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Chemical Analysis of Natural Objects by Ion Chromatographic Method in Combination with a priori Calculations using IONCHROM Software

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Abstract—This paper briefly describes original developments in the theoretical and practical ion chromatography. It is demonstrated that new methods may be applied for the highly-selective analysis of complex natural objects. The determination of different species of sulfur and other ions in the condensates of fumarolic gases is considered in detail as an example.

Keywords: ion chromatography, chemical analysis, numerical modeling, natural waters, fumarolic gases

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INTRODUCTION

Ion chromatographic (IC) method is applied for the qualitative and quantitative determination of a mixture of ionic species as aqueous electrolyte solutions (Small et al., 1975). Ions are identified with allowance for element oxidation state. The lowest analyte concentrations determined using standard device are around tens of picograms. The class of analyzed components is only limited by their ability to form ionic species in aqueous solutions.

Depending on the type of ion exchange separation, the ion chromatography is subdivided into cation- and anion-exchange chromatography. This method is applied to determine mineral, organic cations and cationic complexes, and mineral, organic anions and anionic complexes. The anion-exchange chromatography finds the widest application as the very informative and best method for analyzing the anion composition of different objects and method of speciation analysis.

IC method is widely used in the analysis of ionic composition of solutions in natural and technogenic objects (waste and technological waters), as well as in chemical, electron, and food industry, in energetics, production of potable water, medicine, and scientific studies (Haddad et al., 2008).

Modern ion chromatographs became standard equipment of multiprofile chemical laboratories. Figure 1 demonstrates a general view of Akvilon ion chromatograph (Moscow, RF) (Akvilon catalogues, 2016).

Dionex Corporation, a leader in IC instrumentation manufacturing, performs a reagent-free simultaneous cationic and anionic analysis using alkaline and acid eluent electrochemically generated from aqueous salt solutions (Dionex catalogues, 2016). In this scheme, initial salts return in the electrochemical generator of eluent after chemical suppression—transformation of eluent into low-conductivity compound in a special device—suppressor located between the separation column and conductivity detector. Only distilled water is consumed during electrodialysis to generate side products: hydrogen and oxygen. Figure 2 demonstrates an example of the implementation of the reagent-free ion chromatographic system in ICS-3000 (Dionex) chromatographs for determination of full ionic composition of sample.

Theoretical studies, numerical modeling, and optimization of IO chromatography have been carried out for thirty years at the Laboratory of Sorption Methods Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences (GEOKhI RAS) (Dolgonosov and Ippolitova, 1993; Dolgonosov, 1994; Prudkovskii and Dolgonosov, 1999; Dolgonosov et al., 2001; Dolgonosov and Prudkovskii, 2002, 2013; Dolgonosov et al., 2007; Prudkovskii, 2013). In order to develop IC method, a series of original technologies was proposed, including a design of new sorbents (Dolgonosov, 1994; Dolgonosov, 1984, 1985; Dolgonosov and Lazeikina, 1988), columns (Dolgonosov et al., 2013), schemes and methods (Dolgonosov, 1992, 1993; Dolgonosov and Krachak, 1993; Dolgonosov, 1995; Kalyakina and Dolgonosov, 2003; Kolotilina and Dolgonosov, 2005; Kolotilina et al., 2007, 2008), and methodology of

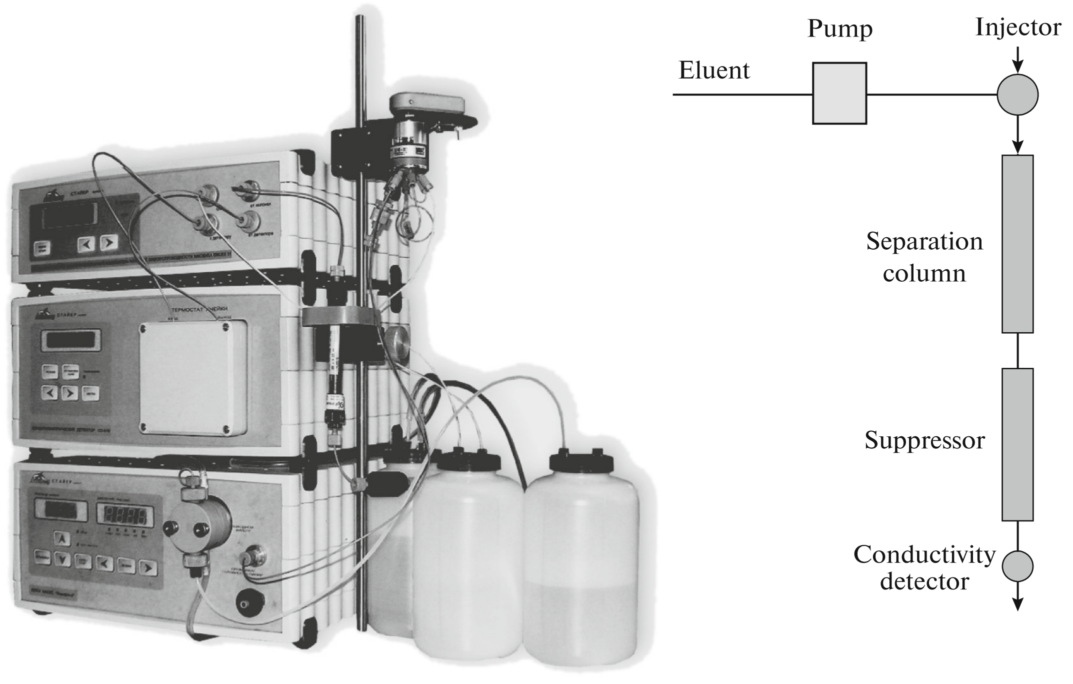

Fig. 1. Stayer ion chromatograph (Akvilon, RF) and a scheme of ionic chromatography with chemical suppression (on the right).

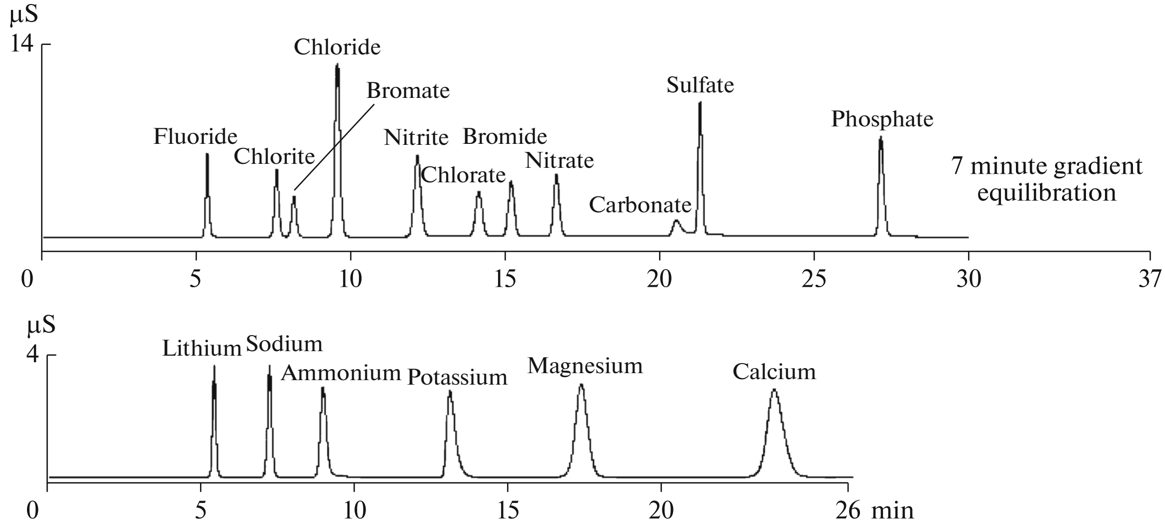

Fig. 2. An example of parallel cation and anion analysis using a reagent-free ion chromatography system. Two separation lines are applied: anionic system with alkaline eluent and gradient mode (upper chromatogram) and cationic eluent with tartrate eluent (isocratic mode).

analyzing complex objects (Dolgonosov, 1991; Kolotilina et al., 2008, 2009). Most of these studies were described and systematized in several monographs (Dolgonosov et al., 1993, 2013, 2015).

The aim of this work was to illustrate the application of new technologies in the field of ion chromatographic analysis of natural objects.

DESCRIPTION OF TECHNOLOGIES EXPANDING THE POSSIBILITIES OF IC METHOD

Methods described below, in addition to chromatographic columns, employ columns with KanK stationary phases that were designed and prepared at the Laboratory of Sorption Methods of GEOKhI RAS

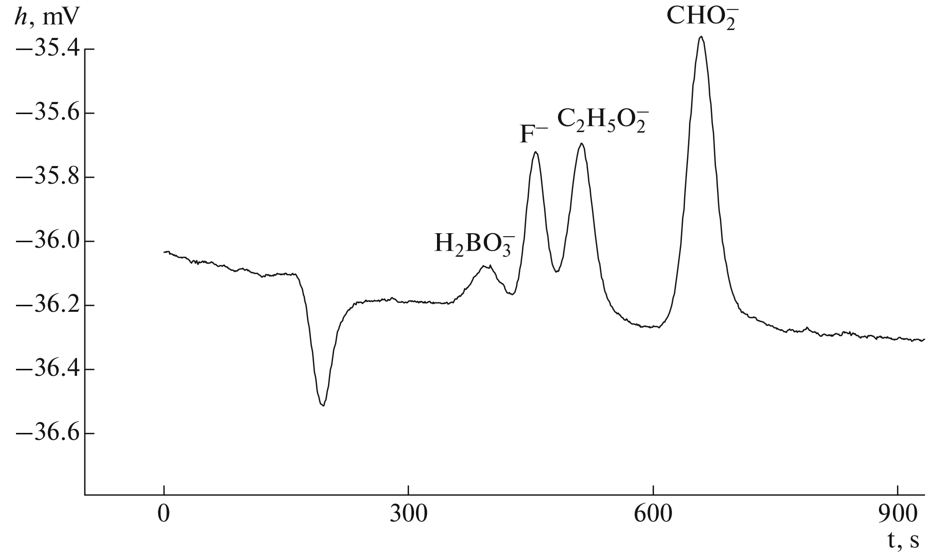

Fig. 3. Separation of a model mixture of four anions with concentrations (mg L): borate—0.2, fluoride—0.04, acetate—0.2, formate—0.2. Two-column chromatographic scheme with conductometric detection: separation column 120 × 5 mm, KanK-ASt (14 μm); suppressor 200 × 6 mm, KU-2 (150 μm) in the mixed H^+/K^+ form. Eluent: 3 mM NaOH, the flow rate of 1.9 mL/min (Kolotilina and Dolgonosov, 2005).

(Dolgonosov, 1994; Dolgonosov, 1984, 1985; Dolgonosov and Lazeikina, 1988).

Method M1: Determination of Weakly Conductive Anions.

After passing through suppressor, eluate is characterized by neutral or weakly acid reaction (pH 5.5–7). Incomplete dissociation of many weak acids under these conditions leads to the decrease of their conductivity signal. Such extremely weak acids as hydrosulphuric, boric, silicic and other acids at pH <7 do not form ionic species and therefore, are not identified using conventional ion chromatographic techniques. This problem may be solved using idea of ion exchange reaction of hydrogen ions for alkali metal ions, which results in the local pH growth in the cation-exchange layer and corresponding dissociation (Kolotilina and Dolgonosov, 2005). This idea may be implemented by location of cation exchanger as potassium ions (or another alkali metal) between supressor in the H form and conductivity detector. Special elution column was mounted for these purposes behind common suppressor. Further conducting detection of weak acids that passed through elution column has one to two orders of magnitude higher sensitivity, while the linear range of the their signal is comparable with that of strong acids.

It is more suitable to treat a small tail part of the suppressor column by potassium salt during its regeneration after counetrflow acid washing. Figure 3 shows the separation of weakly retained anions of monobasic carbonic acids, fluorine, and borate on a standard two-column ion chromatographic system containing separation column filled with KanK-ASt sorbent (GEOKhI RAS) with particle size of 14 μm, capacity of 10 μequiv/mL. Alkaline eluent 3 mM NaOH was used. Suppressor column was filled with strong acid cation exchanger KU-2x8, particle size of 150 μm, in the H^+-form, while the end of suppressor column is saturated in potassium ions.

Method M2: Selective Absorption of Ions during Analysis

The wide application of conductivity detection does not exclude the development of highly selective ionic chromatographic methods.

The interfering effect of one component on the determination of another component during ion chromatographic analysis may be eliminated by postcolumn reactions prior to detection (Dolgonosov and Lazeikina, 1988; Kalyakina and Dolgonosov, 2003). This increases the resolution of this method, provides more reliable identification of mixture components, and expands a set of analyzed objects.

Following ion exchange precipitation reactions were used for the selective anion absorption of sample (R^- is the cation exchanger of the suppression column):

$$R^-Ag^+ + NaCl \rightarrow R^-Na^+ + AgCl\downarrow,$$

$$R^-Ag^+ + NaBr \rightarrow R^-Na^+ + AgBr\downarrow,$$

$$R_3^-Al^{3+} + 3NaF \rightarrow 3R^-Na^+ + AlF_3\downarrow,$$

$$R_2^-Pb^{2+} + 2NaF \rightarrow 2R^-Na^+ + PbF_2\downarrow,$$

$$R_2^-Pb^{2+} + Na_2HPO_4 \rightarrow 2R^-Na^+ + PbHPO_4\downarrow.$$

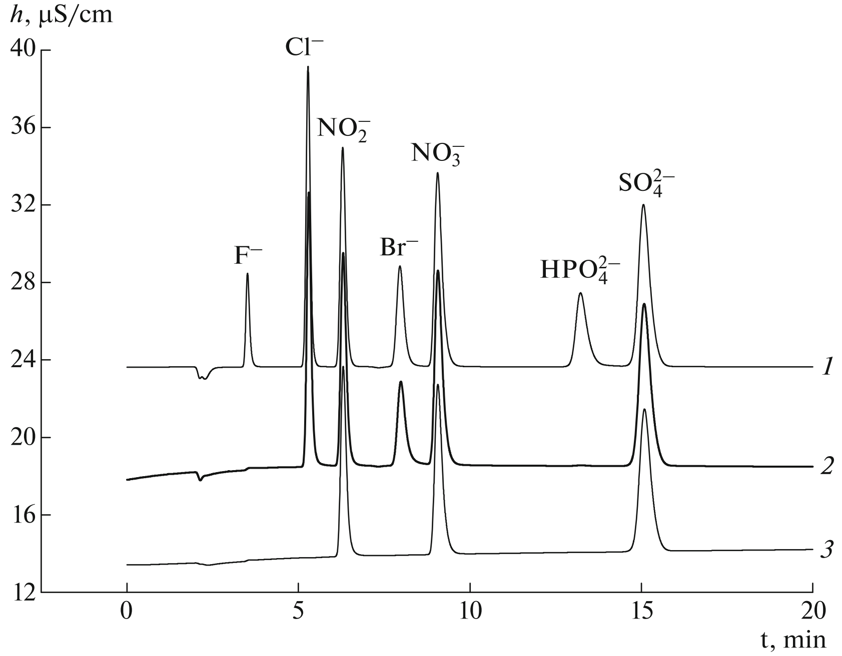

Fig. 4. Illustration of absorption column method by the example of analysis of standard mixture of inorganic anions with concentrations (mg/L): fluoride—2, chloride—10, nitrite—15, phosphate—25, bromide—15, nitrate—20, sulfate—20. *1*—basic chromatogram; *2*—chromatogram after SC treatment by Pb^{2+} ions; *3*—chromatogram after SC treatment by Ag^+ and Pb^{2+}. Chromatograph METROHM 883 Basic IC plus, separating column Metrosep A Supp 5—150/4.0 with precolumn Metrosep A Supp 4/5 Guard/4.0, cluster with three MSM miniature suppression columns. Elution rate of 0.7 mL/min, sample volume of 20 μL.

Known anions were absorbed from eluate as precipitate in the column zones with cationite in form of the above mentioned metals. Such column was installed either behind the suppressor or supplemented the suppressor column (SC). The amount and dispersion of sediments were insignificant enough to be removed with eluate immediately after formation. As experience shows, by-reactions between eluent ions and ionic species of cationite did not affect the level and shape of conductivity signal. Thus, the removed components may be identified using not only retention time but also their participation in the above mentioned absorption reactions. Analysis technique included two stages: 1) conventional determination of anionic composition (basic case using SC in the pure H-form) and treatment with metal salts of suppressor column during washing; 2) determination of anionic composition with a selective absorption of anions in SC treated with metal salts. Obtained chromatograms were subtracted to determine absorbed components. The second chromatogram contained information on the components undetected during standard determination.

Presented below examples that illustrate this method were performed on a modern ion chromatograph METROHM 883 Basic IC plus (http://www.metrohm.com, 2016). Figure 4 illustrates the application of the absorption columns for determination of standard mixture consisting of seven anions. Chromatogram *1* corresponds to the basic case of anion chromatography with SC containing no metal ions. Curve *2* was obtained for the same mixture and under the same conditions, but using SC containing the admixture of Pb^{2+} ions in addition to hydrogen ions; curve *3* was obtained for chromatographic system with SC containing Ag^+ and Pb^{2+}. The comparison of chromatograms indicates a complete removal of absorbed ions and the preservation of sensitivity for other ions, which is very conveniently during analysis.

Highly selective methods M3—M5 are based on the bipolarity of separation sorbents and on the performance of selective reactions that transform the studied cations either in non-conductive compounds or in anions.

Method M3: Simultaneous Determination of Ammonium and Weakly Retained Anions

This method is based on the selective reaction between ammmonia and nitrous acid with formation of nitrogen and water molecules on suppress sorbent in the H^+-form (Dolgonosov and Krachak, 1993):

$$NH_3 + HNO_2 \rightarrow H_2O + N_2\uparrow.$$

The eluent selected to retain ammonium on a cation-exchange layer of the KanK-BP separating sorbent (GEOKhI RAS) and on the sodium form of suppressing sorbent KU-2 was weak but sufficient for the

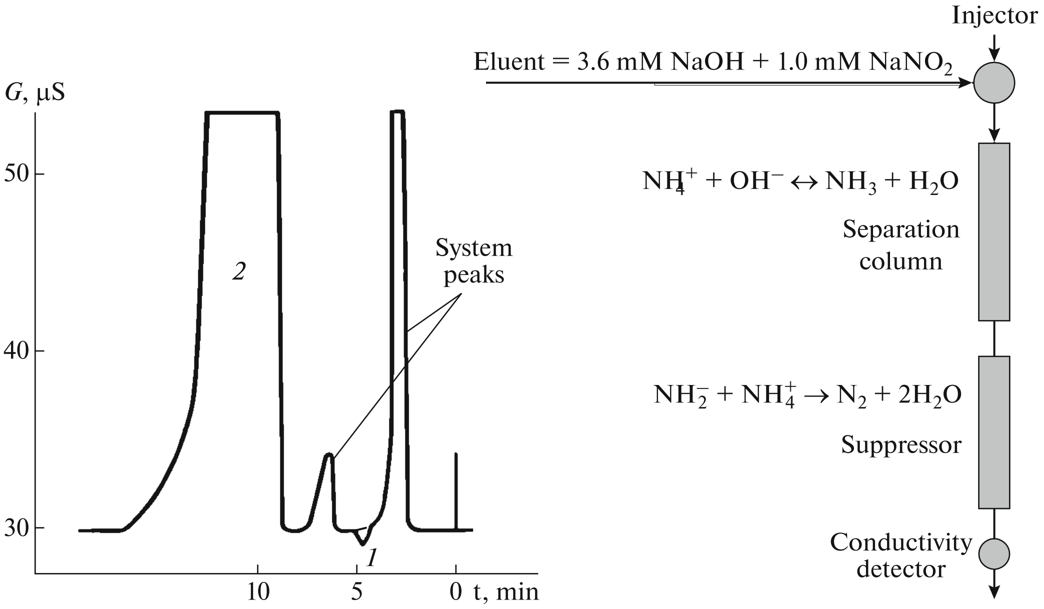

Fig. 5. Determination of ammonium ions in a mixture containing 100-fold excess of Na^+ (5 mM) and K^+ (5 mM). A scheme of chromatographic system (on the right) and experimental chromatogram (on the left). Peaks in the chromatogram: *1*—0.1 mM NH_4^+; *2*—10.1 mM Cl^-. Chromatograph KhPI-1, separation column 120 × 5 mm, KanK-BP, capacity of 0.2 mequiv/mL, 14 μm; suppression column 120 × 5 mm, KU-2 in the H-form, 50 μm; eluent: 1.0 mM $NaNO_2$ + 3.6 mM NaOH + 0.03% CH_2O; flow rate of 0.9 mL/min; sample volume of 300 μL (Dolgonosov A.M. and Krachak A.N., 1993).

separation of the ammonium peak from water peak; the eluent contains hydroxyl ions to convert most part of the ammonium ions in ammonia molecules and nitrite ions to execute the above indicated reaction. Thus, the suppression column serves as a postcolumn reactor adjusted to ammonium ions. In addition, since the system is anion exchangeable, it is possible to determine the weakly retained anions (Fig. 5).

The express routine determination of ammonium is performed using ion-exchange separation of anions. This decreases the analysis time to 2–3 min, allows the analysis selectivity of 100 with respect to other cations, and ammonium detection limit of around 0.1 mg/L.

Two other methods of simultaneous determination of cations and anions were developed to increase significantly the selectivity and sensitivity of the determination of transition metal ions. They may be defined as methods of anion chromatography based on the controlled on-column (in situ) transformation of analyzed cations into anions.

These methods are based of the following principles:

1. Separation of ions according to the charge sign: retention of cations and elution of anions,

2. Injection of reactant to transform quantitatively the metal cations in anions;

3. Elution of the resultant anions after the sample anions.

The required properties of the system are as follows:

—separating sorbent should be bipolar and highly efficient with respect to anion separation,

—injected reactants under conditions kept in the separation system should either form strong anion complexes or oxidize metal ions to their oxoanions;

—eluent should be able to separate efficiently anions and prevent rapid metal hydrolysis.

Method M4: in situ Controlled Formation of Anion Complexes of Metals

Let us consider the first method. The aim of this method is highly selective analysis of *anionic* and *cationic* composition of aqueous solutions during *single* injection of sample using *anion-exchange* ion chromatographic system with chemical suppression without *sample preparation* and during reasonable time (around 20 min).

This method was described in (Dolgonosov, 1992, 1994). Complexes are formed using ethylenediaminetetraacetic acid (EDTA). EDTA forms strong two-charged MEDTA-type anionic complexes with transition metal (M), including Pb, Cd, Zn, Cu etc. The injection of excess EDTA in the system leads to the quantitative transformation of metal cations preliminarily retained in the starting layer of separation column into anionic complexes.

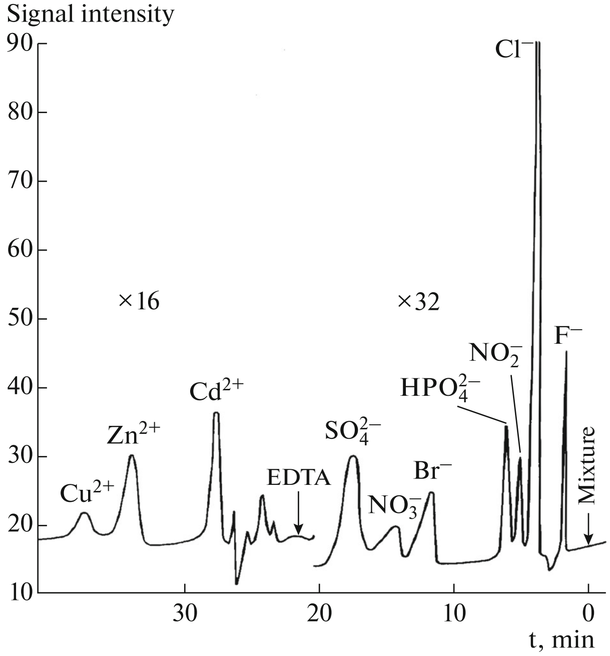

Fig. 6. Separation of model mixture containing ten components: seven anions (F^-, Cl^-, NO_2^-, HPO_4^{2-}, Br^-, NO_3^-, SO_4^{2-}) and three transition metals (Cd^{2+}, Zn^{2+}, Cu^{2+}). Chromatograph Tsvet-3006, separation column 100 × 4 mm, KanK-ASt; suppression column 120 × 5 mm, KU-2 in the H-form; eluent: 3.5 mM Na_2CO_3 + 1.5 mM NH_4HCO_3; flow rate of 2 mL/min; reagent: 5 mM Na_2EDTA; sample loop volume 30 μL (Dolgonosov A.M., 1994).

Obtained and associated anions in analyzed solution are eluted using carbonate eluent, which differ from the common eluent in the presence of ammonium ions, which retard the metal hydrolysis (Fig. 6). This provides the separation of model mixture consisting of ten components: seven anions (F^-, Cl^-, NO_2^-, HPO_4^{2-}, Br^-, NO_3^-, SO_4^{2-}) and three transition metals (Cd^{2+}, Zn^{2+}, Cu^{2+}), under following conditions: chromatograph Tsvet-3006, separation column 100 × 4 mm, KanK-ASt (GEOKhI RAS); suppressor column 120 × 5 mm, KU-2 in the H-form; eluent: 3.5 mM Na_2CO_3 + 1.5 mM NH_4HCO_3; flow rate of 2 mL/min; reagent: 5 mM Na_2EDTA; sample loop volume 30 μL.

In experiments performed on a METROHM 883 Basic IC plus ion chromatograph, this device was represented by specially prepared precolumn (Metrosep A Supp 4/5 Guard/4.0). The precolumn was treated to obtain cation-exchange properties in an off-line mode by flowing of nano-cationite solution with particle size of 100 nm. Model experiments were performed using standard solution of given composition of seven anions and four cations (mg/L): 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+}, 10—Cu^{2+}). Composition of eluent: 1 mM $NaHCO_3$ and 3.2 mM Na_2CO_3, flow rate of 0.7 mL/min. Solution of chelating ligand: 4 mM disodium EDTA in water. All anions and cations were subsequently eluted in a single chromatogram field. Full time of analysis was 21 min (Fig. 7).

Method M5: Controlled in Situ Oxidation of Metal Cations to Their Oxoanions

The second version is based on the oxidation reaction (Dolgonosov, 1993, 1995). Hydrogen peroxide may be used as reactant. It has an oxidizing potential of –0.88 in alkaline environment, which is sufficient to oxidize transition metal ions to their oxoanions. For instance, the redox potential of the reaction

$$Cr(OH)_3 + 5OH^- = CrO_4^{2-} + 4H_2O + 3e^-$$

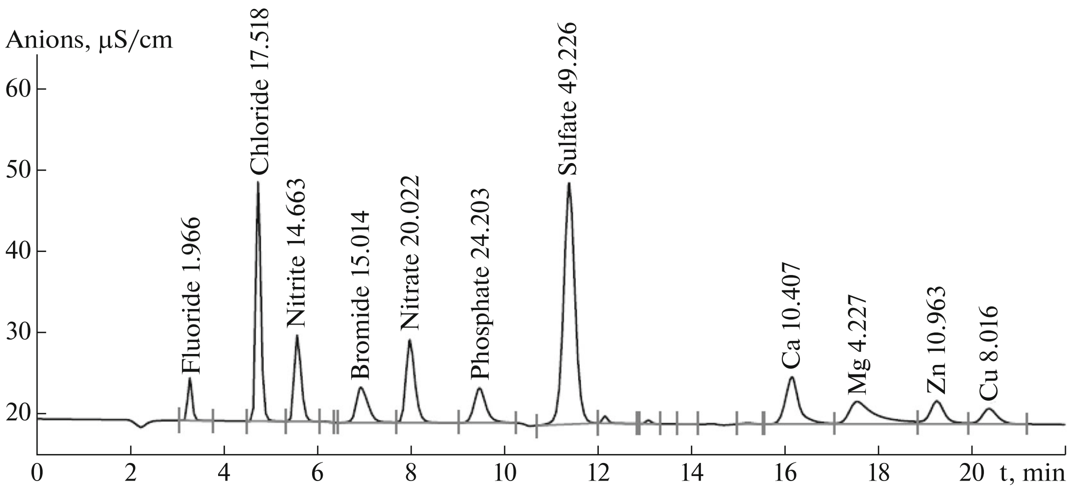

Fig. 7. Chromatogram of simultaneous highly-selective determination of anions and cations obtained on the Metrohm 883 Basic IC plus system for standard solution containing eleven determinable components.

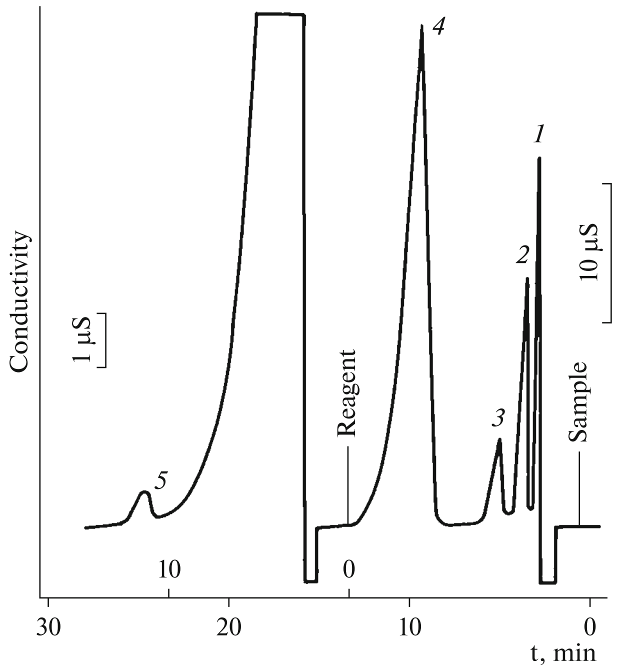

Fig. 8. Simultaneous determination of chromium ions in different degree of oxidation and inorganic anions. *1*—Cl^-; *2*—SO_4^{2-}; *3*—NO_3^-; *4*—$Cr_2O_7^{2-}$ (50 mg/L); *5*— Cr^{3+} (0.5 mg/L). Chromatograph KhPI-1, separation column 100 × 3 mm, KanK-ASt; suppression column 120 × 5 mm, КУ-2 in the H-form; eluent: 5 mM Na_2CO_3 + 0.2 mM KIO_3; flow rate of 0.9 mL/min; reagent: 20% H_2O_2; sample loop volume 30 µL (Dolgonosov, 1995).

equals 0.13 V and, hence, permits the application of hydrogen peroxide for Cr(III) oxidation to Cr(VI) in an alkaline eluent environment. Injection of 20–40% hydrogen peroxide in an eluent flow leads to the quantitative transformation of chromium cations prestopped at the beginning of column into chromate ions. Elution was performed using a carbonate eluent of approximately double force with a small addition of weak oxidizer, which neutralizes the reducing potential of the separation system containing metallic elements. Iodate ion is suitable as such additive.

The frequent difficult analytical task of the separate determination of simultaneously present chromium species can be easily solved using this method. Analyzed sample containing both chromium species is injected without changes in a flow of the above described eluent. The ion chromatograph system contains a separation column with bipolar KanK-ASt sorbent (GEOKhI RAS) and a suppression column with cationite KU-2 in the H-form. The chromium cations are retained by starting layer of the separation sorbent, while anions, including the chromate ions, participate in the chromatographic separation, and their peaks are recorded in the chromatogram. After elution of all anions and establishment of baseline, the oxidizer is injected in the system and quantitatively transforms initially retained chromium cations into chromate ions. The peak of the latters is well separated from the peaks of oxidizer anions and recorded with the corresponding retention time counted from the moment of reactant injection (Fig. 8).

The described method has satisfactory sensitivity and selectivity of determination of the chromium species in different aqueous solutions. Simultaneous determination of chromium ions in different oxidation states and inorganic anions (Cl^-; SO_4^{2-}; NO_3^-; $Cr_2O_7^{2-}$; Cr^{3+}) may be implemented under conditions presented in notes to Fig. 8.

Method M6: Method of Numerical Simulation of IC

The problems of increase of the reliability of ion chromatographic method were considered in (Kolotilina et al., 2007, 2008), where their solution with application of theoretical knowledge and numerical modeling using computer softwares is demonstrated by the example of complex natural and archeological objects. The main developments of the models and theoretical approaches to the description of the high-performance chromatography methods are given in (Dolgonosov et al., 1993, 2013, 2015).

Principles and possibilities of mathematical description based on the theory of sorption dynamics adopted to the ion chromatographic (IC) features were described in (Dolgonosov and Ippolitova, 1993; Dolgonosov, 1994; Prutkovskii and Dolgonosov, 1999; Dolgonosov et al., 2001; Dolgonosov and Prudkovskii, 2002; Dolgonosov et al., 2007; Prudkovskii, 2013; Dolgonosov and Prudkovskii, 2013). An **Ion-Chrom**© software was developed using a DELPHI algorithm (Dolgonosov and Prudkovskii, 2002). The program was applied to solve the direct, optimization, and inverse problems of multicolumn IC with isocratic and gradient elution (Dolgonosov and Prudkovskii, 2002, 2013; Dolgonosov et al. 2007; Prudkovskii, 2013).

A scheme of ion chromatograph (Fig. 9) taken for modeling contains following elements:

1. Eluants: eluant 1—solvents, eluant; 2—acids, eluant; 3—a set of bases;
2. Mixer of flows for obtaining the required composition of mobile phase;
3. High-pressure pump;
4. Injector;
5. Separation column;
6. Suppressor;
7. Conductivity detector and connecting pipes;
8. Computer calculations and data processing.

IONCHROM program is universal enough to simulate ion chromatography, to choose conditions, and

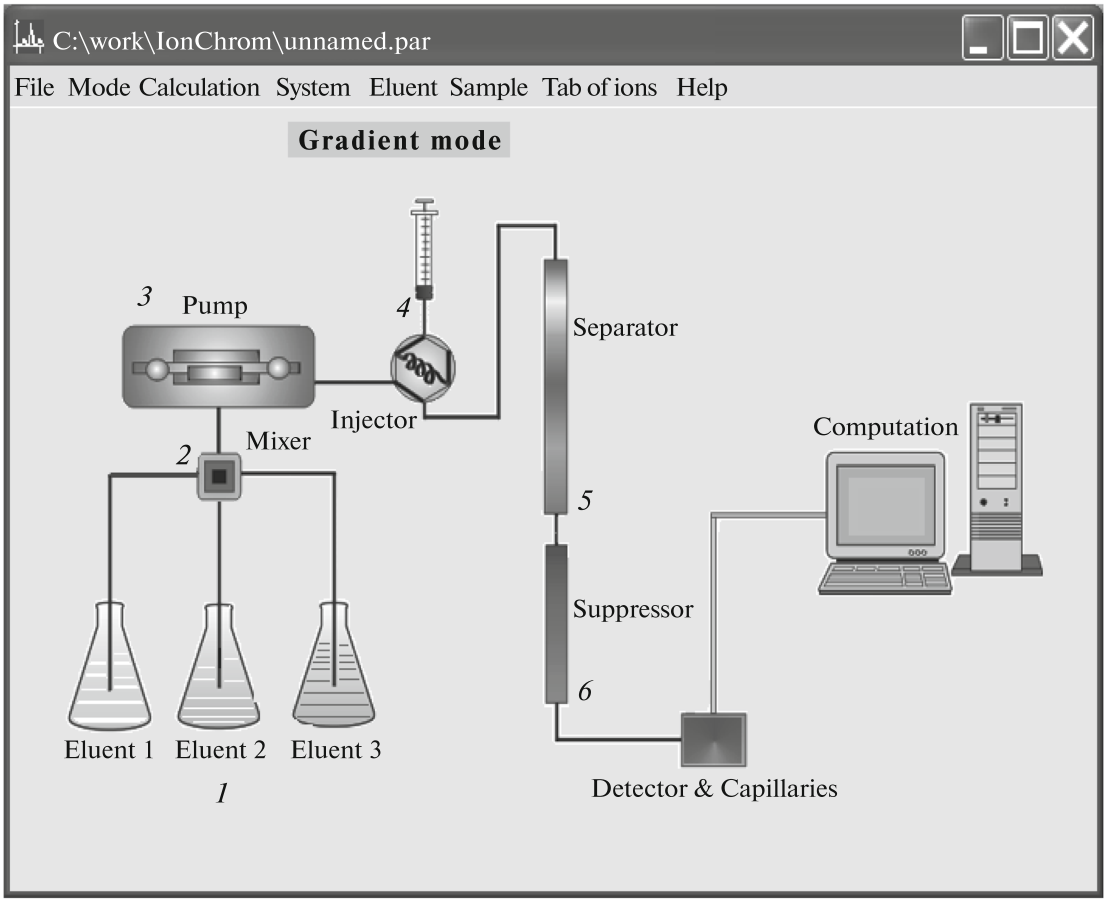

Fig. 9. Scheme of ion chromatograph taken for modeling.

to predict the results of separation on ion chromatographs of different types (Dolgonosov et al., 2007).

Application of Methods M1–M6 in Analyzing the Natural Objects

The application of method M1 provided direct determination of boron at MPC level in potable water (Fig. 10) and even in seawater at corresponding dilution (Kolotilina and Dolgonosov, 2005).

The anions of strong acids do not interfere with boron. The retention time of chloride, which is the main component of all natural and potable waters, is approximately 25 min, which allows the successive analysis of three samples of weakly mineralized waters for borate ions before the elution of interfering peaks. Sulfate- and nitrate ions are retained so strictly that the corresponding peaks are diffuse and do not interfere with the analysis.

Method M2 makes it possible to determine the trace components interfered by peaks of major components both in potable and strongly mineralized waters. Figure 11 demonstrates the determination of iodate and fluoride ions in a mixture, which is very

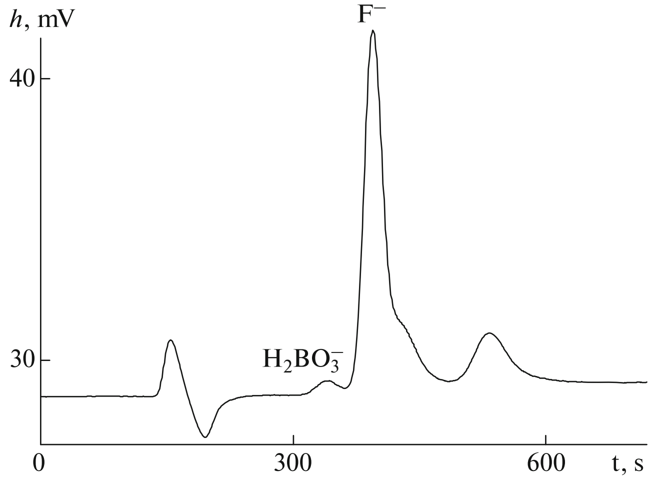

Fig. 10. Chromatogram of boron determination at 0.1 mg/L level in potable water. Chromatograph Tsvet 3006. Three-column scheme: separation column 120 × 5 mm with KanK-ASt, suppression column 120 × 5 mm with cationite Dowex 50 × 5 mm in the hydrogen form, eluent column 100 × 3 mm with cationite SPS-SAC(8). Eluent 2.5 mM NaOH, flow rate of 1.9 mL/min, sample loop volume 300 μL.

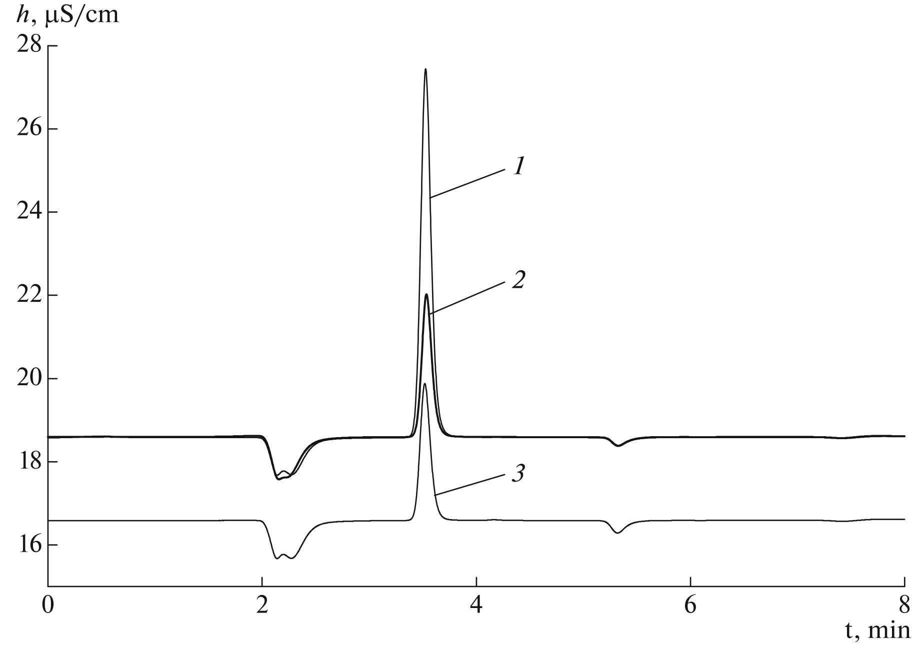

Fig. 11. Determination of iodate- (10 mg/L) and fluoride- (2 mg/L F^-) ions. *1*—Total peak at the first stage; 2—peak of unsorbed iodate ion at the second stage; *3*—peak of standard solution with iodate concentration of 10 mg/L, obtained in independent experiment. Chromatograph METROHM 883 Basic IC plus, separation column Metrosep A Supp 5—150/4.0 with precolumn Metrosep A Supp 4/5 Guard/4.0, cluster with three miniature suppression columns MSM. Elution rate of 0.7 mL/min, sample volume—20 μL.

important task during analysis of mineral water, since both these components have great physiological significance. However, these anions always have similar retention time: under different conditions of ion chromatography and for different separation columns. A method of absorption columns is suitable to determine these trace components in mineral waters.

In the model experiment with sample containing 2 mg/L F^- and 10 mg/L IO_3^- we at first calculated the area of the total peak (curve *1*) and then calculated the area of peak of iodate remained after fluoride consumption by SC (curve *2*). To determine the completeness of determination, we draw curve *3*—results of determination of iodate ion standard (10 mg/L) by conventional technique. The content of the iodate ion in natural waters is usually two to three orders of magnitude lower, which makes its determination more sensitive to interfering components.

It is difficult to determine nitrite pollutant against the background high chloride concentrations in strongly mineralized waters. We analyzed model solution containing 10 mg/L nitrite and 1.8 g/L chloride (Fig. 12). As seen from the figure, the large peak of chloride removed by described method contains peak, whose retention time, shape, and intensity correspond to nitrite obtained from individual solution with concentration. The selectivity coefficient of the chloride/nitrite pair is about 200, which has been previously reached using off-line sample preparation procedure.

Method M4 developed for the simultaneous highly selective determination of anions and cations seemed to be very suitable for express analysis of natural, potable, and mineral waters. An example of such analysis is given below (Fig. 13). Based on the results of 21-minute analysis, the "Lipteskii byuvet" natural potable water contains (mg/L): fluoride—0.086, chloride—10.5, bromide—0.253, nitrate—6.35, sulfate—7.18, calcium ions—27.4, magnesium—5.70; ions of zinc and copper, nitrite, and phosphate are absent (less than 0.05—0.1 mg/L).

Implementation of the considered principle provides the high sensitivity and selectivity in the determination of transition metal ions, for instance, during analysis of sea water (Dolgonosov, 1994).

Methods M1, M3, and M6 were applied to the analysis of complex geological object—fumarolic gases in form of condensates and alkaline concentrates (Kolotilina et al., 2007, 2008). Samples for analysis and primary data on the object were given by M.E. Zelensky (Institute of Experimental Mineralogy of the Russian Academy of Sciences). Volcanic (fumarolic) gases are formed during release of volatile components from magma. The main gas component is water vapor (90—99%). In addition to water, the gases also include acid components (CO_2, SO_2, H_2S, HCl,

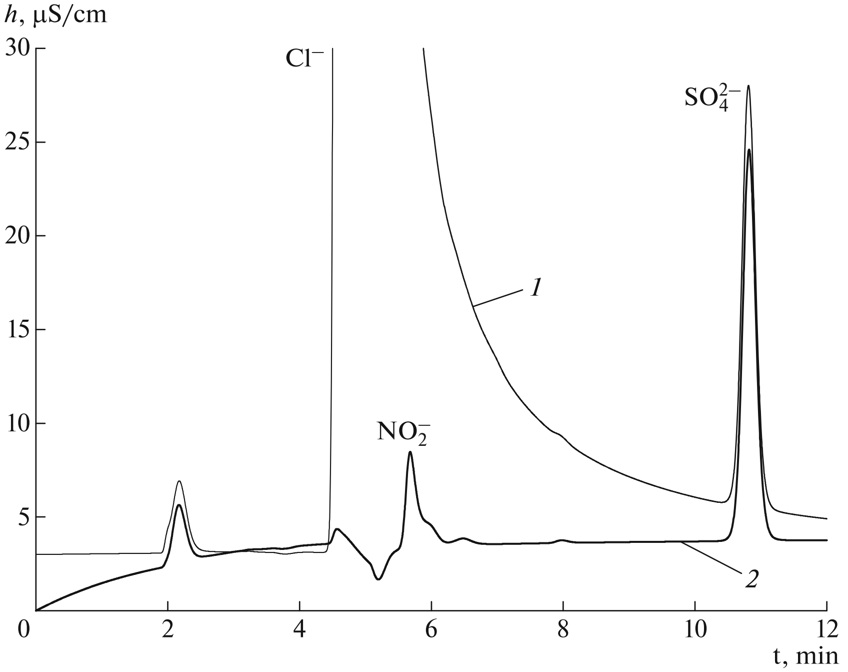

Fig. 12. Determination of trace component nitrite-ion (10 mg/L) against 180-fold excess of chloride-ion (1.8 g/L). *1*—basic chromatogram; *2*—chromatogram after SC treatment by Ag^+ ions. Chromatograph METROHM 883 Basic IC plus, separating column Metrosep A Supp 5—150/4.0 with precolumn Metrosep A Supp 4/5 Guard/4.0, cluster with three suppression columns MSM. Elution rate of 0.7 mL/min, sample volume of 20 μL.

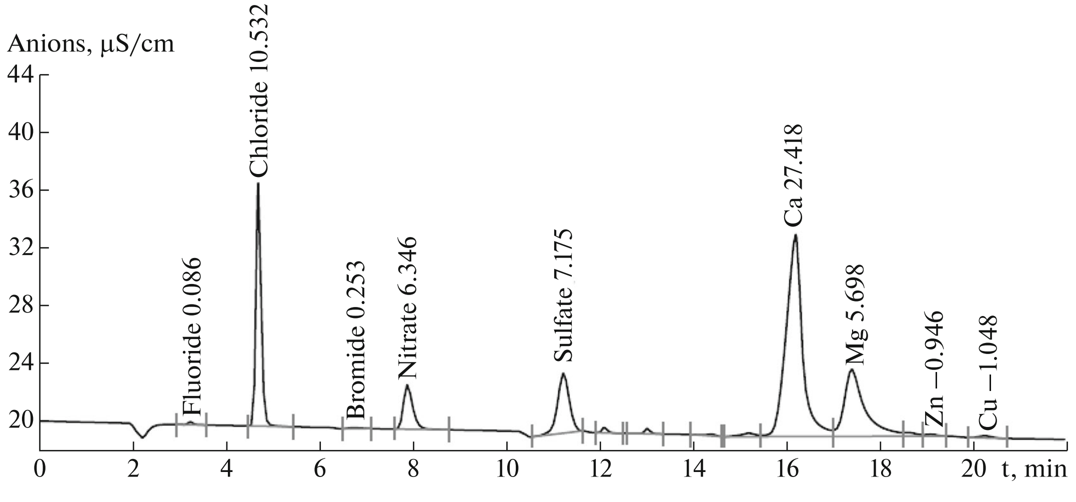

Fig. 13. Analysis of “Lipetskii byuvet” potable water. Chromatograph METROHM 883 Basic IC plus, separation column Metrosep A Supp 5—150/4.0 with precolumn Metrosep A Supp 4/5 Guard/4.0, cluster with three suppressing columns MSM. Elution rate of 0.7 mL/min, sample volume—20 μL.

HF), with lesser amounts of H_2, N_2, O_2, HBr, HI, inert gases, hydrocarbons, and ammonia, and volatile compounds of some metals. Samples were taken from gas condensate and by absorption of volcanic gases with 4M potassium hydroxide solution. A list of the components to be determined is as follows:

1. Possible ionic species of sulfur: sulfide, sulfite, sulfate, and thiosulfate anions;

2. Halogenides: fluoride-, chloride, and bromide ions;

3. Ammonium ion.

Two column chromatographic system with conductivity detector was taken as the basic technique for the determination of most medium-retained anions (Fig. 1). The measurements were conducted on a Tsvet-3006 chromatograph (DOKBA, RF).

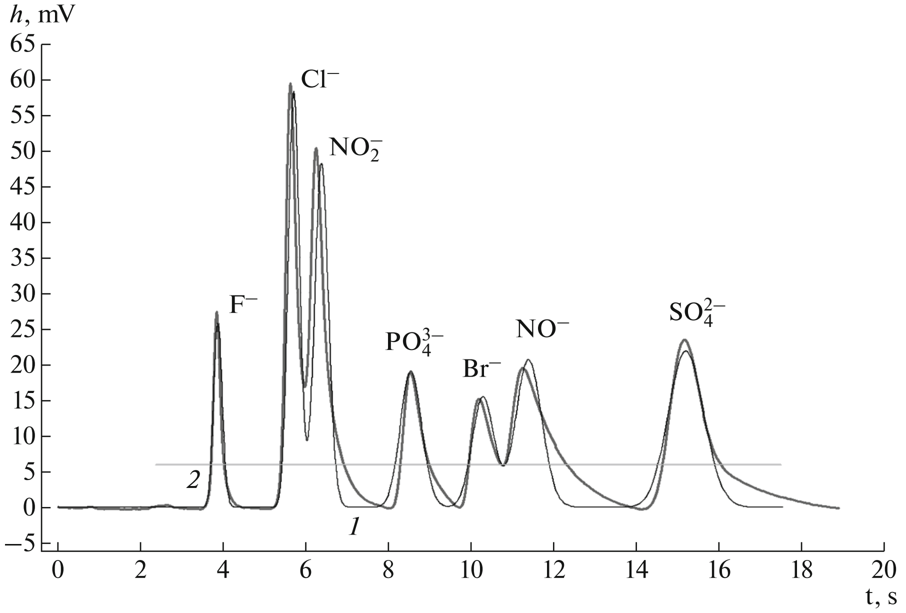

Fig. 14. Chromatogram of the separation of a model mixture of seven anions with concentrations (mg/L): fluoride—2, chloride—10, nitrite—15, phosphate—25, bromide—15, nitrate—20, sulfate—20: *1*—experimental; *2* –theoretical. Two-column scheme: separation column 120 × 5 mm with KanK-ASt grain size of 14 μm, capacity of 0.01 mequiv/mL; suppression column 100 × 10 mm with SPS-SAC particle size 50 μm in the H-form. Composition of eluant: 2.5 mM Na_2CO_3, 3.0 mM $NaHCO_3$, flow rate 1.7 mL/min. Sample volume—30 μL.

With respect to the basic technique, the presented above mixture was qualified as containing polymorphic element (sulfur) and two elements that are undetectable under given conditions (sulfide and ammonium ions). Additional methods are required to determine the latter components.

IONCHROM software was calibrated for numerical simulation of chromatographic analysis of object by basic technique. When corresponding initial data were input in the program, the correctness of modeling was testified by the comparison of theoretical and experimental chromatograms of separation of basic mixture of seven medium-retained anions (Fig. 14).

The comparison of the retention times of anions of a model mixture of seven anions, sulfite, and thiosulfate, during separation by basic method allowed us to specify the character of the analyzed object, which, in addition, could contain two hardly separable anions (bromide and sulfide) and strongly retained thiosulfate ion with retention time around an hour (Table 1).

After complete description of the object as a mixture of ions, including undetectable polymorphic components, a pair of hardly separatable anions, and one strongly retained component, we compiled a plan of experiments (including numerical simulation) on solving this analytical task:

1. determination of fluoride, chloride, and sulfate anions by basic technique;
2. choice of conditions for separation of bromide and sulfite anions using numerical method;
3. identification of components of fumarolic gas condensates under new elution conditions;
4. choice of conditions of thiosulfate determination using numerical method;
5. determination of thiosulfate in sample;
6. determination of sulfide in the fumarolic gas condensate using technique for weakly dissociating acids;
7. determination of ammonium ion using highly selective method.

Results of experiment on the determination of main anions in a sample are presented in Fig. 15.

Fluoride, chloride, and sulfate anions present in sample were identified and quantitatively determined. In terms of retention time, the fourth peak of chromatogram in Fig. 15 may be ascribed to both bromide and sulfate ions, however the joint presence of bromide and sulfite is also possible.

Table 1. Retention time of some anions under conditions of standard experiments.

Anion	Retention time, s
Br^-	583 ± 7
SO_3^-	582 ± 7
$S_2O_3^{2-}$	≈3600

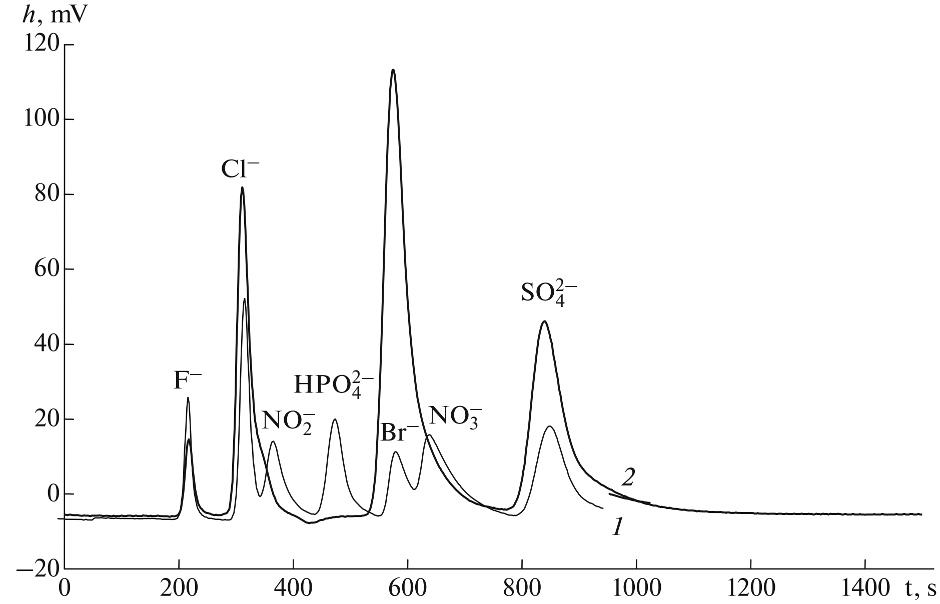

Fig. 15. Chromatograms of a model mixture of seven anions (*1*) with concentrations of components (mg/L): fluoride—2, chloride—10, nitrite—15, phosphate—25, bromide—15, nitrate—20, sulfate—20; 100-fold diluted sample (*2*).

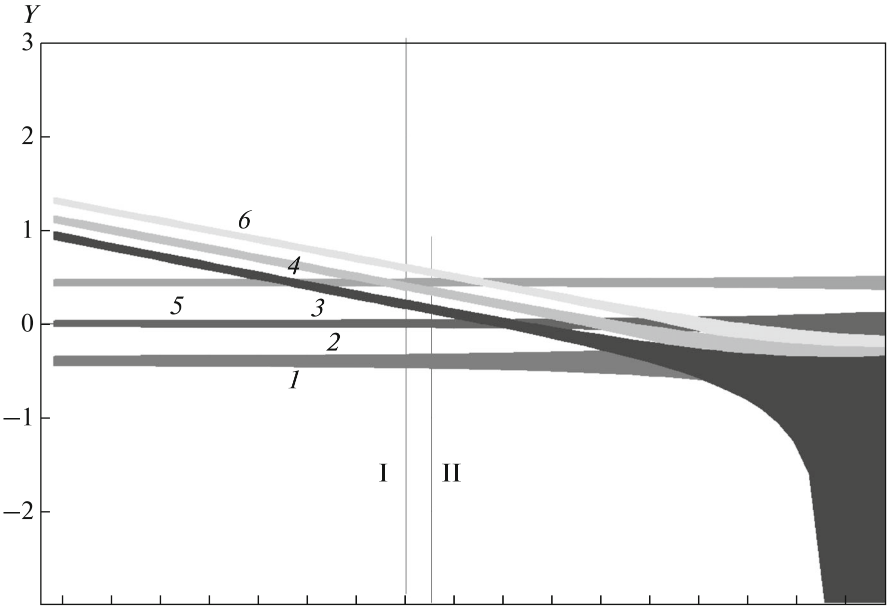

Fig. 16. Dynamic map of chromatographic system. Logarithmic coordinates: Y—selectivity, X—eluent power. Correspondence of DMCS bands to the separated anions: *1*—fluoride, *2*—chloride, *3*—phosphate, *4*—sulfite, *5*—bromide, *6*—сульфат. Vertical line I corresponds to the initial separation conditions: eluent 2.5 mM Na_2CO_3 and 3.0 mM $NaHCO_3$ (sulfite and bromide bands are overlapped). Vertical line II is drawn in the region of band resolution. New eluent—3.2 mM Na_2CO_3 and 3.3 mM $NaHCO_3$.

Conditions of separation of these components were determined using IONCHROM software. Numerical experiment allowed us to obtain a theoretical chromatogram of a mixture containing weakly separable anion pair (basic technique) and a dynamic map of the chromatographic scheme (DMCS). This map demonstrates all possible variations of separation of the given ionic mixture in the given chromatographic system, which allows the rapid correction of eluent composition and finding the conditions of the separation of the considered anion pair. Such conditions are met in the diagram region, where bands corresponding to sulfite (4) and bromide (5) are not overlapped.

Vertical line *I* in Fig. 16 is shown in compliance with the composition of standard eluent: 2.5 mM Na_2CO_3 and 3.0 mM $NaHCO_3$. Vertical line *II* was

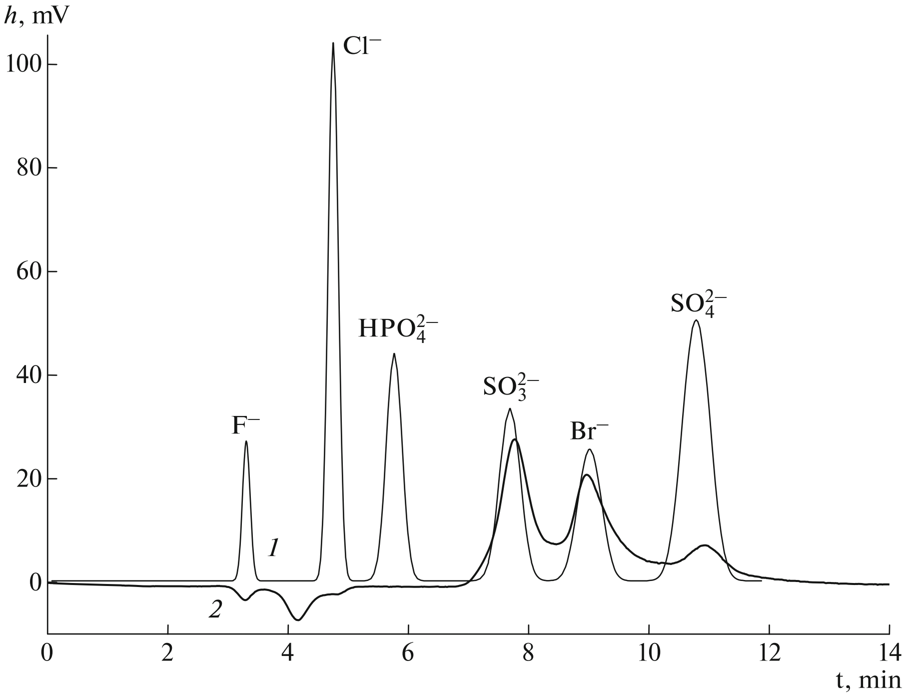

Рис. 17. Chromatograms: *1*—theoretical, separation of anionic mixture with concentrations (mg/L): fluoride—2, chloride—10, phosphate—25, sulfite—20, bromide—15, sulfate—20. Chromatogram *2*—experimental, separation of anionic mixture with concentrations (mg/L):: sulfite—20, bromide—15, sulfate—3. Separation column 120 × 5 mm, KanK-Ast; suppression column 100 × 10 mm, SPS-SAC in the H^+—form. Composition of eluent—3.2 mM Na_2CO_3 and 3.3 mM $NaHCO_3$, flow rate 1.7 mL/min. Sample volume 30 μL.

drawn in the nearest region of the resolution of bromide and sulfate anions bands. The intersection point of vertical line with x-axis determined a new composition of eluent: 3.2 mM Na_2CO_3 and 3.3 mM $NaHCO_3$.

Under determined separation conditions, we performed numerical and natural experiments on the separation of model anion mixture containing both SO_3^{2-} and Br^-. Figure 17 demonstrates the calculated and experimental chromatograms.

Further experiments were carried out to identify bromide and sulfite in the fumarolic gas condensate. The studies showed that the sample contains sulfite ion and no bromide-ion (Fig. 18).

Numerical method M6 was used again to find conditions for determination of strongly retained thiosulfate ion. Using DMCS, we determined the composition of eluent at which the retention time of thiosulfate decreases to 14 minutes. Theoretical chromatogram of separation of the anion mixture (F^-, Cl^-, PO_4^{2-}, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$) was calculated for new conditions. Experiment on the determination of thiosulfate ion in samples was carried out under the same conditions. The comparison of theoretical and experimental chromatograms is given in Fig. 19

Sulfide and ammonium ions are not detected using selected basic method. In order to determine the sulfide ion, we applied method M1, according to which the eluent column with cationite in the hydrogen form was installed beyond the suppressor in the potassium form. Resultant weakly dissociating hydrosulfuric acid was conversed in well-conductive potassium salt and the sensitivity of determination sharply increased. Figure 20 shows the results of the determination of sulfide ion in sample.

Method M3 was used to determine the ammonium contents in samples. Suppressor in the hydrogen form is applied as postcolumn reactor, whereas nitrite ion was involved in the composition of alkaline eluent. Ion exchange separation of anions was used prior to sample injection in chromatograph. Ammonium ion was determined as a negative peak against the highly conductive eluent.

Results of determination of ammonium ion in sample with described method are shown in Fig. 21.

Results of the solution of the analytical task are presented in Table 2.

CONCLUSIONS

This work presents some results of studies of the Laboratory of Sorption Methods in the theoretical and practical IC, including the development of new methods (M1—M6) for sensitive and highly selective determination of ionic composition and chemical analysis of complex natural objects.

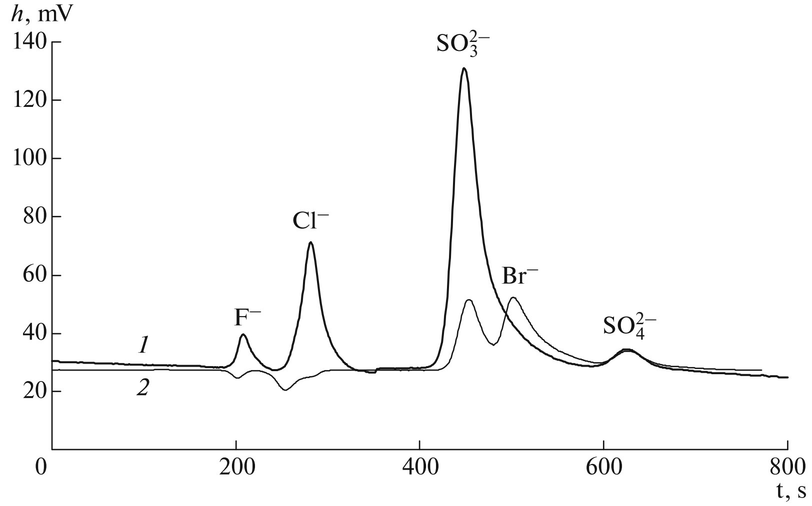

Fig. 18. Chromatograms: *1*—studied sample of fumarolic gas condensate 100-fold diluted; *2*—standard solution containing 20 mg/L bromide-ion and 15 mg/L sulfate-ion. Separation column 120 × 5 mm, KanK-ASt; suppression column 100 × 10 mm, SPS-SAC in the H-form. Composition of eluent 3.2 mM Na_2CO_3 and 3.3 mM $NaHCO_3$, flow rate 1.7 mL/min. Sample volume 30 μL.

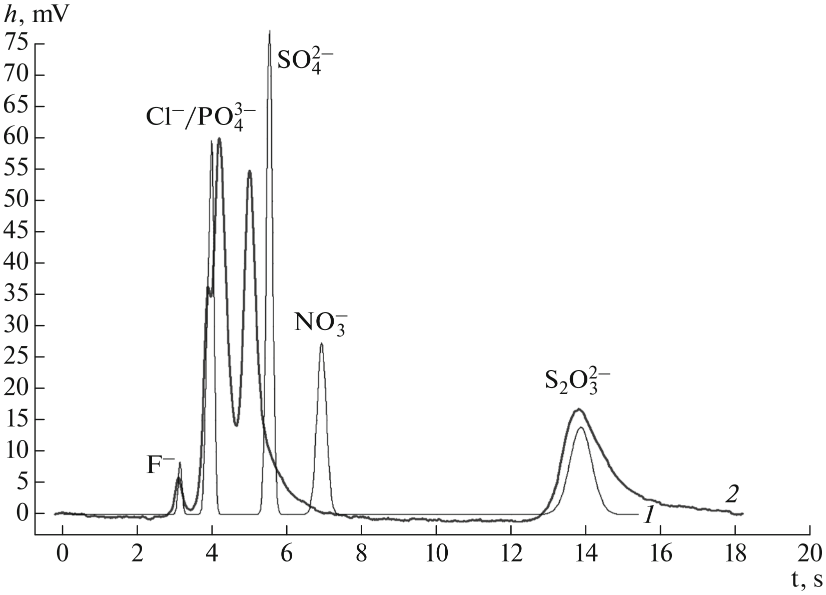

Fig. 19. Calculated (*1*) and experimental (*2*) chromatograms for conditions of thiosulfate determination. Calculation was carried out for a mixture of anions with concentrations (mg/L): fluoride—2, chloride—10, phosphate - 25, sulfate—20, thiosulfate—20. Experiment was carried out for 100-fold diluted sample. Separation column 120 × 5 mm, KanK-ASt; suppression column 100 × 10 mm, SPS-SAC in H^+—forme. Eluent—13.42 mM Na_2CO_3 and 3.84 mM $NaHCO_3$, elution rate of 1.6 mL/min. sample volume of 30 μL.

A described systematic procedure of the ion chromatographic analysis of condensate of fumarolic gases demonstrated the efficiency of applied methodology of analyzing the multicomponent electrolyte solutions. Our studies were planned on the basis of a priori characteristics of object and analytical task. Numerical IC modeling using corresponding program became an important part of the analytical procedure. The

Table 2. Results of anion determination in the condensate of fumarolic gases

Ions, g/L						
F^-	Cl^-	SO_3^{2-}	S^{2-}	SO_4^{2-}	$S_2O_3^{2-}$	NH_4^+
0.10 ± 0.01	1.70 ± 0.05	10.5 ± 0.5	0.90 ± 0.04	2.2 ± 0.2	7.0 ± 0.5	0.004 ± 0.001

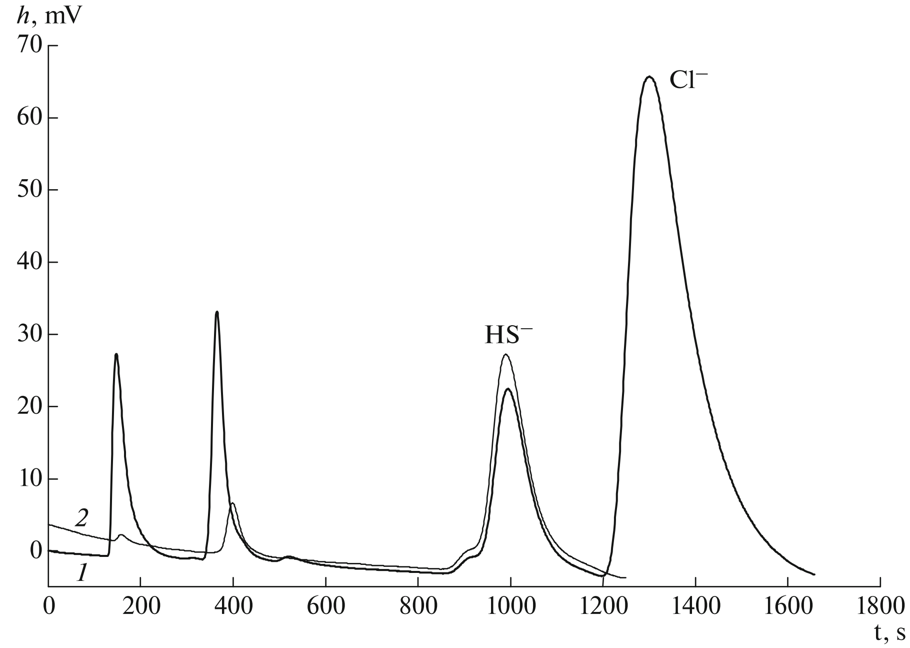

Fig. 20. Chromatograms: *1*—110-fold diluted sample; *2*—model solution of sodium sulfide with sulfur concentration of 9.6 mg/L. Peaks of components with retention time up to 600 s were not identified. Separation column 120x5 mm, KanK-ASt, suppression column 120 × 5 mm, SPS-SAC-8 in the H^+-form, eluent column 100 × 3 mm, SPS-SAC-8 in the K^+-form. Eluant 3 mm NaOH, flow rate 1.9 mL/min. Sample volume of 30 μL.

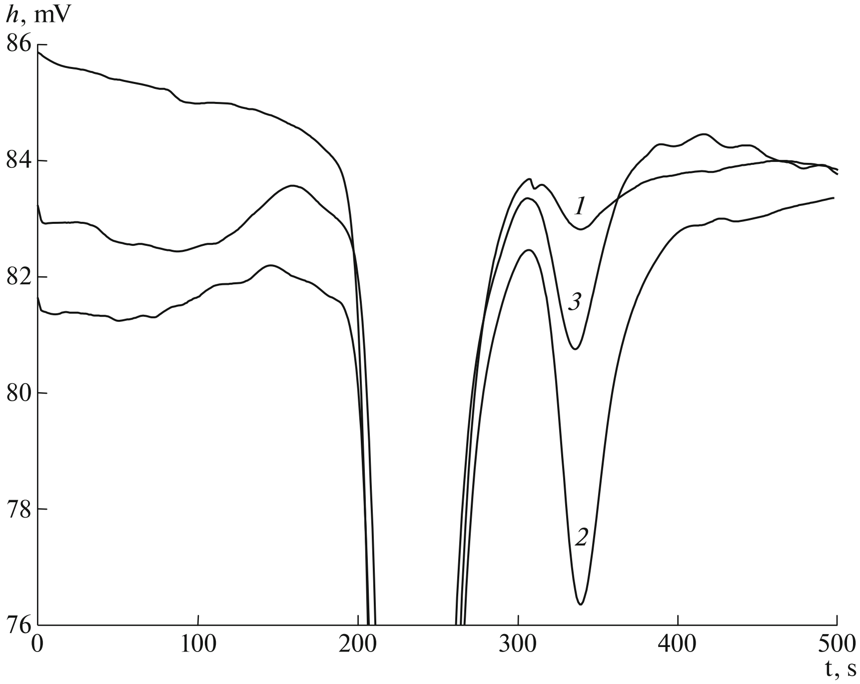

Fig. 21. Chromatograms: *1* and *2*—model solutions of ammonium ion with concentrations 1.8 and 10 mg/L, respectively; *3*—analyzed sample, 10-fold diluted. Separation column: 100 × 4 mm, KanK-BP; suppression column 100 × 8 mm, SPS-SAC-8 in the H^+-form. Eluent: 4.8 mM NaOH and 1.1 mM $NaNO_2$, flow rate of 1.2 mL/min. Sample volume 30 μL.

application of IONCHROM software allowed us to solve the problems of identification of complex ionic mixtures and to improve the quality of analysis, minimizing routine procedures.

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