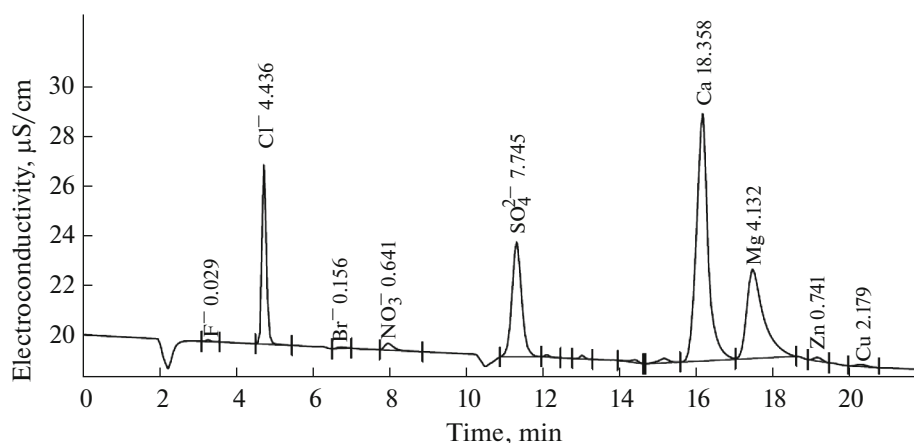


Fig. 5. A chromatogram of a tap water sample (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, July 10, 2015; sample was fivefold diluted; the found values of ion concentrations, ppm, are shown).

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