

Matrix Influences on the Determination of Common Ions by using Ion Chromatography Part 1—Determination of Inorganic Anions

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Ion chromatography is the most popular instrumental analytical method used for the determination of anions and cations in water and wastewater. Isocratic ion chromatography with suppressed conductivity detection is frequently used in laboratories carrying out routine analyses of inorganic anions. The paper presents the results of the research into the influence of selected inorganic anions dominant in environmental samples (Cl^- , NO_3^- , SO_4^{2-}) on the possibility of simultaneous determination of F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} with the application of this most popular ion chromatography type in standard separation conditions. Four Dionex and four Metrohm anion-exchange columns were tested in standard separation conditions recommended by their manufacturers with both standard solutions and environmental samples with complex matrix.

Introduction

Chromatography as a separation method had been known since the beginning of the twentieth century, yet its rapid development took place approximately fifty years later. Presently, chromatographic methods are among the most common instrumental methods in analytical chemistry, because they allow quick separation and determination of substances in complex matrix samples.

Currently used ion determination methods (titration, gravimetric, colorimetric, electrolytic and other methods) are cheap and readily available, but they are also laborious and often require the use of toxic reagents. On the other hand, until the 1970s, the chromatographic methods were almost solely used for the separation and determination of organic compounds. Research into the application of chromatographic methods for separation of inorganic substances was intensively conducted during WWII within the framework of the atomic bomb construction works (the Manhattan Project). Nevertheless, the breakthrough was achieved in 1971, when Small and his team propounded and examined the chromatographic method of lithium, sodium and potassium separation with ion exchange and conductivity detection (1).

Ion chromatography (IC) in which high-performance analytical columns filled with small-diameter homogenous particles, and often conductivity detection, are employed originates from ion-exchange chromatography (2). Compared to the traditional ion-exchange chromatography, ion chromatography is more efficient, faster and more sensitive and provides suitable result repeatability. Its popularity results from its various advantages, among which the most important are:

- (i) The possibility of the simultaneous determination of several ions within a short time (5–30 min);
- (ii) A small amount of the sample required for the analysis (approximately 0.1 mL);
- (iii) The possibility of deploying various detectors (conductivity detectors, UV-Vis, amperometric, potentiometric, fluorescence, chemiluminescence and mass spectrometry) (3);
- (iv) A simple method of sample preparation (4);
- (v) The possibility of simultaneous determination of cations and anions or organic and inorganic ions;
- (vi) High selectivity of separation;
- (vii) The possibility of determining ions of the same element with different oxidation states (speciation analytics) (5, 6); and
- (viii) Safety and low costs (green chemistry).

These characteristics contributed to the fact that many standardized methodologies (used for the determination of anions and cations in water and wastewater) were elaborated soon after ion chromatography was established (7).

Ion chromatography evolved from a relatively simple method of determination of inorganic ions at the level of mg/L concentrations into an elaborate method of separation and determination of organic and inorganic substances at the trace level (8), including analyses of complex matrix samples (9). Ion chromatography (the same as other chromatographic methods) is most efficient when the sample matrix is not too complex and the analyzed samples contain analytes whose specific concentrations are similar. The situation becomes more complicated when real samples are analyzed. In this case, the concentrations of specific analytes vary. Moreover, the complex sample matrix hinders or even precludes proper ion separation and hence, their reliable determination.

In such a situation, a suitable preparation of the sample for the analysis is necessary (10). Unfortunately, in the laboratory practice, especially in the case of routine analyses, analysts do not have either time or access to the sophisticated methods of sample preparation that eradicate the interferences that hinder determination processes. If, for various reasons, no sophisticated sample preparation method is employed (except for indispensable filtration), the optimization of the separation process may be the best method to use for obtaining reliable analysis results. This consists of the selection of a suitable analytical column, eluent type and concentration, as well as its pH and flow rate. Regrettably, even these possibilities are limited if a given laboratory possesses only one analytical column and a

sole conductivity detector. Under such circumstances, the options are limited to the changes of the eluent concentration and/or its flow rate.

The primary issue in the application of ion chromatography for analysis of real samples (e.g., water and wastewater) is related to the matrix composition, including the necessity of the simultaneous determination of F^- , NO_2^- and PO_4^{3-} anions in the presence of high concentrations of anions dominant in environmental samples such as Cl^- , NO_3^- and SO_4^{2-} (11).

A similar problem occurs in the process of determination of inorganic cations, i.e., a suitable separation of K^+ , NH_4^+ and Mg^{2+} ions in the presence of excess Na^+ or Ca^{2+} ions.

Anion exchangers contain alkanol or alkyl quaternary amine functional groups, and the variation in their selectivity has been obtained by modifying the structures of the ion-exchange sites. Anion exchangers are divided into polymer-based anion exchangers [styrene–divinylbenzene (PS–DVB), ethylvinylbenzene–divinylbenzene (EVB–DVB), polymethacrylate and polyvinyl copolymers], latex-agglomerated anion exchangers, silica-based and others (12). Stationary phases used in ion chromatography differ, not only in the type of support material, but also according to their different pore sizes and ion-exchange capacities.

Isocratic elution with carbonate eluents is the most commonly used version of ion chromatography. Since the introduction of gradient elution in ion chromatography in 1987, hydroxide-selective latex-based anion exchangers have also been developed.

The experience of over twenty years and the contacts with laboratory workers that conduct water and wastewater analyses with ion chromatography on a regular basis have convinced the authors of this article that laboratory staff most often make use of standard analytical conditions recommended by the column manufacturers. Additionally, there is frequently either no time or no willingness to carry out optimization processes for specific types of matrices. These facts have persuaded the authors to examine eight typical anion-exchange columns that have dominated the ion chromatography market, i.e., columns produced by American company Dionex (Sunnyvale, CA) and Swiss company Metrohm (Herisau, Switzerland).

Both manufacturers produce and sell anion-exchange and cation-exchange columns that differ in terms of their stationary phases, and consequently the applied eluent, its flow rate and the possibility of the application of organic modifiers. Both standard solutions of inorganic ions with variable concentrations and environmental samples with complex matrices were used in the course of the examination. The inorganic anions that dominate in environmental samples are Cl^- , NO_3^- and SO_4^{2-} ions. It often occurs that their high concentrations hinder or preclude the determination of other anions present in the sample (e.g., F^- , NO_2^- , ClO_2^- , BrO_3^- and Br^-). The aim of the research was to define the influence of the increasing concentration of the primary inorganic anions (Cl^- , NO_3^- and SO_4^{2-}) on the possibility of simultaneous separation and determination of other anions (such as F^- , NO_2^- and PO_4^{3-}) with the employment of the standard separation conditions recommended by the column manufacturers.

Experimental

The following apparatus was used in the course of examinations: Metrohm ion chromatograph equipped with: IC 818 pump; IC 837 eluent degasser; IC 830 interface; IC 820 separation center; Valco injection valve; Metrodata 2.3 software; IC 838 autosampler; MSM suppressor and IC 819 conductivity detector.

Reagents

$NaHCO_3$ and Na_2CO_3 with analytical purity produced by Fluka (Steinheim, Switzerland) were used to prepare eluents. Eluents with suitable compositions and concentrations recommended by the column manufacturers were prepared by weighing proper $NaHCO_3$ and/or Na_2CO_3 sample masses. Afterward, they were dissolved in a 2-liter laboratory flask and diluted to obtain the value of the specified concentration.

Solutions produced by Fluka were employed to prepare standard solutions of particular anions (F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-}) at the concentration level of $1,000 \pm 2$ mg/L. Water used for the eluent preparation came from a Millipore deionizer (Bedford, MA) and had electrical conductivity < 0.05 $\mu S/cm$. Calibration solutions were prepared with the dilution of the suitable standard solutions just before their application. All solutions were stored in high-density polyethylene (HDPE) vessels at room temperature.

Anion-exchange columns

Four Dionex anion-exchange columns (IonPac AS4-SC, IonPac AS9-HC, IonPac AS14 and IonPac AS22) and four Metrohm anion-exchange columns (Metrosep A Supp 1, Metrosep A Supp 3, Metrosep A Supp 5 and Metrosep A Supp 7) were chosen from the variety of anion-exchange columns produced by the primary global manufacturers of ion chromatography apparatus and accessories. Their detailed characteristics, encompassing data such as the type of the stationary phase, dimensions, pH range of the eluents used, the possibility of the application of eluent organic modifiers, exchange capacity, diameters of stationary phase particles, recommended eluents and flow rates are presented in Table I. The column selection depended, on one hand, on the popularity of their application in the laboratories that perform routine water and wastewater analyses, and on the other hand, on the diversity of column qualities, especially in terms of the exchange capacity.

Seven standard solutions of inorganic anions with the invariable content of fluoride, nitrite and phosphate ions and the increasing amount of the primary anions, i.e., chloride, nitrate and sulfate ions, were prepared. Their composition, given in Table II, was arranged in such a way that it was similar to the composition of the selected real samples analyzed with ion chromatography and that it would not cause the analytical column to overload.

The standard samples, numbered 1–7, underwent chromatographic analysis in the standard separation conditions recommended by the manufacturer of a given analytical column. The obtained results are presented in Figures 1–8.

The second stage of the research consisted of the examination of the analytical columns by means of real samples with

Table I

Characteristics of the Examined Anion-Exchange Columns

Column name	Metrosep A Supp 1	Metrosep A Supp 3	Metrosep A Supp 5	Metrosep A Supp 7	IonPac AS4-SC	IonPac AS 14	IonPac AS9-HC	IonPac AS 22
Manufacturer	Metrohm				Dionex			
Stationary phase type	PS–DVB copolymer with quaternary ammonium groups	PS–DVB copolymer with quaternary ammonium groups	Polyvinyl alcohol with quaternary ammonium groups	Polyvinyl alcohol with quaternary ammonium groups	EVB–DVB copolymer with quaternary ammonium groups and latex particles	EVB–DVB copolymer with quaternary ammonium groups	EVB–DVB copolymer with quaternary ammonium groups and latex particles	EVB–DVB copolymer with quaternary ammonium groups and latex particles
Column dimensions (mm)	250 × 4.6	250 × 4.6	250 × 4.0	250 × 4.0	250 × 4.0	250 × 4.0	250 × 4.0	250 × 4.0
pH range	1–13	1–13	3–12	3–12	0–14	2–11	0–12	0–14
Resistance to organic solvents (%)	100	100	100	100	100	100	100	100
Exchange capacity (μM Cl ⁻)	64	33	107	108	20	65	190	210
Particles diameter (μm)	7	9	5	5	13	9	9	6.5
Recommended eluent	3.0 mM Na ₂ CO ₃	1.7 mM NaHCO ₃ + 1.8 mM Na ₂ CO ₃	1.0 mM NaHCO ₃ + 3.2 mM Na ₂ CO ₃	3.6 mM Na ₂ CO ₃ + 2% acetone	1.7 mM NaHCO ₃ + 1.8 mM Na ₂ CO ₃	1.0 mM NaHCO ₃ + 3.5 mM Na ₂ CO ₃	9.0 mM Na ₂ CO ₃	1.4 mM NaHCO ₃ + 4.5 mM Na ₂ CO ₃
Recommended eluent flow (mL/min)	1.0	1.0	0.7	0.8	2.0	1.2	1.0	1.2
Recommended for the determination of	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and SCN ⁻ ; SO ₃ ²⁻ , ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₄ ⁻ and CN ⁻ and S ²⁻ ions (amperometric detection)	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and SCN ⁻ ; SO ₃ ²⁻ , S ₂ O ₃ ²⁻ and polyphosphates	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , CrO ₄ ²⁻	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , ClO ₄ ⁻ , CrO ₄ ²⁻ dichloroacetic acid	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and SCN ⁻ , SO ₃ ²⁻ , SO ₃ ⁻ and SO ₄ ²⁻	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , BrO ₄ ⁻ , CrO ₄ ²⁻ recommended for analysis of BrO ₃ ⁻ ions	Main inorganic anions: F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ and ClO ₂ ⁻ , ClO ₃ ⁻ , ClO ₄ ⁻ , BrO ₃ ⁻ , BrO ₄ ⁻ , CrO ₄ ²⁻

Table II

Quantitative and Qualitative Composition (mg/L) of Standard Samples of the Selected Inorganic Anions

Sample	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
1	0.5	10	2.0	5	5.0	10
2		50		25		50
3		100		50		100
4		150		75		150
5		200		100		200
6		250		125		250
7		300		150		300

complex matrix. They encompassed samples of coal mine water from the Maciej Shaft (in Zabrze, Poland), whose content of Cl⁻ and SO₄²⁻ is very high, and water collected from the Bytomka River (in Zabrze, Poland), which is the place of wastewater discharge for many plants in the Upper Silesia. The physico-chemical composition of Maciej Shaft and Bytomka river water samples is given in Table III.

Chromatograms of inorganic anions in the analyzed real samples obtained for the tested analytical columns, together with the chromatogram of standard Sample 1, which serves as the reference sample, are presented in Figures 9–16. The effect of eluent concentrations on the quality of the separation of major inorganic anions using the two selected columns, Dionex and Metrohm, are shown in Figures 17 and 18.

Results and Discussion

The aim of the work was not to choose which of the IC manufacturers produce better columns, but to define the influence of the increasing concentration of the primary inorganic anions (Cl⁻, NO₃⁻ and SO₄²⁻) on the possibility of simultaneous separation and determination of other anions and influence of eluent concentration on separation quality.

As mentioned previously, the quality of the separation and the obtained results are mostly dependent on the type of stationary phase, cross-linking, exchange capacity and particles size, as well as the eluent type and its flow rate. Because most laboratories conducting routine analyses of ions in water and wastewater with ion chromatography frequently have only one specific analytical column, then what might be altered within the optimization process framework are usually the last two parameters, i.e., the eluent type and its flow rate. Regrettably, most laboratories do not do this, instead strictly following the column manufacturer recommendations.

All tested Dionex columns had dimensions of 250 × 4.0 mm and contained a stationary phase consisting of EVB–DVB copolymers. The pH of eluents used for Dionex IonPac AS4-SC and IonPac AS22 columns ranged between 0 and 14, while pH of other eluents was slightly lower, ranging between 2 and 11 for the IonPac AS14 column and between 0 and 12 for the IonPac AS9-HC column.

The discussed columns are highly diversified in terms of their exchange capacity. The IonPac AS4-SC column is characterized

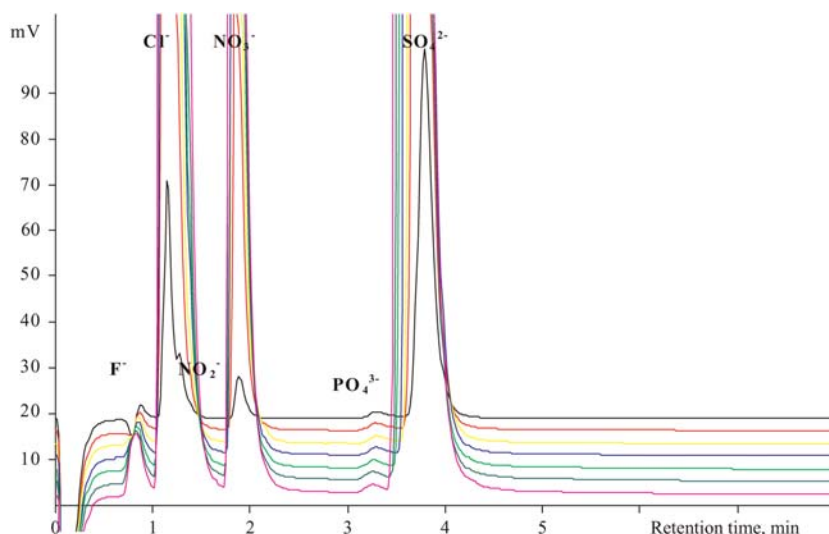


Figure 1. Chromatograms of standard samples numbered 1–7 obtained for Dionex AS4-SC column.

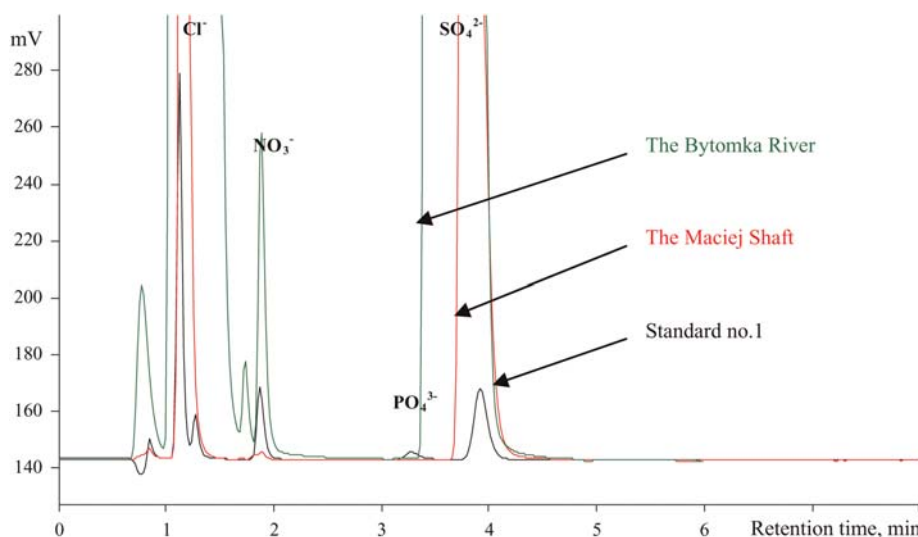


Figure 2. Chromatograms of real samples obtained for Dionex AS4-SC column.

by the lowest capacity, which amounts to a mere 20 μM Cl^- , whereas the IonPac AS9-HC and IonPac AS22 columns have exchange capacities of 190 and 210 μM Cl^- , respectively. The differences determine the concentration of the applied NaHCO_3 – Na_2CO_3 eluent. It is the lowest in the case of the Dionex IonPac AS4-SC column, equal to 1.7 mM NaHCO_3 + 1.8 mM Na_2CO_3 with a high eluent flow rate of 2.0 mL/min.

The eluent concentration is much higher for other Dionex columns, but the flow rate is twice as low. Hence, it is necessary to use a stronger eluent at lower flow rates to leach separated analyte ions from the analytical column within the specified time.

The most important conclusions drawn from the examinations carried out in the standard separation conditions for each anion-exchange column are given in the following. Figure 1 shows seven overlapping chromatograms obtained for the Dionex IonPac AS4-SC anion-exchange column and standard samples numbered 1–7. The results prove that this column is

well suited for a quick separation (less than five-min) of the primary inorganic ions (Cl^- , NO_3^- , SO_4^{2-}). At the same time, the simultaneous determination of trace amounts of F^- and PO_4^{3-} ions is difficult, whereas the determination of NO_2^- is virtually impossible, because the retention times of chloride and nitrite ions are too similar.

Figure 2 presents chromatograms of water samples collected from the Maciej Shaft and the Bytomka River obtained for the Dionex IonPac AS4-SC column. The chromatograms corroborate the aforementioned conclusions. Slightly better results were obtained for the popular Dionex IonPac AS14 anion-exchange column (Figure 3). When the chloride content exceeds 150 mg/L, the simultaneous Cl^- and NO_2^- determination is impossible with the application of the standard separation conditions and isocratic suppressed ion chromatography. This column is suitable for quick analysis of inorganic ions in samples in which their concentrations are at comparable

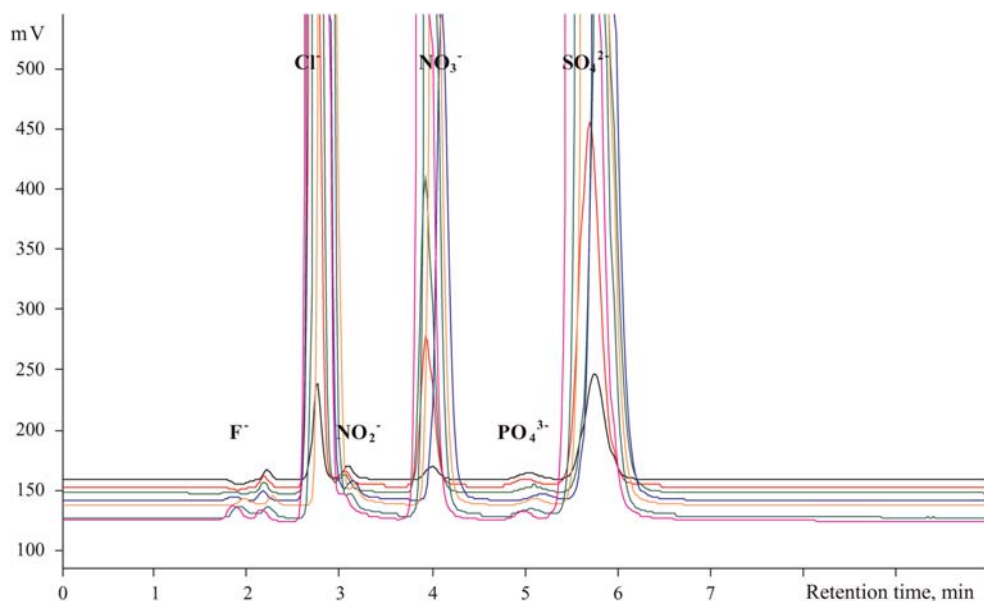


Figure 3. Chromatograms of standard samples numbered 1–7 obtained for Dionex AS14 column.

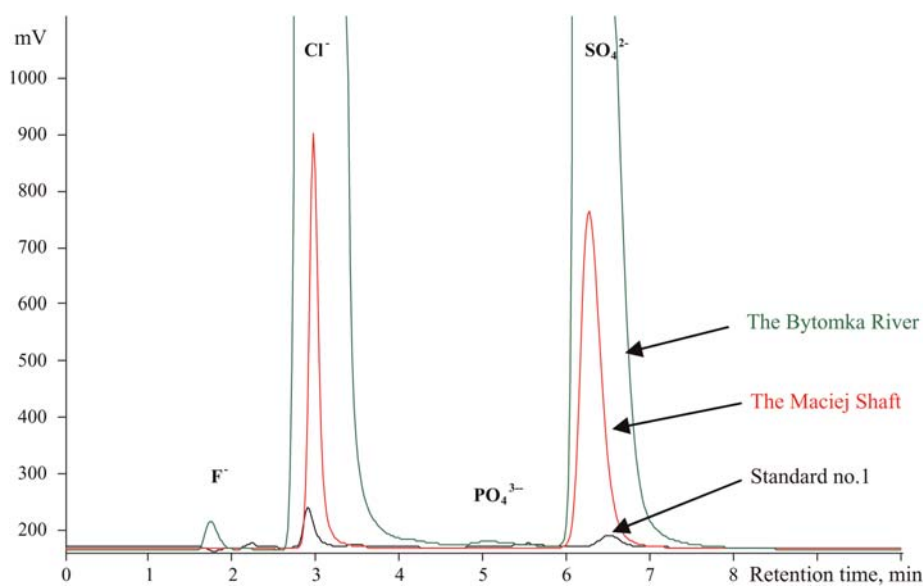


Figure 4. Chromatograms of real samples obtained for Dionex IonPac AS14 column.

concentration levels. Chromatograms of real samples given in Figure 4 confirm this finding.

On the other hand, chromatograms obtained for the Dionex IonPac AS9-HC anion-exchange column and standard samples numbered 1–7 (Figure 5) illustrate that this column is well matched for isocratic and simultaneous separation and determination of F^- , Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} ions. Admittedly, the retention times are longer (25 min in the analytical conditions recommended by the column manufacturer) due to its high exchange capacity ($190 \mu M Cl^-$), but the peak resolution is very good and also enables the separation of other ions (such as Br^- , ClO_2^- and ClO_3^-) present in the sample.

This column is recommended for the determination of carcinogenic bromate ions in drinking water. The chromatograms presented in Figure 5 demonstrate that it allows simultaneous separation and determination of trace amounts of F^- , NO_2^- and PO_4^{3-} ions in samples whose concentrations of Cl^- , NO_3^- and SO_4^{2-} significantly exceed 500 mg/L.

Even better results were obtained for the IonPac AS22 column (Figure 7). The total time of main anions separation does not exceed 13 min (it is 10 min longer for the IonPac AS9-HC column). Columns with high exchange capacity such as Dionex IonPac AS9-HC or Dionex IonPac AS22 are excellent for the analysis of complex matrix samples with isocratic ion chromatography with suppressed conductivity detection.

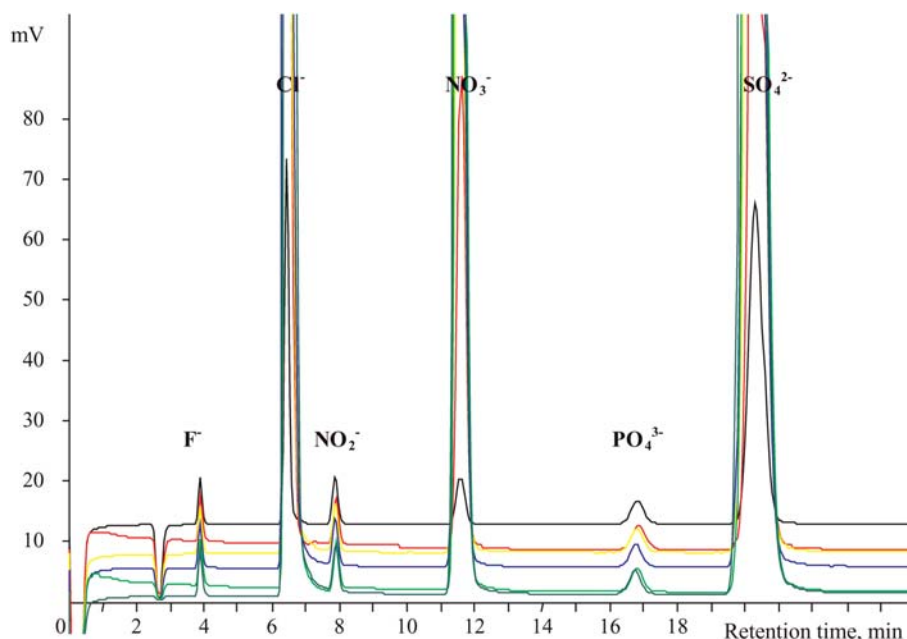


Figure 5. Chromatograms of standard samples numbered 1–7 obtained for Dionex AS9-HC column.

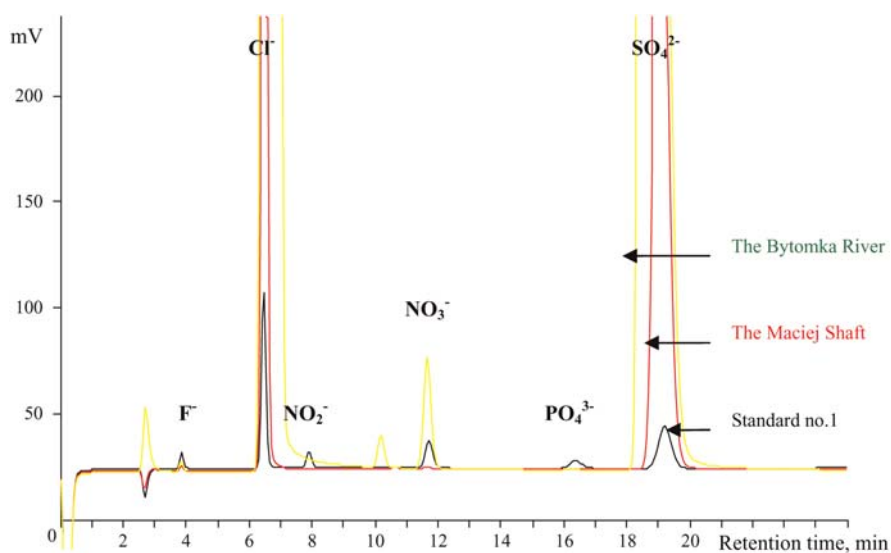


Figure 6. Chromatograms of real samples obtained for Dionex IonPac AS9-HC column.

The examined Metrohm columns had the following dimensions: 250×4.6 mm (Metrosep Supp 1 and Supp 3) or 250×4.0 mm (Metrosep Supp 5 and Supp 7). The column stationary phases consisted of copolymer PS–DVB (Metrosep A Supp 5 column) and polyvinyl alcohol with quaternary ammonium groups (the other three columns). The pH ranged between 1 and 13 (Metrosep A Supp 1 and 3) and between 3 and 12 (Metrosep A Supp 5 and 7). Eluents with the addition of organic solvents could be used with all the columns.

The tested Metrohm anion-exchange columns did not have as highly diversified exchange capacity as Dionex columns; it ranged between 33 and $108 \mu\text{M Cl}^-$. Such values determine

the concentration of the applied eluent and its flow rate. Generally, flow rates recommended for Metrohm columns are lower than those suggested for Dionex. Interestingly, the eluent recommended for the Metrosep Anion Supp 7 column is Na_2CO_3 -based on the addition of 2% acetone. Addition of organic solvents improves the shape of the peaks and shortens retention times of late-eluting ions.

Figure 9 displays seven overlapping chromatograms obtained for the Metrohm Metrosep A Supp 1 anion-exchange column and standard samples numbered 1–7. It shows that the column is suitable for the simultaneous separation and determination of the primary inorganic anions (Cl^- , NO_3^- and SO_4^{2-}) and

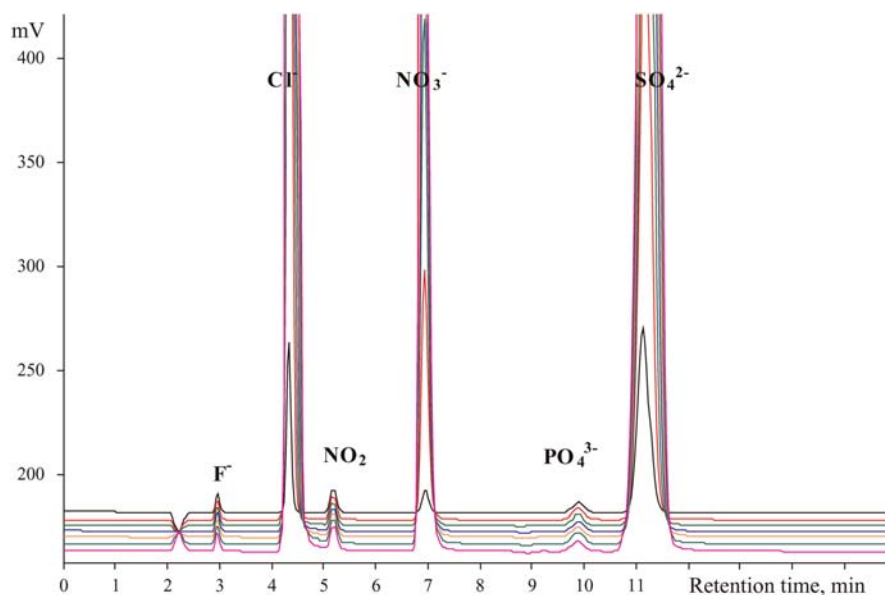


Figure 7. Chromatograms of standard samples numbered 1–7 obtained for Dionex IonPac AS22 column.

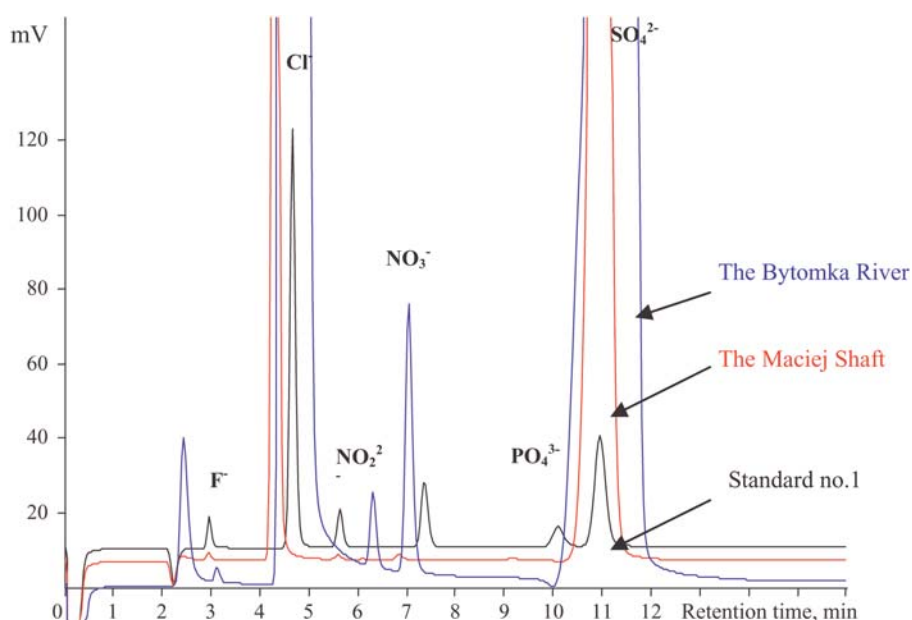


Figure 8. Chromatograms of real samples obtained for Dionex IonPac AS22 column.

trace amounts of F^- and PO_4^{3-} ions. Unfortunately, the separation of Cl^- and NO_2^- peaks in the conditions recommended by the column manufacturer is difficult and virtually impossible when the ratio of their concentrations $>25:1$.

This column also enables direct analysis of real samples with high content of chlorides and sulfates, exceeding 800 mg/L, such as the collected water samples from the Maciej Shaft and the Bytomka River (with the exclusion of the NO_2^- ion), without any specific sample preparation except for standard filtration through a filter with 0.45 μm pores (Figure 10).

Figures 11 and 12 demonstrate that the Metrosep A Supp 3 column allows quick separation and determination of the

main inorganic anions in the conditions recommended by the manufacturer. Nevertheless, both the determination of phosphates when the ratio of $PO_4^{3-}:SO_4^{2-}$ is $>1:10$ and simultaneous determination of Cl^- and NO_2^- ions when their ratio is $>25:1$ are impossible. The obvious advantage of the discussed column consists of quick separation of the primary anions (Cl^- , NO_3^- , SO_4^{2-}) within a 10-min time period and suitable separation of fluoride ions in the presence of the injection peak.

These conclusions are supported by the results of separation of inorganic anions in real samples with matrices as complex as those in the water samples from the

Table III

Physico-Chemical Parameters of Analyzed Real Samples

Parameter	Water from Maciej Shaft (mg/dm ³)	Water from Bytomka River (mg/dm ³)
pH	7.73	8.28
Electrical conductivity (μS/cm)	992	6770
F ⁻	0.32	0.34
Cl ⁻	70.99	1,587.14
NO ₂ ⁻	<0.05	<0.05
Br ⁻	0.54	6.99
NO ₃ ⁻	2.18	14.18
PO ₄ ³⁻	1.01	1.40
SO ₄ ²⁻	185.67	840.80
Li ⁺	<0.05	<0.05
Na ⁺	62.87	1,220.08
NH ₄ ⁺	<0.05	<0.05
Mg ²⁺	21.03	74.66
Ca ²⁺	141.02	151.2

Maciej Shaft and the highly contaminated Bytomka River (Figure 12).

Considerably better separation results were obtained for the examined Metrohm Metrosep A Supp 5 (Figure 13) and Metrosep A Supp 7 (Figure 15) anion-exchange columns. All analyzed ions are well separated and the total separation time amounts to approximately 30 min. They also allow determination of highly contaminated samples, such as the analyzed coal mine and river water samples (Figures 14 and 16), without any special sample preparation except for filtration.

The chromatograms in Figures 17 and 18 show that, depending on the concentration of carbonate/bicarbonate in the eluent, and their mutual relations, the retention times of separated inorganic anions are strongly differentiated. This can be very beneficial for specific determination and sample matrices. For example, when analyzing samples with high

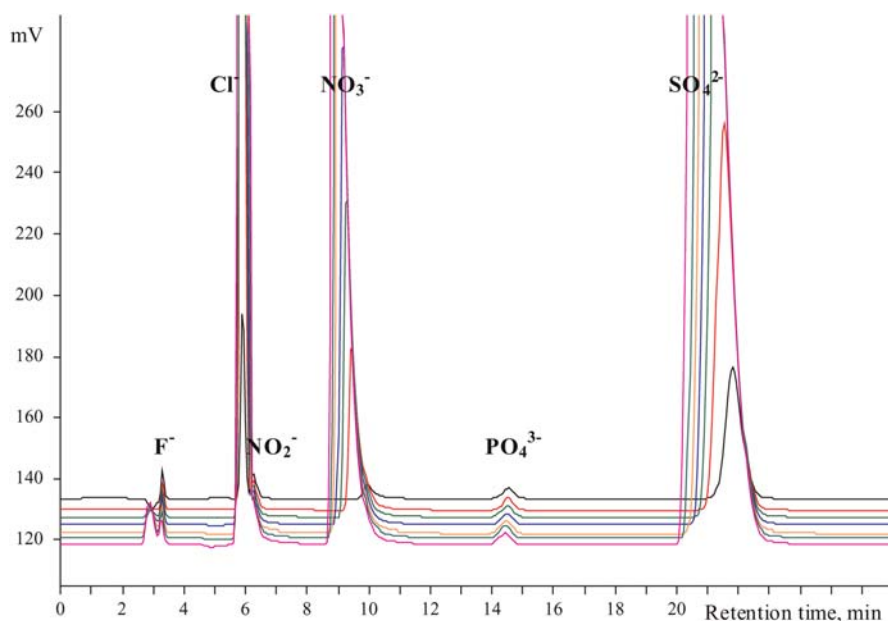


Figure 9. Chromatograms of standard samples numbered 1–7 obtained for Metrohm A Supp 1 column.

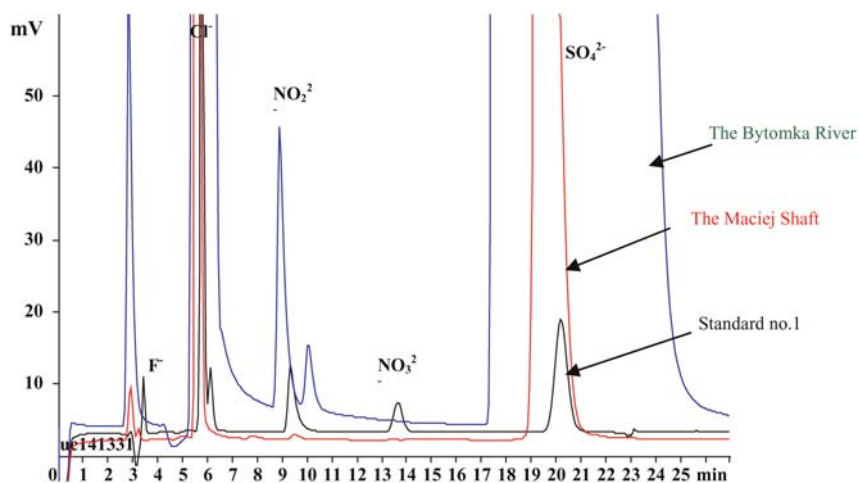


Figure 10. Chromatograms of real samples obtained for Metrohm A Supp 1 column.

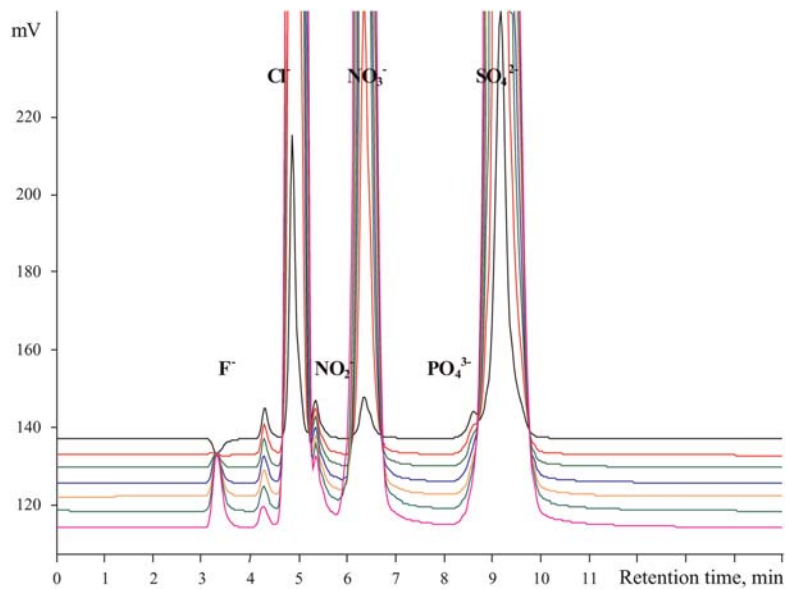


Figure 11. Chromatograms of standard samples numbered 1–7 obtained for Metrohm A Supp 3 column.

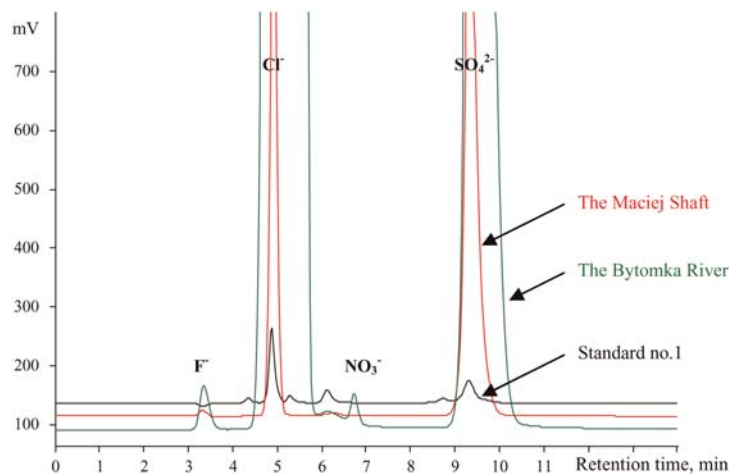


Figure 12. Chromatograms of real samples obtained for Metrohm A Supp 3 column.

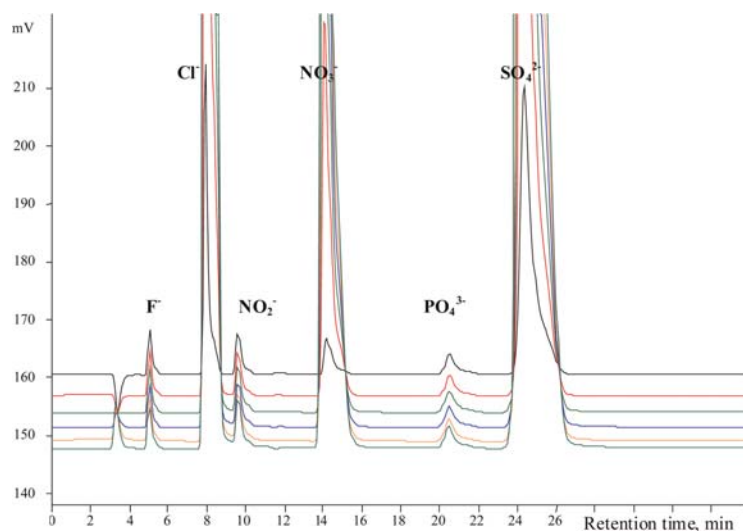


Figure 13. Chromatograms of standard samples numbered 1–7 obtained for Metrohm Metrosep A Supp 5 column.

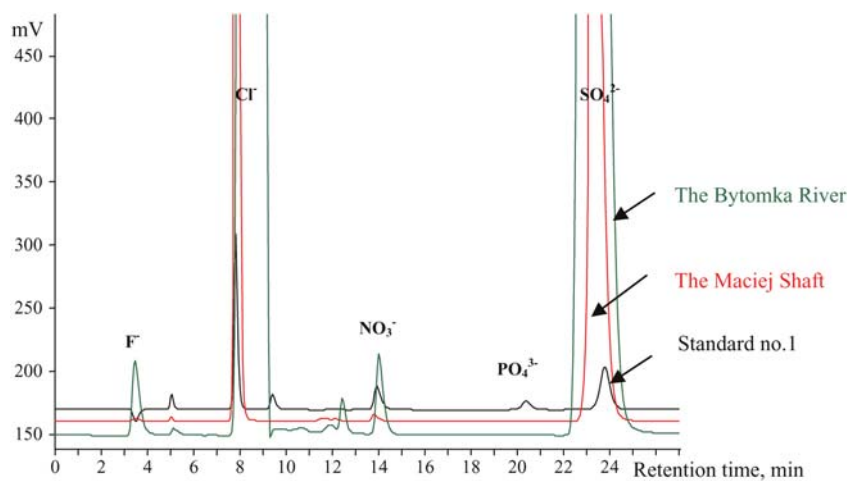


Figure 14. Chromatograms of real samples obtained for Metrohm A Supp 5 column.

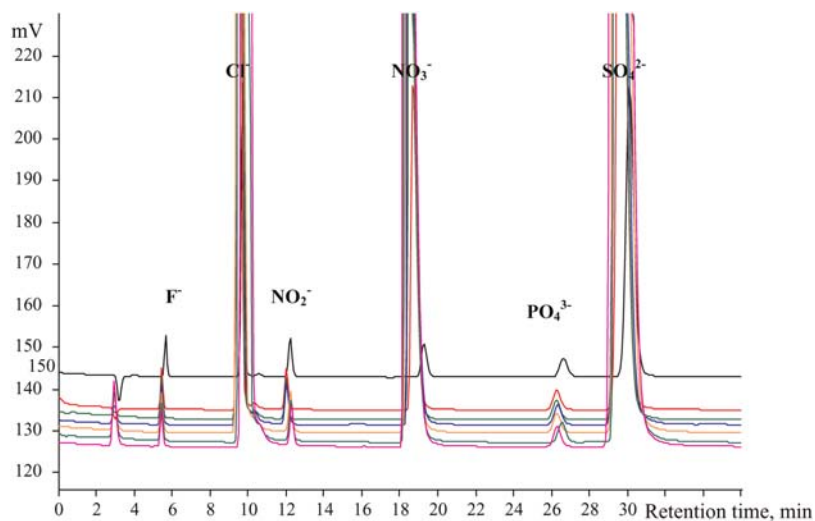


Figure 15. Chromatograms of standard samples numbered 1–7 obtained for Metrohm A Supp 7 column.

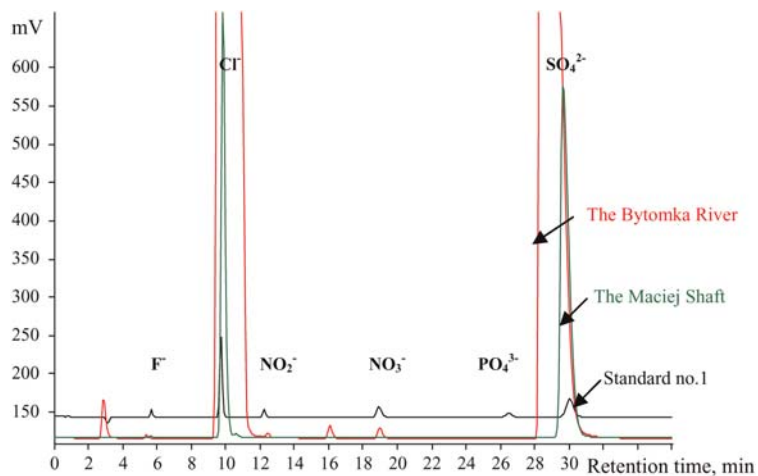


Figure 16. Chromatograms of real samples obtained for Metrohm A Supp 7 column.

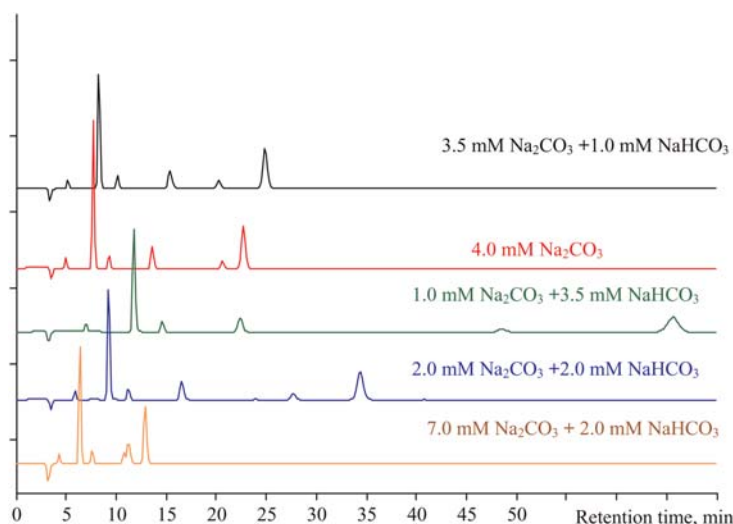


Figure 17. Chromatograms of standard anions separation using Metrohm A Supp 5 column and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluents with different concentration.

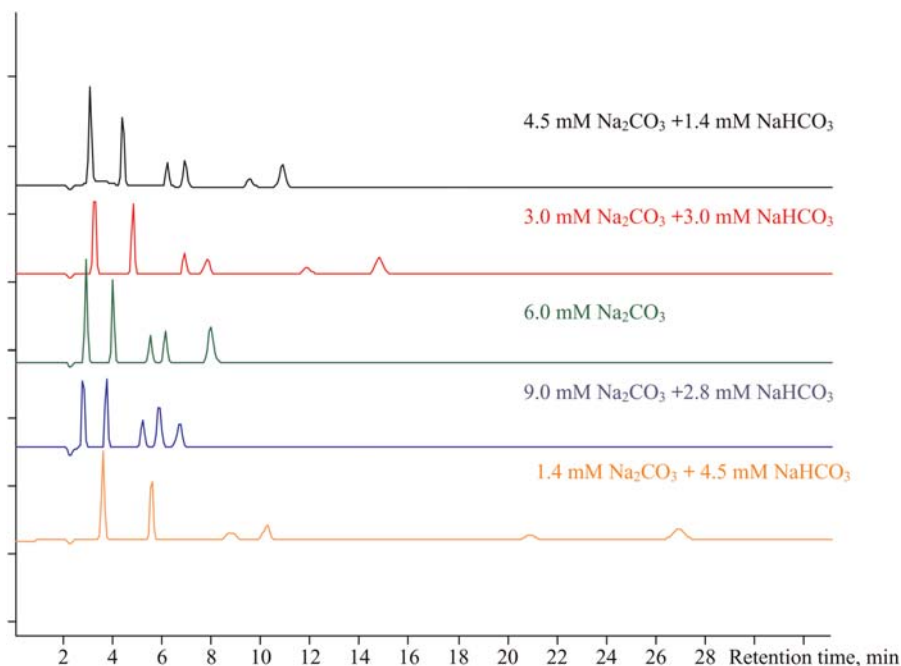


Figure 18. Chromatograms of standard anions separation using Dionex IonPac AS 22 column and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluents with different concentration.

content of ions such as SO_4^{2-} and trace contents of NO_3^- , using a Metrohm A Supp 5 column with 2.0 mM NaHCO_3 and 2.0 mM Na_2CO_3 makes it possible to simultaneously separate and determine these ions without any special sample preparation.

Conclusions

Isocratic ion chromatography with suppressed conductivity detection is the most popular instrumental method, enabling determination of inorganic anions and cations in water and wastewater. The laboratories that perform routine analyses

usually own only one anion-exchange column and the separation of the analyte ions takes place in the standard conditions recommended by the column manufacturers.

The paper presents the results of separation of selected inorganic anions in standard samples containing variable concentrations of F^- , NO_2^- and PO_4^{3-} ions and increasing concentrations of ions dominant in environmental samples (Cl^- , NO_3^- and SO_4^{2-}) with the application of four Dionex and four Metrohm anion-exchange columns working under standard separation conditions. The investigated columns were also employed in the analyses of real samples with complex matrix (coal mine water and water from a highly contaminated river).

The conducted tests point out the advantages and limitations of both the anion-exchange columns and analytical conditions and indicate the need to adapt the appropriate column to specific determinations.

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