

Ion-chromatographic determination of common anions in drinking water in some regions of the Republic of Armenia

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Abstract

The present study investigated the anion composition of drinking water from various cities and villages in Armenia, including spring water and tap water samples. The simultaneous separation was achieved for fluoride, chloride, bromide, nitrite, nitrate, sulfate, and phosphate anions with the correlation coefficients >0.998 . Validation of the method was carried out in accordance with the requirements of guidelines in terms of selectivity, specificity, system suitability, linearity, accuracy, precision, lower limits of detection and quantitation, robustness, and stability. The method was suitable for routine drinking water quality assessment in line with the national or World Health Organization (WHO) regulations. The validated method was further used to analyze drinking water samples from different regions of Armenia. The observed concentrations for the anions in drinking water complied with the WHO limits for drinking water with some exceptions. The test method can be submitted to quality control laboratories as a convenient and practical tool for routine analysis and monitoring studies.

Keywords

anion composition, comparative study, method validation, water analysis

Introduction

Water is called the matrix of life because it is an integral part of all living systems and the medium from which life has evolved and exists. Fresh water is a limited and valuable resource necessary to maintain life and health and to ensure the preservation of ecosystems (Franks 2000). The growth of population combined with rapid urbanization, changes

in lifestyle, and economic development resulted in an increased load on water resources, and there is evidence of a global water crisis. More than 1 billion people do not have access to safe drinking water, and it is estimated that 80% of childhood deaths from digestive diseases such as diarrhea (about 2 million annually) are caused by consumption of contaminated drinking water (Balbus and Lang 2001). In this regard, the resolution of the European Union (EU) of

May 30, 2002, approved the EU Water Initiative (Dondeynaz et al. 2010), which emphasizes the importance of integrated water resources management. Despite significant efforts of the national and international authorities, there is evidence that it is not easy to achieve the correct quality of drinking water. Disinfection is undoubtedly important to provide safe drinking water; however, lack of supervision and control can lead to deterioration of water quality (Cidu et al. 2011).

In aquatic systems, elements are present as dissolved ions and complexes, suspended colloidal ions, and solids in sediments. The concentration of these ions highly depends on biological processes, redox potential, ionic strength, pH, organic and inorganic activity, and purification processes (Brahman et al. 2013). Normal values for drinking water have been obtained for many chemical components. A standard value is commonly a concentration of a component that does not pose a significant health risk over a lifetime of consumption. In this article, we refer to the recommendations of the WHO for drinking water (WHO 2022) because they represent reference values for developing national standards. High levels of anions in drinking water can be toxic.

The main sources of fluoride ion (F^-) in natural waters are fluoride-containing minerals (fluorite, fluorapatite, cryolite, and apophyllite), as well as clay minerals (Dey et al. 2012). Its concentration in groundwater depends on pH, the intensity of the weathering process, and the amount of clay in the aquifer material (Saxena and Ahmed 2001). Fluoride ions in small amounts are a necessary component for the proper bone mineralization and the formation of tooth enamel (Everett 2011; Carey 2014). The main source of F for the human body is usually drinking water, constituting about 75–90% of daily intake (Zohouri and Rugg-Gunn 2000). A small number of countries practice artificial fluoridation to protect against dental caries in children and adults. The amounts added to drinking water are such that the final concentration is usually between 0.5 and 1 mg/L. High fluoride concentrations exceeding 4 mg/L cause dental fluorosis, and higher concentrations cause skeletal fluorosis (Chen et al. 1997; Benson et al. 2013; Peroš et al. 2013), cancer, arthritis, and other diseases (Li et al. 1995; Waldbott 1998). There is strong evidence of increased risk of skeletal effects at total intakes of more than 6 mg/day (Haguenaer et al. 2000; Brahman et al. 2013). About 200 million people from 25 countries are exposed to health risks due to high fluoride levels in groundwater (Ayooob and Gupta 2006; Rafique et al. 2009). The preliminary normative value of fluoride concentration in drinking water established by the WHO is 1.5 mg/L (WHO 2011).

Nitrate ion (NO_3^-) occurs naturally in the environment and is an important plant nutrient. The nitrite ion (NO_2^-) is usually not present in significant concentrations except in a reducing environment since nitrate is a more stable oxidation state. Nitrates can enter both surface and groundwater due to agricultural activities (including excessive use of inorganic nitrogen fertilizers and manures), wastewater discharge, and the oxidation of nitrogenous wastes. Nitrates can affect the oxygen transport capacity in the human body and cause methemoglobinemia, which

can be fatal for infants (Brunato et al. 2003). The recommended values for nitrate and nitrite are 50 mg/L and 3 mg/L, respectively, to protect the health of the most sensitive artificially fed population groups (WHO 2022).

Chloride ions can give water a salty or unpleasant taste, cause hypertension, etc. Taste thresholds of chloride depend on the cation associated with it and are in the range of 200–300 mg/L for sodium, potassium, and calcium chloride. Chloride in drinking water originates from natural sources, wastewaters and industrial effluents, urban runoff containing de-icing salt, and saline intrusion. Excessive chloride concentrations increase the rate of metal corrosion in the distribution system depending on the alkalinity of water. This can lead to an increased concentration of metals in supplies (WHO 2003).

The bromide ion does not pose a direct risk to humans or the environment, but it can react with other compounds and natural organic matters to form brominated organic compounds that are actually dangerous to health. During water treatment (disinfection), bromide can interact with natural organic matters in water and strong oxidizers such as chlorine and ozone with the formation of brominated or mixed chlorobrominated byproducts—bromate (BrO_3^-), etc. (WHO 2009; Alomirah et al. 2020).

The presence of sulfate in drinking water can cause a noticeable taste, and high levels can cause a laxative effect in unaccustomed consumers. The worsening of taste depends on the nature of the corresponding cation. Taste thresholds have been found to range from 250 mg/L for sodium sulfate to 1000 mg/L for calcium sulfate. Taste deterioration is generally considered to be minimal at levels below 250 mg/L (WHO 2004).

Ion chromatography is a sensitive, robust, and simple method for the determination of inorganic anions in various matrices. The use of suppressors provides constant suppression of the eluent conductivity and strengthens the response of the analyte before it enters the detector (Manickum et al. 2019).

The aim of the present study is the assessment of a simple, fast, and accurate method for the determination of anions (fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate) in various samples of drinking water from different regions of Armenia using ion chromatography equipped with a conductometric detector in a suppression mode. Full validation of the method was carried out in accordance with the requirements of accreditation tests ISO 17025 and ICH harmonized tripartite guidelines (ICH 2005; ISO 17025 1999). When validating the method, its selectivity, specificity, system suitability, linearity, accuracy, precision (repeatability), lower limits of detection and quantitation, robustness, and stability were observed. The validated method was used for the first time for the determination of anions in drinking water samples from different geographical regions of Armenia. The samples included spring water and tap water taken from various cities and villages in Armenia.

The test results may be useful for improving the current drinking water regulations as well as for assisting consumers.

Materials and methods

Reagents and standards

Certified standard solution, analytical grade reagents were obtained from CertiPUR®, Merck, Darmstadt, Germany, and ultrapure water (Millipore, Milli-Q RG, Thermo Scientific, Waltham, MA, USA) was used in sample preparation and also mobile phase used for analysis. Certified multi-anions standard for ion chromatography 7 elements: bromide (Br⁻): 100 mg/L, sulfate (SO₄²⁻): 150 mg/L, phosphate (PO₄³⁻): 50 mg/L, chloride (Cl⁻): 30 mg/L, nitrite (NO₂⁻): 30 mg/L, nitrate (NO₃⁻): 20 mg/L, fluoride (F⁻): 20 mg/L, matrix: water (Stock Anion Standard Solution) were purchased from Carlo Erba. Working Standard Solution (WS) was prepared by 20-fold dilution of Stock Anion Standard Solution with ultra-pure deionized water (F⁻ 1 mg/L, Cl⁻ 1.5 mg/L, NO₂⁻ 1.5 mg/L, Br⁻ 5 mg/L, NO₃⁻ 1 mg/L, PO₄³⁻ 2.5 mg/L, SO₄²⁻ 7.5 mg/L), which was used to determine the validation parameters such as selectivity/specificity, system suitability, repeatability, and robustness. All calibration solutions were prepared by appropriate dilution of Stock Anion Standard Solution with ultra-pure deionized water, and their concentrations are presented in Table 2. For method accuracy assessment, control samples of standard solution (QC samples) were prepared by appropriate dilution of stock anion standard solution with ultra-pure deionized water, and their concentrations are presented in Suppl. material 1: table S1.

The volumetric glassware used for standard solution preparation was of class A.

Sample collection and preparation

In this study, 14 samples of drinking water from 5 regions of Armenia (Yerevan, 3 samples; Aparan, Aragacotn region, 1 sample; Goris, Syunik region, 1 sample; Tavush region, 7 samples; Eghegnadzor, Vayots dzor, 2 samples) were studied, including 9 samples of tap water and 5 samples of spring water (Table 3). The location of water samples is shown in Fig. 1.

The water samples were collected in March–May 2023. All drinking water samples were stored in tightly closed containers at 4 °C. Before injection, the sample was filtered through a 0.22 µm membrane syringe filter (Macherey-Nagel, Germany) and then was analyzed without any dilution.

Instrument and ion chromatographic conditions

The separation of anions was performed using an ion chromatographic system (Knauer Azura, Berlin, Germany), equipped with a Dionex IonPac AS22 Analytical 4×250 mm analytical column and ASUREX-A100 regenerator with XAMS Anion membrane suppressor (Self-Regenerating, 4 mm, recycle mode, 50 mA current) and conductivity detector CDD-10Avp (Knauer Azura, Berlin, Germany). The eluent solution was prepared by dissolving the following salts in Milli-Q water to obtain 4.5 mM/L sodium carbonate (Na₂CO₃) and 1.4 mM/L sodium hydrogen carbonate (NaHCO₃) and degassing in an ultrasonic bath for 10 min. All chromatographic experiments were carried out in the isocratic mode at 30 °C. The



Figure 1. Location of water samples.

operating conditions were: 1.2 mL/min eluent flow rate, 10 μ L injection volume and 25 μ L injection loop volume, and 31 mA current in a suppressor. Data processing was carried out with ClarityChrom chromatography software (Knauer Azura, Germany, Berlin) and Excel.

When validating the method, selectivity, specificity, linearity, accuracy, precision, and lower limits of detection and quantification, robustness, and stability were taken into account.

Results and discussion

According to the literature (Zhu et al. 2008; Cidu et al. 2011), the IonPac AS22 column has high ion exchange performance and can efficiently separate anions (Fig. 2). This effective separation was achieved within 15 min. The anions were well separated with the sequence presented in the chromatogram (Fig. 2), obtained at the concentrations of WS.

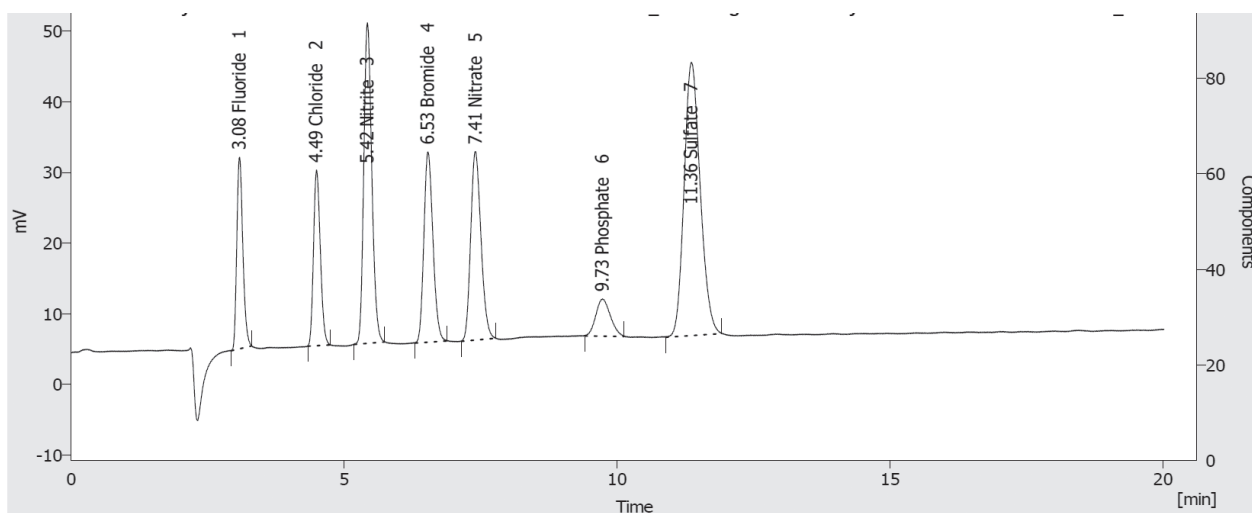


Figure 2. Separation of seven low-mg/L inorganic anion standard solutions: 1-F⁻ 1 mg/L, 2-Cl⁻ 1.5 mg/L, 3-NO₂⁻ 1.5 mg/L, 4-Br⁻ 5 mg/L, 5-NO₃⁻ 1 mg/L, 6-PO₄³⁻ 2.5 mg/L, 7-SO₄²⁻ 7.5 mg/L.

Validation of the method

Selectivity / specificity

The selectivity of the method was assessed based on retention time and resolution for each analyte and compared with the retention time standards of anions by examining the relative standard deviation (% RSD) of retention times and peak areas for a series of 6 injections at the

above-mentioned concentrations of WS. The mean retention time (RT), the value of the peak area (PA), standard deviations (SD), and relative standard deviations (% RSD) are presented in Table 1.

Since in all cases the relative standard deviation is less than 2%, the method is considered selective according to the requirements of the ICH harmonized tripartite guideline (ICH 2005).

To determine the **system suitability**, six injections of the WS were carried out, and the resolution factor and peak asymmetry were calculated. Peak symmetry and resolution are important factors to ensure that the separation profile is optimized. Peaks in Fig. 2 are symmetric, without tails or fronts. The resolution was determined by the difference in the elution time of the peaks and their width. The data are presented in Table 1. As follows from the data presented in the table, the resolution factor and peak asymmetry meet the stated requirements: Resolution factor ≥ 1.5 and asymmetry ≤ 1.5 .

Linearity / calibration range

Linearity is the ability of a method (within a certain range) to get test results that are in direct proportion to the concentration (amount) of analyte in the sample. Linearity is determined by analyzing calibration standards (at least four, including the blank) and obtaining the correlation coefficient (R^2) (Miskaki et al. 2007; Ivanova et al. 2018). The value of R^2 should be ≥ 0.995 . The linearity of the

Table 1. Method specificity test results for identifying fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate ions ($n = 6$).

Analyte	Retention time (min) \pm SD	RSD for RT	Peak area \pm SD	RSD for PA	Asymmetry	Resolution factor
F ⁻	3.07 \pm 0.006	0.207	235.6 \pm 3.687	1.565	1.500	-
Cl ⁻	4.46 \pm 0.009	0.205	265.5 \pm 2.835	1.068	1.331	5.790
NO ₂ ⁻	5.38 \pm 0.007	0.133	455.3 \pm 6.230	1.370	1.298	3.357
Br ⁻	6.47 \pm 0.0063	0.098	298.9 \pm 2.817	0.942	1.242	3.532
NO ₃ ⁻	7.33 \pm 0.01	0.138	357.3 \pm 4.240	1.187	1.204	2.435
PO ₄ ³⁻	9.22 \pm 0.013	0.139	161.7 \pm 1.559	0.964	1.301	4.326
SO ₄ ²⁻	11.13 \pm 0.017	0.151	796.6 \pm 8.495	1.066	1.343	3.636

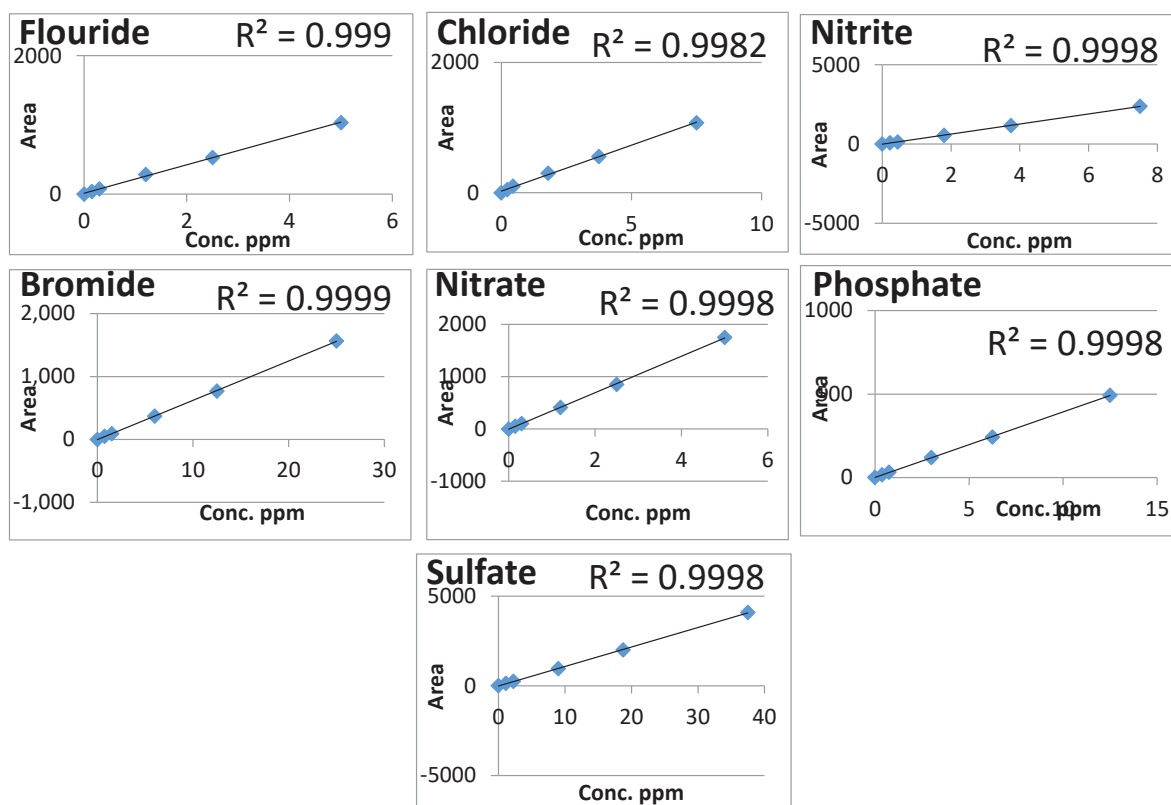


Figure 3. Calibration curves of analyzed anions.

method under consideration was estimated for the following anions: fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfates. Calibration curves were obtained in the concentration range of 0.015–5 mg/L for F⁻, 0.225–7.5 mg/L for Cl⁻, 0.225–7.5 mg/L for NO₂⁻, 0.75–25 mg/L for Br⁻, 0.15–5 mg/L for NO₃⁻, 1.125–37.5 mg/L for SO₄²⁻, and 0.375–12.5 mg/L for PO₄³⁻ (Table 2). Measurements were carried out 3 times for 5 concentration levels of multi-ion standards, and mean values were used to construct calibration curves (Fig. 3). For each concentration, mean value, relative deviation (RD), and relative standard deviation (RSD) that did not exceed 2% were calculated.

Regression analysis was used in accordance with IUPAC validation guidelines (Thompson et al. 2002). The results are presented in Table 2. Calibration curves showed a linear relationship between peak area and concentration over a wide range of concentrations for all target analytes. The correlation coefficient (R^2) met the IUPAC requirements and was ≥ 0.995 .

Quantification and detection limit

LOD is the lowest concentration of analyte in a test sample that can be reliably distinguished from the zero concentration and is determined by the signal-to-noise ratio. The signal-to-noise ratio is determined by comparing a known low concentration of analyte with a sample containing no analyte (blank), setting the lowest concentration possible to detect. To assess the detection limit, a signal-to-noise ratio of 3:1 is acceptable. The LOD values of the proposed ion chromatography method were calculated by three-

time introduction of the standard sample with the following concentrations: Br⁻ 0.2 mg/L, SO₄²⁻ 0.3 mg/L, PO₄³⁻ 0.1 mg/L, Cl⁻ 0.06 mg/L, NO₂⁻ 0.06 mg/L, NO₃⁻ 0.04 mg/L, and F⁻ 0.04 mg/L.

The limit of LOQ quantification is the lowest concentration of analyte in a sample that can be determined with an acceptable level of repeatability (% RSD $\leq 10\%$) and recovery (80–120%) accuracy. To evaluate the quantitative limit, a signal-to-noise ratio of 10:1 is acceptable. The relative standard deviation (RSD) of six measurements should not exceed 10%. To determine the lower limits of quantification, a standard sample was prepared with the following concentrations: Br⁻ 0.6 mg/L, SO₄²⁻ 0.9 mg/L, PO₄³⁻ 0.3 mg/L, Cl⁻ 0.18 mg/L, NO₂⁻ 0.18 mg/L, NO₃⁻ 0.12 mg/L, and F⁻ 0.12 mg/L. For all anions, the relative standard deviation of six performed measurements did not exceed the admissible limit; all anions had a low variation of RSD 0.1–1.7%, while considerable variation was apparent in peak area of NO₃⁻, with a value of 5.8% RSD. LOD and LOQ concentrations are given in Table 2.

Accuracy is an indicator of how close the test results are to a known value. Accuracy can be assessed by adding a standard solution to samples of deionized water and determining the extracted analyte. To determine the accuracy of the method, control samples (QC samples) of anions standard solution were prepared at three different concentrations (low, medium, and high), selected so that they were within the range of the calibration curve but did not repeat the concentration of the curve. The concentrations of the QC samples are presented in Suppl. material 1: table S1. Only for chlorine ions, 2 concentrations were

Table 2. The calibration parameters, LOD, and LOQ concentrations of the proposed method (n = 6).

Analyte	Concentration of external standards [mg/L]	Correlation coefficient (R^2)	LOD [mg/L]	LOQ [mg/L]
F ⁻	0.15, 0.3, 1.2, 2.5, 5	0.999	0.04	0.12
Cl ⁻	0.225, 0.45, 1.8, 3.75, 7.5	0.998	0.06	0.18
NO ₂ ⁻	0.225, 0.45, 1.8, 3.75, 7.5	0.999	0.06	0.18
Br ⁻	0.75, 1.5, 6, 12.5, 25	0.999	0.20	0.60
NO ₃ ⁻	0.15, 0.3, 1.2, 2.5, 5	0.999	0.04	0.12
PO ₄ ³⁻	0.375, 0.75, 3, 6.25, 12.5	0.999	0.10	0.30
SO ₄ ²⁻	1.125, 2.25, 9, 18.75, 37.5	0.999	0.30	0.90

chosen. Each concentration was injected 3 times. Accuracy was expressed as percentage recovery (% recovery) by comparing the obtained value with the theoretical value. The acceptable percentage error should be within $\pm 20\%$, i.e., the concentration of the extracted analyte should be between 80% and 120% of the added concentration. The equation for calculating recovery is given below:

$$\% \text{ recovery} = \frac{\text{measured concentration}}{\text{actual prepared concentration}} \times 100$$

The recovery values were 92.74–114.67% (Suppl. material 1: table S1). The closeness of the results to 100% confirmed the rather good accuracy of the ion chromatography method.

Repeatability precision gives an idea of the kind of variability to be expected when the method is performed by a single analyst over a short period of time. This was determined at the system suitability stage by analyzing six replicates of the Working Standard Solution and calculating % RSD. As shown in Table 1, the excellent precision values were achieved with < 1% RSD for retention time and < 2% RSD for the peak area.

Robustness

It gives an idea of the kind of variability to be expected when the method is performed by one or different analysts under different conditions over a long period of time. As an indicator of the robustness of the analytical method, the stability of the test standard solution was monitored over short and long periods of time. To control stability, Working Standard Solution was injected six times. The test was done on the first day of validation, then the same solution was stored under room conditions and tested after 24 hours (short-term stability) and stored in a refrigerator at 2–8 °C and then tested after 9 days (long-term stability). The relative standard deviation (% RSD) of the retention times and peak areas for a series of 6 injections at the above concentrations of WS was assessed. Data from all measurements are presented in Suppl. material 1: table S2.

Since in all cases the relative standard deviation of peak areas varies from 0.10 to 1.79, which meets the stated requirements and is less than 2%, the method is considered robust in terms of stability according to the ICH harmonized tripartite guideline and the Horwitz equation at the concentration levels used (ICH 2005; Rivera and Rodriguez 2014).

Drinking water analysis

The validated method was used to determine anions in drinking water samples from different geographical regions of Armenia. The samples included spring water and tap water taken from various cities and villages in Armenia. Four river water samples were also studied to compare the ion quantities and the applicability of the method. The water of the Getar river flowing through the city of Yerevan and the water of 3 tributaries of the Voghji river flowing through the city of Kapan of Syunik's region were selected. Sample preparation was simple and involved only filtration. Each sample was injected 3 times. Fig. 4 shows a typical chromatogram of inorganic anions in drinking water from Yerevan obtained using a Dionex IonPac AS22 ion-exchange column.

Separation of all 7 anions was achieved in 15 min. The analysis of water samples for anion content is presented in Table 3. It can be seen that all 7 target anions can be detected in the water samples, including fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate. The concentration of analyzed anions varied among samples. The contents of highly concentrated sulfates, chlorides, and nitrates were calculated from diluted samples (1/10 by volume) to quantify all target compounds within the calibration operating concentration range. The concentration of residual anions was calculated from undiluted samples.

In an attempt to evaluate the quality of the tested water, the water samples were compared with the WHO drinking water recommendations (WHO 2022) and with the national water quality regulations. Table 3 shows that bromide-anion was detected in all water samples except the Aparan sample. The bromide content in drinking water varied from 0.08 mg/L from Goris to 1.029 mg/L from Yeghegnadzor, Areni, and Akhtaghbyur. The amount of bromide in 7 samples from different regions of Armenia exceeded the WHO normative value (WHO 2022). The chloride content varied from 0.84 mg/L from Goris to 28.83 mg/L for Yeghegnadzor, Areni, and Akhtaghbyur. The content of sulfates and phosphates varied between 2.32–107.62 mg/L and 0.136–0.593 mg/L, respectively. No phosphate ion was detected in five drinking water samples. The nitrite ion was not detected in any drinking water sample. It was detected only in trace amounts in two river water samples. As to nitrate-ion, it was detected in all samples of drinking water, and its amount varied from 6.07 mg/L to 89.20 mg/L; its amount in two samples of the Voskevan region exceeded the WHO normative value. A

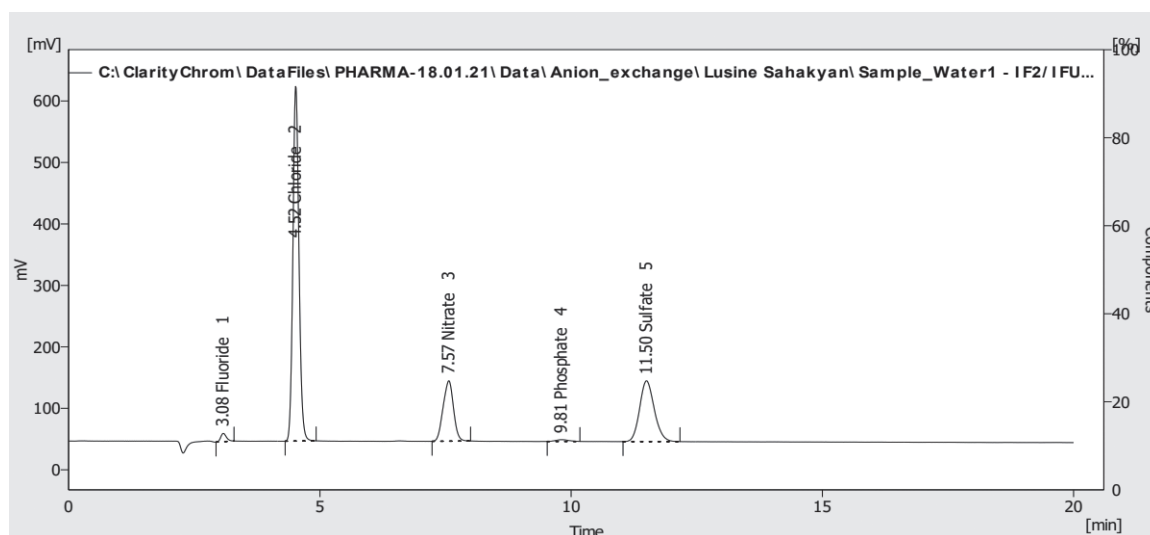


Figure 4. Chromatogram of inorganic anions in drinking water from Yerevan, Kentron district.

Table 3. Concentration of anions in drinking water samples from different regions of Armenia (n = 3, P = 95%).

Water samples location /matrix	Anions concentration Mean* (mg/L)						
	Br	SO ₄ ^{2-**}	PO ₄ ³⁻	Cl ^{**}	NO ₂ ⁻	NO ₃ ^{**}	F ⁻
	Recommended values (mg/L)						
	0.2	250	3.5	250	0.5	50	1.5
Yerevan, Davtashen dist. /tap water	0.146	0.444	0.347	0.277	< LOQ	2.430	0.198
Yerevan, Kentron dist./tap water	0.460	2.160	< LOQ	18.670	< LOQ	3.450	< LOQ
Yerevan, Khorenatsi str. /tap water	0.206	1.211	0.274	2.286	< LOQ	2.845	0.328
Aparan, Aragatsotn region /tap water	< LOQ	0.284	0.234	0.085	< LOQ	1.301	0.147
Goris, Syunik region/tap water	0.080	0.448	0.593	0.084	< LOQ	0.726	0.183
Voskevan No1, Tavush region /tap water	0.570	5.650	< LOQ	0.233	< LOQ	2.323	0.316
Voskevan No2, Tavush region /tap water	0.502	5.469	0.143	1.185	< LOQ	8.896	0.286
Koghb, Tavush region/tap water	0.726	10.762	0.266	0.732	< LOQ	2.517	0.374
Berdavan, Tavush region /tap water	0.183	0.375	0.256	0.451	< LOQ	1.404	0.180
Voskevan, Nav, Tavush region /spring water	0.603	5.499	< LOQ	1.181	< LOQ	8.920	0.295
Dilijan, Tavush region /spring water	0.096	0.837	< LOQ	0.389	< LOQ	0.607	0.139
Gosh, Tavush region /spring water	0.331	1.361	0.136	0.129	< LOQ	0.735	0.099
Areni, Akhtaghbyur, Yeghegnadzor, Vayots dzor /spring water	1.029	< LOQ	< LOQ	2.883	< LOQ	3.410	0.407
Areni, Kapaghbyur, Yeghegnadzor, Vayots dzor /spring water	0.340	0.232	< LOQ	0.096	< LOQ	1.575	0.169
Vachagan, Kapan, Syunik region /river water	0.209	1.3700	< LOQ	0.360	0.029	0.282	0.115
Artsvanik, Kapan, Syunik region /river water	0.261	2.9354	< LOQ	0.708	< LOQ	0.613	0.125
Jradzor, Kapan, Syunik region /river water	0.239	0.022	< LOQ	1.085	0.017	< LOQ	0.171
Getar, Yerevan / river water	< LOQ	3.15	< LOQ	6.780	< LOQ	< LOQ	0.508

* Mean of three measurements

** Sample diluted 1/10, by volume.

fluoride ion was detected in all tested samples of drinking water. The fluoride content in drinking water in Armenia was presented in the following range: 0.099 mg/L for Gosh, up to 0.407 mg/L for Yeghegnadzor, Areni, and Akhtaghbyur, and was within the permissible value.

Only a few ions, such as fluoride and nitrate, when present in high quantities in drinking water were detected to cause widespread health problems in humans (WHO 2022). It can be seen that most samples are in compliance with guidelines.

In conclusion, it should be noted that the method of ion chromatography using a CDD-10Avp conductivity detector has been successfully applied to determine anions in

drinking water samples. The above results show that this method is fast, accurate, sensitive, and suitable for analyzing water samples. Some differences were found in the amounts of anions between tap water and spring water.

Conclusion

An ion chromatographic test method for low-level quantification of inorganic anions (fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulfate) in drinking water (tap and spring water) samples was fully validated and successfully applied. Investigation results indicate that

the validated ion chromatographic test method is rapid, suitable, sensitive, precise, and accurate for various drinking water matrices for the routine simultaneous quantification of the key anions over the concentration range: 0.225–7.5 mg/L for chloride and nitrite, 0.15–5 mg/L for nitrate and fluoride, 1.125–37.5 mg/L for sulfate, 0.0375–12.5 mg/L for phosphate, and 0.075–25 mg/L for bromide, with correlation coefficients >0.998. Since the relative standard deviation of retention times was smaller than 1% and the peak resolution factor exceeded the 1.5, the method was declared selective. The low value of the LOD proves the applicability of the method in other samples where low concentrations of anions are present. Good accuracy (the recovery values 92.74–114.67%) and precision values (< 1% RSD) were achieved. The method is also considered robust in terms of stability in accordance with the ICH harmonized tripartite guideline and the Horwitz equation at the concentration levels used, since in all cases the relative standard deviation of peak areas varies from

0.10 to 1.79, which meets the stated requirements and is less than 2%.

The method was further used to analyze the anion content in drinking water samples from different regions of Armenia. Some variations in amounts of anions between tap water and spring water were detected. The observed concentrations for the anions in drinking water complied with the WHO limits for drinking water with some exceptions. The test method will be submitted to the quality control laboratory of the Pharmacy Institute of Yerevan State University as a convenient and practical tool for routine analysis and monitoring studies.

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Supplementary material 1

Supplementary tables

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Data type: docx

Explanation note: **table S1**. Recovery data for the anions from spiked QC samples, n = 3; **table S2**. Stability data for the anions solution, n = 6.

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