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Professional paper

Validation of ion chromatographic method for determination of inorganic anions in bottled water

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Abstract

This study validates a method for the determination of anions in drinking water using ion chromatography (IC), with a focus on accuracy, precision, and reliability, aligned with regulatory requirements for water quality monitoring. The method focuses on detecting common anions, including fluoride, chloride, nitrite, nitrate, sulfate, and phosphate, in compliance with international water quality standards. The anions were separated and examined by using a Dionex IonPacTM AS22 column (4 x 250 mm), with a flow rate of 1.2 mL/min, using 4.5 mM Na_2CO_3 /1.4 mM $NaHCO_3$ as eluent and DS6 heated conductivity detector. The validation of the analytical method was studied in terms of selectivity, linearity, accuracy, sensitivity, precision, and measurement uncertainty. The method demonstrated robust validity, characterized by high selectivity and excellent linearity between 0.9975 and 0.9999. Accuracy ranged from 98.87 to 100.80%, with precision reflected in low RSD values (0.05 – 2.85%). Sensitivity was evident from LOD (0.003 – 0.02 mg/L) and LOQ (0.009 – 0.05 mg/L) values. Measurement uncertainty was minimal, ranging from 2.43 to 4.88% confirming the method's reliability for quantitative analysis. The method has been tested on bottled water samples taken from four different places in North Macedonia (Debar, Bitola, Kratovo and Gevgelija) during the period May 2023 to April 2024, a time interval for which sufficient information on the quality of drinking water can be obtained. These findings confirm the method's applicability for routine monitoring of drinking water quality in line with international standards.

Key words: method validation, ion chromatography, anions, bottled water

Introduction

Analytical methods based on chromatography have become essential for the detection of diverse compounds in drinking water, including anions such as fluoride, chloride, nitrite, nitrate, phosphate, and sulfate. The presence of these anions serves as a crucial indicator of water quality, significantly contributing to environmental monitoring, adherence to regulations, and the protection of public health. The remarkable evolution of chromatography, particularly ion chromatography (IC), in the last half-century, is primarily a result of its unparalleled speed, user-friendliness, relatively low cost, and extensive versatility as a powerful separation technique for the quantitative evaluation of separated components (Dimitrovska et al., 2020).

To achieve reliable and reproducible results from chromatographic methods, these methods must be fully validated. Validation consists of a detailed evaluation of

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method parameters such as accuracy, precision, linearity, and sensitivity. This approach ensures that the method is suitable for its designated purpose, delivering accurate and reproducible results under defined conditions (Ermer and Nethercote, 2014; Hibbert, 2007; ICH, 2005). Validated methods are essential for the analysis of drinking water, as they facilitate the monitoring of compliance with the EN ISO/IEC 17025 standards, which define the general requirements for laboratory competence and testing set forth by the Institute for Accreditation of the Republic of North Macedonia and the Food and Veterinary Agency of the Republic of North Macedonia. This study contributes to ensuring public health protection and consumer trust through validated chromatographic determination of key anions in drinking water, enabling regulatory compliance and accurate product labeling in North Macedonia.

Material and methods

Instrumentation and ion chromatographic conditions

The analysis of inorganic anions in drinking water was performed using a Dionex Aquion ion chromatography system (Thermo Fisher Scientific), equipped with an isocratic pump, a Dionex IonPac™ AS22 analytical column (4 x 250 mm), an AG22 guard column, a DS6 heated conductivity detector, a Dionex AERS 500 Carbonate suppressor (4 mm), and an AS-DV autosampler. An isocratic eluent composed of carbonate/bicarbonate ensured efficient separation of fluoride, chloride, nitrite, nitrate, phosphate, and sulfate anions. To minimize baseline noise (approximately 0.99 µS/cm), the suppressor was chemically regenerated using 100 mM sulfuric acid, as recommended by Ivanova et al. (2018). A summary of the optimized chromatographic conditions is provided in Table 1.

Chemicals and standards

Ultrapure water with conductivity below 0.05 µS/cm, produced by a Direct-Q® 5 UV system (Merck), was used for all solution preparations. This water was free from the target anions. The suppressor was regenerated using sulfuric acid (AR grade, S.G. ~1.83; Fisher Chemical). The eluent was prepared by diluting Thermo Scientific Dionex AS22 Eluent Concentrate at a 1:100 ratio with ultrapure water, resulting in a working concentration of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$.

A certified Dionex Seven Anion Standard (Thermo Scientific Fisher), containing 20 mg/L fluoride, 30 mg/L chloride, 100 mg/L nitrite and nitrate, and 150 mg/L phosphate and sulfate, was used to prepare working calibration standards through serial dilution. All standard solutions were prepared using class A volumetric glassware.

Sample preparation followed the EN ISO 10304-1 standard. Prior to analysis, samples were filtered through 0.45 µm membrane filters and transferred to polyethylene vessels. Instrument control and data acquisition were carried out using Chromeleon® Version 7.3 (Thermo Fisher Scientific, 2018).

Table 1. Optimized condition for ion chromatographic measurement

Parameter	*Value*
Column	Dionex IonPac™ AS22 Analytical (4 x 250 mm)
Precolumn	AG22 Guard (4 x 50 mm)
Eluent	4.5 mM Na_2CO_3/1.4 mM $NaHCO_3$
Eluent flow rate	1.2 mL/min
Elution mode	Isocratic
Column temperature	30°C
Detection	Suppressed Conductivity
Suppressor	Dionex Anion Self-Regenerating Suppressor (Dionex AERS 500 Carbonate 4mm)
Applied Current	41 mA
Injection volume	10 µL
Storage solution	100 mM Sodium bicarbonate
Determination mode	Peak area

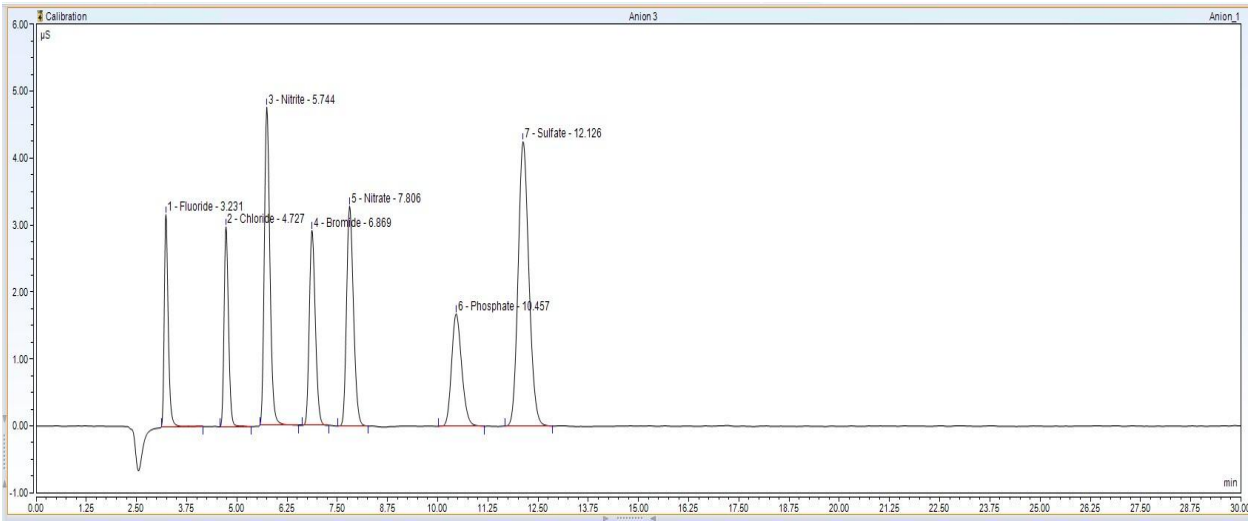


Fig. 1. Typical anion chromatogram in the following concentrations 2 mg/L F^-, 3 mg/L Cl^-, 10 mg/L NO_2^- and NO_3^-, 15 mg/L PO_4^{3-} and SO_4^{2-} produced by the method presented.

Table 2. Method selectivity (%RSD)

	Retention time (min)	*SD (min)*	*RSD (%)*
F^-	3.24	0.014	0.44
Cl^-	4.73	0.011	0.24
NO_2^-	5.76	0.032	0.55
NO_3^-	7.8	0.013	0.17
PO_4^{3-}	10.45	0.013	0.12
SO_4^{2-}	12.15	0.043	0.36

Results and discussion

The tested anions (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) were successfully separated under optimized chromatographic conditions using an eluent containing 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$, as presented in Table 1. Figure 1 shows a representative chromatogram corresponding to the following concentrations: 2 mg/L F^-, 3 mg/L Cl^-, 10 mg/L NO_2^- and NO_3^-, and 15 mg/L PO_4^{3-} and SO_4^{2-}. Complete separation of all analytes was achieved within 20 minutes.

Selectivity

Selectivity is a critical parameter in chromatographic method validation, ensuring the method's ability to quantify analytes in the presence of potential interferences. It was assessed by evaluating the relative standard deviations (RSD) of retention times across ten replicate injections at five concentration levels: 0.2–20 mg/L for F^-, 0.3–30 mg/L for Cl^-, 1–100 mg/L for NO_2^- and NO_3^-, and 1.5–150 mg/L for PO_4^{3-} and SO_4^{2-}.

As shown in Table 2, the RSD values for all analytes were consistently below 1%, indicating highly stable retention times regardless of concentration. This consistency, further illustrated in Figure 2, demonstrates that the peak positions were unaffected by concentration variations, confirming the selectivity and robustness of the analytical method.

In chromatographic systems, the degree of separation between two analytes is quantitatively evaluated by the column resolution (R_S). This parameter reflects the column's ability to resolve adjacent peaks and is critical for ensuring accurate quantification. The resolution is calculated using the retention times (t_{R1} and t_{R2}) and peak widths (w_1 and w_2) of two neighboring peaks, as shown in Figure 3.

According to the EN ISO 10304-1:2007 guidelines, the minimum acceptable resolution between the target anion peak and the nearest adjacent peak should not be less than 1.3. The resolution values calculated using Chromeleon® 7.3 software (Thermo Fisher Scientific, 2018) and summarized in Table 3 demonstrate sufficient separation at all tested concentration levels. These results confirm the adequacy of the chromatographic conditions for reliable anion analysis.

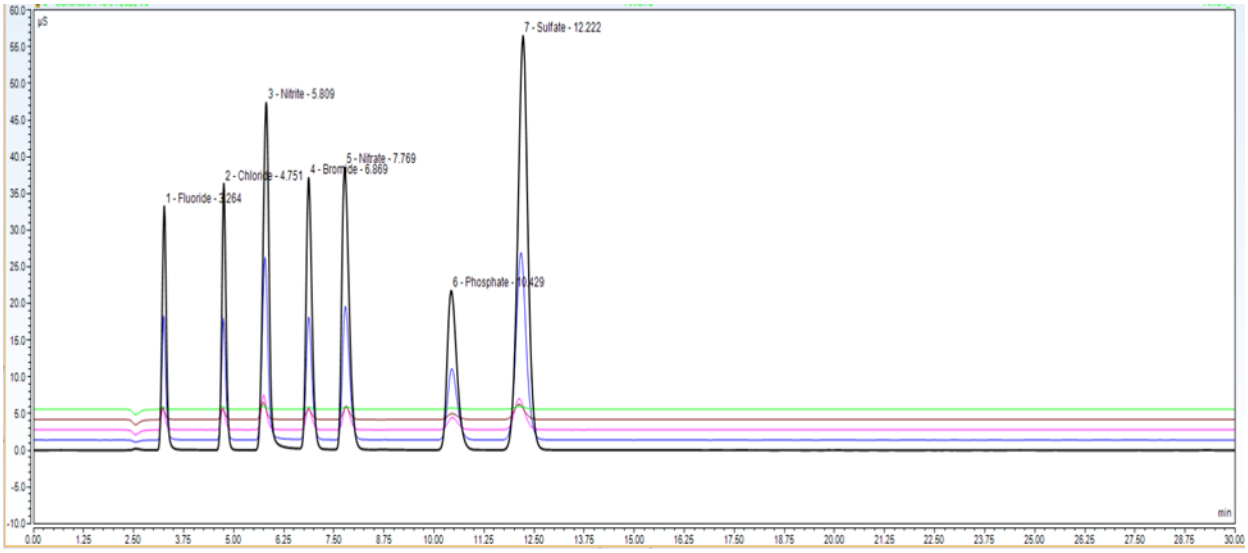
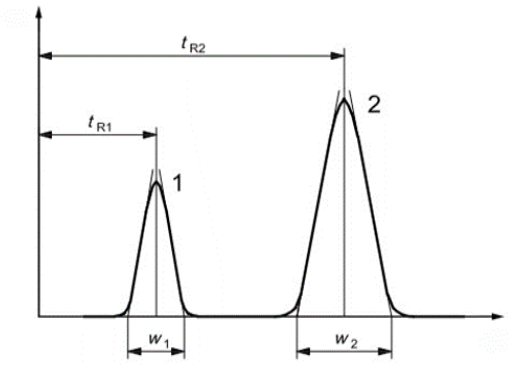


Fig. 2. Overlaid chromatogram of the anions at the various calibration standard concentrations: 0.2-20 mg/L for F^-; 0.3-30 mg/L for Cl^-; 1-100 mg/L for NO_2^- and NO_3^-; and 1.5-150 mg/L for PO_4^{3-} and SO_4^{2-}.



$$R_s = \frac{2(t_{R2} - t_{R1})}{w_1 + w_2}$$

Fig. 3. Graphical representation of the parameters and equation to calculate the peak resolution, R_S.

Table 3. Method selectivity (R_S)

	R_s (min)				
	Anion 1	Anion 2	Anion 3	Anion 4	Anion 5
F^-	7.88	8.15	8.07	8.01	7.79
Cl^-	4.54	4.61	4.53	4.49	4.48
NO_2^-	3.89	4.15	4.3	4.29	4.28
NO_3^-	6.87	7.00	6.89	6.87	6.63
PO_4^{3-}	4.00	3.85	3.54	3.51	3.36
SO_4^{2-}	n.a.	n.a.	n.a.	n.a.	n.a.

Linearity and range

Linearity refers to the ability of an analytical method to produce results that are directly proportional to the concentration of the analyte within a specified range. According to established guidelines, the linearity assessment requires a minimum of five calibration standards and a correlation coefficient (R^2) of at least 0.995 (Miskaki et al., 2007). In this study, calibration standards were prepared across the following concentration ranges: 0.2–20 mg/L for fluoride, 0.3–30 mg/L for chloride, 1–100 mg/L for both nitrite and nitrate, and 1.5–150 mg/L for phosphate and sulfate. Each concentration level was measured in triplicate, and the mean values were used to construct the calibration curves (Fig. 4).

Regression results presented in Table 4 demonstrate strong linear correlations between peak area and analyte concentration across all tested ranges. To validate the model, residual analysis was applied. The standardized residuals revealed no significant outliers, confirming the appropriateness of the linear regression models used (Băjenaru et al., 2015). These outcomes underscore the method's reliability for quantitative analysis in accordance with regulatory requirements.

Method accuracy

The accuracy of an analytical method reflects the closeness of agreement between a test result and the accepted reference value (ICH, 2005). One approach to evaluating accuracy is through the use of certified reference materials (CRMs), whereby the systematic error (bias) is calculated. A bias within ±5% is generally accepted as a valid threshold (Manickum et al., 2019) and is determined using the following equation:

Bias = (obtained value − true value) / true value × 100%.

Another widely used approach is the standard addition method, where accuracy is expressed as analytical recovery - the percentage of analyte recovered after the analytical procedure. Acceptable recovery values are typically within 90% to 110%, corresponding to a percentage error of ±10% (Ivanova et al., 2018; Manickum et al., 2019). The recovery is calculated as:

$$\text{Recovery (\%)} = (C_S - C) / S \times 100,$$

where C_S is the measured concentration in the spiked sample, C is the concentration in the blank, and S is the spiked amount.

To validate method accuracy, six replicates at low, medium, and high concentration levels were analyzed. The results, summarized in Table 5, show recovery values between 96.70% and 100.36%, with bias around ±5%, confirming the method's accuracy for determining anions by ion chromatography.

Method detection limits and quantification limits

The limit of detection (LOD) is defined as the lowest concentration of an analyte that can be reliably distinguished from background noise, though not necessarily quantified. In contrast, the limit of quantification (LOQ) represents the lowest concentration at which the analyte can be quantified with acceptable precision and accuracy (ICH, 2005).

The determination of LOD and LOQ relies on the standard deviation of the response (σ) and the slope (S) of the calibration curve, according to the following equations:

$$LOD = (3.3 \times \sigma) / S \qquad LOQ = (10 \times \sigma) / S$$

where σ is either the residual standard deviation of the regression line (s_y) or the standard deviation of the intercept (s_a).

The results presented in Table 6 were derived using the data from Table 4. It is important to note that the LOD and LOQ values are influenced by the method of calculating σ. In all cases, the values calculated using the residual standard deviation were higher compared to those based on the intercept, indicating a more conservative estimation (Ermer and Nethercote, 2014).

Table 4. Regression analysis results for the calibration curves

Anion	*Linear range (mg/L)*	*Slope (b)*	*Slope standard deviation, (s_b)*	*Intercept (a)*	*Intercept standard deviation (s_a)*	*Correlation coefficient (R^2)*	*Residual standard deviation (s_y)*
F^-	0,2-20	0.203	1.97E-05	-0.032	1.98E-04	0.9995	3.32E-04
Cl^-	0,3-30	0.146	4.35E-05	-0.046	6.56E-04	0.9986	1.10E-03
NO_2^-	1-100	0.086	1.59E-06	-0.052	7.99E-05	0.9999	1.34E-04
NO_3^-	1-100	0.081	3.14E-06	-0.122	1.58E-04	0.9980	2.65E-04
PO_4^{3-}	1.5-150	0.040	2.51E-06	-0.099	1.89E-04	0.9975	3.17E-04
SO_4^{2-}	1.5-150	0.111	2.26E-06	-0.272	1.70E-04	0.9980	2.86E-04

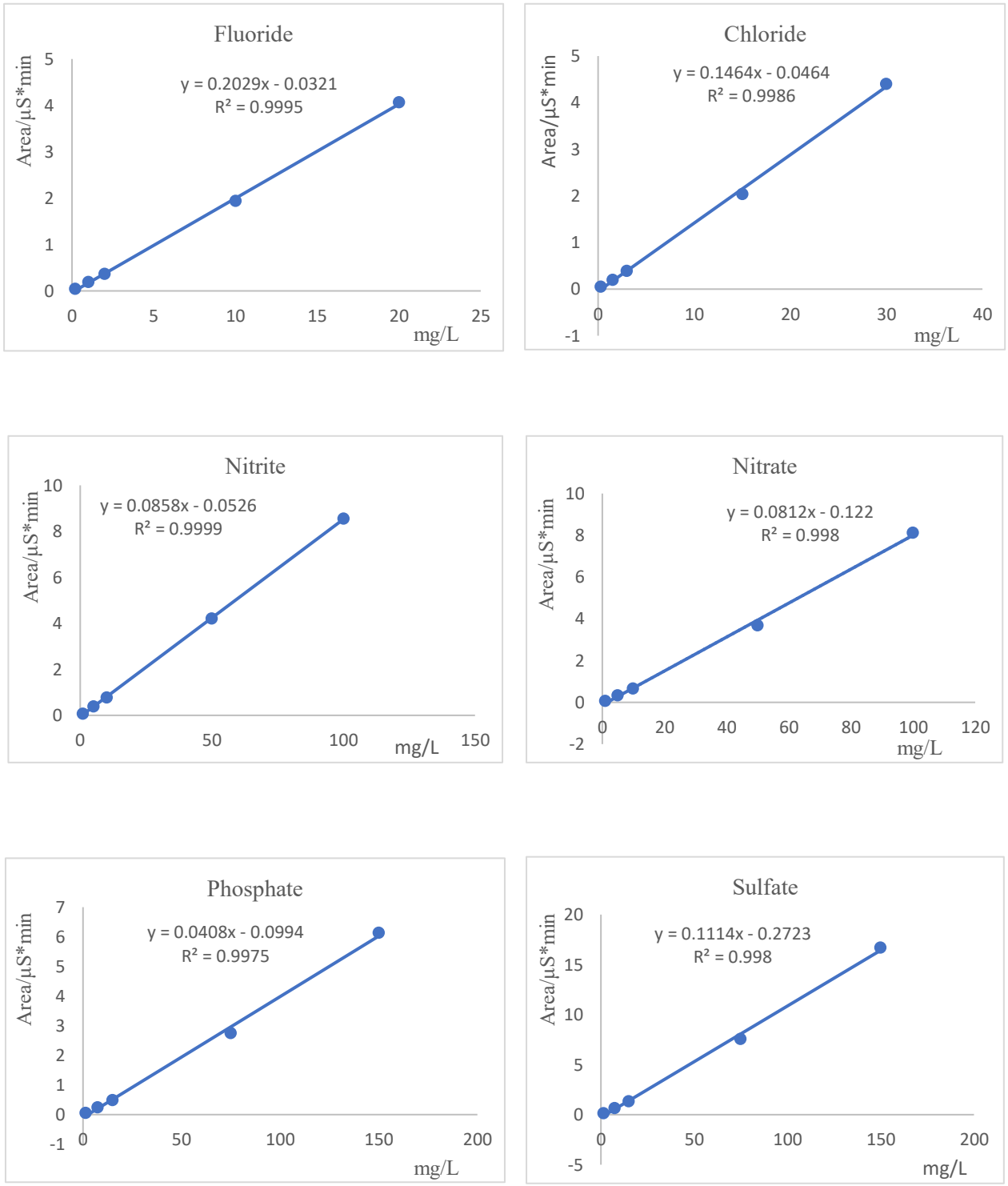


Fig. 4. Calibration curves for F^- (0.2-20 mg/L), Cl^- (0.3-30 mg/L), NO_2^- (1-100 mg/L), NO_3^- (1-100 mg/L), SO_4^{2-} (1.5-150 mg/L) and PO_4^{3-} (1.5-150 mg/L).

Table 5. Method accuracy

Analyte	*Concentration level (%)*	*Amount added (mg/L)*	*Amount found (mg/L)*	*Recovery (%)*	*RSD (%) (n=3)*	*Bias (%)*
F^-	50	2.50	2.50	100.13	2.83	0.13
	100	5.00	5.06	100.17	1.62	1.17
	150	7.50	7.55	100.62	0.70	0.62
Cl^-	50	25.00	25.00	100.01	2.75	0.01
	100	50.00	50.08	100.16	1.19	0.16
	150	75.00	74.88	99.84	0.48	-0.16
NO_2^-	50	2.50	2.52	100.80	2.85	0.80
	100	5.00	4.95	99.03	1.94	-0.97
	150	7.50	7.51	100.11	0.69	0.11
NO_3^-	50	25.00	24.98	99.91	2.84	-0.09
	100	50.00	50.31	100.63	0.93	0.63
	150	75.00	74.93	99.90	0.37	-0.10
PO_4^{3-}	50	2.50	2.51	100.20	2.08	0.20
	100	5.00	5.03	100.67	1.82	0.67
	150	7.50	7.54	100.56	0.72	0.56
SO_4^{2-}	50	25.00	25.03	100.13	1.59	0.13
	100	50.00	50.14	100.28	0.75	0.28
	150	75.00	74.16	98.87	0.35	-1.13

Table 6. Method detection limits and quantification limits

	LOD (mg/L)		*LOQ (mg/L)*	
Anion	*Calibration data SD of intercept (s_a)*	*Calibration data residual SD (s_y)*	*Calibration data SD of intercept (s_a)*	*Calibration data residual SD (s_y)*
F^-	0.0032	0.0054	0.0097	0.0164
Cl^-	0.0148	0.0248	0.0448	0.0752
NO_2^-	0.0030	0.0052	0.0093	0.0156
NO_3^-	0.0064	0.0108	0.0194	0.0326
PO_4^{3-}	0.0153	0.0257	0.0463	0.0778
SO_4^{2-}	0.0050	0.0085	0.0153	0.0257

Table 7. Method repeatability

Analyte	*No. of replicates*	*Low standard concentration*		*Medium standard concentration*		*High standard concentration*	
		SD (mg/L)	*RSD (%)*	*SD (mg/L)*	*RSD (%)*	*SD (mg/L)*	*RSD (%)*
F^-	6	0.06	2.38	0.08	1.62	0.05	0.70
Cl^-	6	0.69	2.75	0.60	1.19	0.36	0.48
NO_2^-	6	0.07	1.85	0.10	1.94	0.05	0.69
NO_3^-	6	0.71	2.84	0.47	0.93	0.27	0.37
PO_4^{3-}	6	0.05	2.08	0.09	1.82	0.05	0.72
SO_4^{2-}	6	0.40	1.59	0.37	0.75	0.26	0.35

Method repeatability and intermediate precision

The determination of method repeatability and intermediate precision was performed according to the guidelines established in the Eurochem Guide (Magnusson and Örnemark, 2014). Repeatability data were obtained by analyzing six replicates of an identical standard solution at three concentration levels: low (2.5 mg/L for F^-, NO_2^-, PO_4^{3-} and 25 mg/L for Cl^-, NO_3^-, SO_4^{2-}), medium (5 mg/L for F^-, NO_2^-, PO_4^{3-} and 50 mg/L for Cl^-, NO_3^-, SO_4^{2-}), and high (7.5 mg/L for F^-, NO_2^-, PO_4^{3-} and 75 mg/L for Cl^-, NO_3^-, SO_4^{2-}). These analyses were carried out within a short time frame by the same analyst using the same instrument, ensuring high precision. The precision of the method is summarized in Table 7.

For evaluating intermediate precision, the method was tested across ten replicates conducted by different analysts on separate days, using the same instrument, at a concentration of 5.0 mg/L for F^-, NO_2^-, and PO_4^{3-}, and 50.0 mg/L for Cl^-, NO_3^-, and SO_4^{2-}. The relative standard deviations, as shown in Table 8, confirm that the method meets the precision criteria outlined in the EN ISO 10304-1:2007 standard.

Recovery test results from spiked water samples

The determination of the analytical recovery of the method was carried out by spiking water samples collected from the regions of Kratovo, Bitola, Gevgelija, and Debar with the following concentrations: 0.5 mg/L and 1.0 mg/L for F^-, NO_2^-, and PO_4^{3-}; and 5.0 mg/L and 10.0 mg/L for Cl^-, NO_3^-, and SO_4^{2-}. The analytical recovery (%) was calculated as the difference between the concentrations in spiked and unspiked samples, relative to the added concentration of the analyte. The data presented in Table 9 show recovery values ranging from 90.30 to 109.86%, which fall within the acceptable range of ±10%. These findings confirm that the matrix composition of the tested natural water samples does not interfere with the validated ion chromatographic method.

Method uncertainty

Measurement uncertainty, often expressed as a standard or expanded standard deviation, represents a parameter accompanying the result of a measurement, indicating the range within which the true value is expected to lie with a specified level of confidence. It was determined by evaluating both type A (derived from method repeatability) and type B (from calibration certificates) uncertainty components. These were converted into relative standard deviation units and combined to calculate the combined measurement uncertainty (u_C), as described by Ellison et al. (2012). The expanded uncertainty (U), corresponding to a 95% confidence level, was calculated as $2 \times u_C$. The results are presented in Table 10.

Table 8. Method intermediate precision

	Analyte concentration (mg/L)	*Analyst 1*	*Analyst 2*	*RSD_r[1] (%)*
		RSD (%)	*RSD (%)*	
F^-	5.0	2.10	1.61	4.1
Cl^-	50.0	1.11	1.17	1.9
NO_2^-	5.0	3.32	2.22	3.5
NO_3^-	50.0	0.91	1.21	2.8
PO_4^{3-}	5.0	2.43	4.42	10.8
SO_4^{2-}	50.0	0.63	0.74	1.6

[1]Values are taken from MKC EN ISO 10304

Table 9. Method recovery

Anion	Spike conc. (mg/L)	Kratovo		Bitola		Gevgelija		Debar	
		c_{cal} (mg/L)	Rec (%)	c_{cal} (mg/L)	Rec (%)	c_{cal} (mg/L)	Rec (%)	c_{cal} (mg/L)	Rec (%)
F^-	-	0.07	-	0.09	-	0.08	-	0.08	-
	0.5	0.53	92.11	0.56	93.33	0.56	97.95	0.56	96.21
	1	0.98	91.28	1.03	94.16	1.03	95.68	0.98	90.30
Cl^-	-	2.71	-	3.28	-	2.83	-	2.85	-
	5	7.78	101.37	8.12	96.67	7.77	98.87	7.45	92.02
	10	12.12	94.11	13.01	97.32	13.36	105.29	12.78	99.30
NO_2^-	-	n.d.	-	n.d.	-	n.d.	-	n.d.	-
	0.5	0.51	101.66	0.52	103.62	0.55	109.86	0.55	109.51
	1	0.99	98.86	1.07	107.67	1.02	101.66	1.03	103.22
NO_3^-	-	4.71	-	0.38	-	1.01	-	0.44	-
	5	9.78	101.5	5.62	104.7	5.85	96.89	5.36	98.51
	10	13.75	90.41	10.34	98.53	10.27	92.59	10.41	99.74
PO_4^{3-}	-	n.d.	-	n.d.	-	0.17	-	n.d.	-
	0.5	0.46	91.36	0.51	103.29	0.65	96.47	0.47	94.06
	1	0.96	95.74	0.99	98.53	1.08	90.82	0.97	96.63
SO_4^{2-}	-	7.96	-	18.61	-	2.5	-	10.49	-
	5	12.86	98.16	23.45	96.74	7.13	92.64	15.36	97.41
	10	17.90	99.42	28.07	94.63	12.17	96.65	19.57	93.4

n.d. = not detected

Table 10. Method uncertainty

Analyte	Concentration level (mg/L)	u_C (mg/L)	U (mg/L)
F^-	5.00	0.10	0.19
Cl^-	50.00	0.94	1.89
NO_2^-	5.00	0.11	0.23
NO_3^-	50.00	0.93	1.87
PO_4^{3-}	5.00	0.09	0.19
SO_4^{2-}	50.00	0.61	1.22

Measurement uncertainty should be reassessed whenever new equipment is introduced, when technical specifications of the current instrumentation are altered, or when significant changes in operating conditions are made.

Results from analysis of bottled drinking water by validated IC method

The analysed samples were packaged natural mineral waters collected from various regions across the country over a one-year period, covering all four seasons. Each sample was analysed in triplicate using a validated ion chromatographic method. The results for all anions are presented in Table 11. Fluoride levels were consistent across all regions and seasons. Chloride concentrations in spring and winter were similar, with a slight decline during summer and autumn. Nitrites were not detected in any sample throughout the year. Nitrate levels showed a similar seasonal pattern, with stable values in spring and winter, and a minor decrease in the warmer seasons; the highest levels were observed in Debar and Bitola during winter. Phosphates were absent in all samples from Kratovo, Debar, and Bitola, but were consistently detected in Gevgelija. Sulfate concentrations in Kratovo, Debar, and Bitola followed a seasonal trend similar to chlorides and nitrates, while Gevgelija showed the highest sulfate levels in autumn. All measured values complied with the national regulation for natural mineral waters (Official Gazette of the Republic of Macedonia No.184/2018), confirming the safety and quality of the tested samples.

The ion chromatographic method for the determination of dissolved anions in packaged drinking water - fluoride, chloride, nitrite, nitrate, phosphate, and sulfate was validated through the assessment of linearity, accuracy, precision, limits of detection and quantification, and measurement uncertainty. Linearity was established over the following concentration ranges: 0.2–20 mg/L for F^-, 0.3–30 mg/L for Cl^-, 1–100 mg/L for NO_2^- and NO_3^-, and 1.5–150 mg/L for PO_4^{3-} and SO_4^{2-}.

Table 11. The results obtained by analyzing the bottled water samples

Location	*Anion*[1]	*Spring*	*Summer*	*Autumn*	*Winter*
		c (mg/L)	*c (mg/L)*	*c (mg/L)*	*c (mg/L)*
Kratovo	F^-	0.22	0.2	0.215	0.282
	Cl^-	1.841	1.764	1.707	1.989
	NO_2^-	n.d.	n.d.	n.d.	n.d.
	NO_3^-	4.924	4.582	4.575	4.943
	PO_4^{3-}	n.d.	n.d.	n.d.	n.d.
	SO_4^{2-}	9.496	9.223	8.662	9.859
Debar	F^-	0.21	0.204	0.22	0.243
	Cl^-	1.566	1.21	1.21	1.557
	NO_2^-	n.d.	n.d.	n.d.	n.d.
	NO_3^-	0.294	0.265	0.2	0.721
	PO_4^{3-}	n.d.	n.d.	n.d.	n.d.
	SO_4^{2-}	10.379	9.892	9.747	12.348
Gevgelija	F^-	0.187	0.187	0.183	0.226
	Cl^-	2.896	1.393	1.313	1.466
	NO_2^-	n.d.	n.d.	n.d.	n.d.
	NO_3^-	2.596	0.915	0.776	1.071
	PO_4^{3-}	2.635	2.723	2.617	2.663
	SO_4^{2-}	6.585	3.698	3.610	4.451
Bitola	F^-	0.224	0.224	0.219	0.242
	Cl^-	1.912	1.87	1.676	1.944
	NO_2^-	n.d.	n.d.	n.d.	n.d.
	NO_3^-	0.18	0.163	0.175	0.376
	PO_4^{3-}	n.d.	n.d.	n.d.	n.d.
	SO_4^{2-}	20.311	18.837	16.477	20.209

[1]Each represents the mean value of three determinations.
n.d. = not detected

Conclusion

The validation process of the chromatographic method for the determination of anions in drinking water, conducted using a Dionex Aquion ion chromatograph, confirmed the method's reliability, precision, and suitability for routine water quality monitoring. By adhering to systematic validation protocols, including assessments of accuracy, precision, specificity, linearity, and sensitivity, the method demonstrates compliance with regulatory standards such as EN ISO/IEC 17025.

The application of the IonPac™ AS22 column and suppressed conductivity detection allowed for effective separation and quantification of key anions (fluoride, chloride, nitrite, nitrate, phosphate, and sulfate), with high sensitivity and reproducibility. The validated method exhibited excellent stability and robustness under varying operational conditions.

Experimental values were compared with the declared values on product labels and found to be largely consistent, with only minor discrepancies. In some cases, the measured concentrations were slightly lower than those stated. All anion levels were below the maximum permissible limits as defined by the Regulation on the special safety requirements for natural mineral waters, spring waters, and other packaged waters (Official Gazette of the Republic of Macedonia, No. 184/2018), thereby confirming compliance with safety and quality standards. While seasonal variations in anion concentrations were minimal, significant differences were observed between various brands of packaged water.

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Резиме

Валидација на методот на јонска хроматографија за определување на неоргански анјони во пакувана вода

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Клучни зборови: валидација на метода, јонска хроматографија, анјони, пакувана вода

Со оваа студија се потврдува валидноста на методот за определување на анјони во водата за пиење со помош на јонска хроматографија (IC), со фокус на точноста, прецизноста и веродостојноста, усогласена со регулаторните барања за следење на квалитетот на водата. Методот се фокусира на откривање вообичаени анјони, вклучувајќи флуориди, хлориди, нитрити, нитрати, фосфати и сулфати, во согласност со меѓународните стандарди за квалитетот на водата. Анјоните се раздвојуваат и испитуваат со употреба на Dionex IonPac^{TM} AS22 (4 x 250 mm) колона, со брзина на проток од 1,2 mL/min, при што како елуент се користи 4,5 mM Na_2CO_3/1,4 mM $NaHCO_3$ и DS6 топлински детектор за спроводливост. Потврдувањето на аналитичкиот метод е проучувано од аспект на селективност, линеарност, точност, сензитивност, прецизност како и мерна неодреденост. Методот покажа висока валидност, карактеризирана со висока селективност и одлична линеарност помеѓу 0,9975 – 0.9999. Точноста на методот е 98,87 до 100,80%, а прецизноста е одразена со ниски вредности на RSD (0,05 – 2,85%). Сензитивноста беше одредена од вредностите за LOD (0,003 – 0,02 mg/L) и LOQ (0,009 – 0.05 mg/L). Мерната неодреденост е минимална и се движи во границите од 2,43 до 4,88% што ја потврдува веродостојноста на методот за квантитативна анализа. Методот е тестиран на примероци од пакувана вода за пиење земени на четири различни места во Северна Македонија (Дебар, Битола, Кратово и Гевгелија) во периодот од мај 2023 до април 2024 година, што е доволен период за кој може да се добијат доволно информации за квалитетот на водата за пиење. Овие наоѓања ја потврдуваат применливоста на методот за рутинско следење на квалитетот на водата за пиење во согласност со меѓународните стандарди.