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Ion chromatography

Water analysis: The role of standardized ion chromatography

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Goal
Present an introductory overview of standard ion chromatography methods employed in water analysis

Introduction
Analytical chemistry is essential to the advancement of our society, providing numerous approaches for the qualitative and quantitative analysis of chemicals that could be harmful to individuals and the environment. The analytical task, based on the physicochemical characteristics of the analytes, their concentration, and the matrix, determines the analytical approach and workflow choice.

Ion chromatography (IC) is a widely employed analytical technique for separating and quantifying ions in various matrices. It is extensively used to analyze water samples from different sources, including potable water, surface water, and wastewater, and allows for accurate identification and precise measurement of ionic or ionizable contaminants.

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Modern IC provides a powerful analytical tool to access dissolved inorganic and organic ions, such as chloride, nitrate, sulfate, phosphate, group I and II cations, organic acids, and amines. These analytes can stem from various sources, natural geological or meteorological conditions, land runoffs, or human interventions, such as agricultural, industrial, or municipal activities, in the form of wastewater. IC can be used to monitor the concentrations of these target analytes, and consequently guide the protection of vital aquatic ecosystems. IC can, for example, measure levels of nitrogen and phosphorus nutrients, excessive amounts of which can cause algal blooms and eutrophication. Additionally, through the combination of IC with modern triple quadruple or high-resolution accurate mass (HRAM) mass spectrometers, compounds, such as disinfection by-products (bromate, chlorate, chlorite, perchlorate) and polar ionic pesticides and their metabolites, can be reliably identified, and quantified. It is important to analyze such compounds due to their potential carcinogenic and pathogenic properties, thus ensuring consumer and environmental protection.

Strict compliance with national and global standards is critical to guarantee the efficacy and dependability of analytical outcomes. This compliance contributes to safeguarding people's well-being and the environment, guaranteeing that water consumed or discharged is safe and devoid of hazardous substances. These benchmarks provide a unified method for analytical assessment, boosting precision and accuracy when performing analysis. Furthermore, they offer an auditable way to evaluate results from disparate countries or regions, ensuring the same parameters are faithfully monitored.

The International Organization for Standardization (ISO)[1] and the American Society for Testing and Materials (ASTM)[2] have been instrumental in developing and preserving standards across multiple industries and analytical chemistry. As an amalgamation of more than 160 national standard bodies, ISO is a global alliance focused on cooperatively founding and protecting international standards for different products and services. ASTM specializes in developing and sustaining standards related to materials, tests, and products in engineering and scientific fields. The United States Environmental Protection Agency (U.S. EPA)[3], one of the foremost national standard organizations' representatives, has considerably influenced standardization initiatives through its published IC standards. The German Institute for Standardization (DIN) was among the first to release national standards for using IC in evaluating anions in aqueous samples in 1985.[4]

Experts in their disciplines volunteer their analytical experience to design national and international analytical standards open to all companies and individuals, creating a level competitive field. With the many national standards for employing IC in water analysis, it can be hard to assess them equally. Therefore, the discussion in this document will center on the international standards published by ISO and ASTM. In addition, the close association between international standardization bodies and national committees causes several national IC standards to be analogous in content to the international ones, encompassing the review of national documents. We encourage readers to investigate the sources thoroughly to become completely familiar with the standard procedures. The following discussions focus on the compliant implementation and application of Thermo Fisher Scientific technology.

Experimental conditions

Thermo Scientific™ Dionex™ Ion Chromatography Systems (ICS)[5], Thermo Scientific™ Dionex™ IonPac™ Columns[6], Thermo Scientific™ Dionex™ Suppressors[7], and the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS).[8] All experiments were conducted with the highest quality chemicals and deionized (DI) water (type 1), as requested by the international standards. The minimum recommendations for DI water type 1 are defined by ASTM[9] and ISO.[10] Water quality is essential to the quality of analytical work, and monitoring it is an integral part of assuring quality control. The specifications of the DI water play a significant role in determining the quality of subsequent analytics—not just those of the IC. When operated, serviced, and maintained correctly, modern laboratory water treatment systems can yield water superior to the specified standards, with an electrical conductivity below 0.056 µS/cm ($> 18\,M\Omega \cdot cm$) at 25 °C and a total organic carbon (TOC) content of less than 5 µg/L.[11]

Given the comprehensive nature of the white paper, a complete overview of all details is not feasible. For additional information, please refer to the accompanying references or contact a Thermo Fisher Scientific sales or support representative.

Discussion

The most relevant ASTM and ISO standards for water analysis are outlined in Tables 1 and 2, arranged by year of publication and last revision, respectively. Supplementary notes on the standards and their references have been included in the tables for further consideration.

Similarities and differences

Table 1. ISO standards describing the use of IC for water analysis

Number	Title	Analytes	Year*	Remarks	Reference	Thermo Scientific Application Notes
ISO 10304-3:1997	Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate	Chromate, iodide, sulfite, thiocyanate and thiosulfate	1997	Detection: suppressed conductivity with UV/VIS detection described	(70)	AppsLab chromate (5 results)[76] AppsLab sulfite (4 results)[77] AppsLab thiosulfate, thiocyanate (9 results)[78]
ISO 14911:1998	Water quality — Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography — Method for water and wastewater	Alkaline and alkaline earth metals, including ammonia	1998	Detection: suppressed and non-suppressed conductivity	(19)	AppsLab cations (7 results)[79]
ISO 15061:2001	Water quality — Determination of dissolved bromate — Method by liquid chromatography of ions	Bromate	2001	Detection: suppressed conductivity. Suggests sample preparation (Ion exchange-SPE, OnGuard cartridges) and inline sample preconcentration. Permits direct injection with or without sample preparation. Matrices: Drinking water, raw water, surface water, partially treated water, or swimming pool water	(31)	AppsLab bromate, bromide, chlorate, chlorite (6 results)[80]
ISO 10304-1:2007	Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate, and sulfate	Bromide, chloride, fluoride, nitrate, nitrite, o-phosphate, and sulfate	2007	Detection: suppressed conductivity and UV/VIS Carbonate and hydrogen carbonate, and hydroxide eluents	(14)	AppsLab anions (31 results)[81]
ISO 11206:2011	Water quality — Determination of dissolved bromate — Method using ion chromatography (IC) and post column reaction (PCR)	Bromate	2011	Detection: Post-column reaction combined with UV detection. Matrices: Drinking water, mineral water, raw water, surface water, partially treated water, or swimming pool water	(32)	AppsLab bromate (6 results)[82]
ISO 19340:2017	Water quality — Determination of dissolved perchlorate — Method using ion chromatography (IC)	Perchlorate	2017	Detection: suppressed conductivity. Allows a direct determination of perchlorate ≥ 1 µg/L. Mass spectrometry detection is mentioned in the informative annex.	(52)	AppsLab perchlorate (22 results)[83]
ISO 10304-4:2022	Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 4: Determination of chlorate, chloride and chlorite in water with low contamination	Chlorate, chlorite, and chloride	2022	Detection: suppressed conductivity. For drinking water, raw water, or swimming pool water.	(18)	Appslab oxychlorides (5 results)[84]

* Publishing year or year of the last update

Table 2. ASTM standards describing the use of IC for water analysis

Number	Titel	Analytes	Year*	Remarks	Reference	Thermo Scientific Application Notes
ASTM D5257-17	Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography	Chromate	2022	Detection: UV absorption; $\lambda_{abs} = 520$ nm after derivatization with 1,5-Diphenylcarbazide. Suitable over the range of approximately 1 to 1000 µg/L. Higher levels can be determined by appropriate dilution Matrices: Wastewater, surface water, and drinking water	(71)	AppsLab chromate (5 results)[76]
ASTM D5996-16	Standard Test Method for Measuring Anionic Contaminants in High-Purity Water by Online Ion Chromatography	Inorganic and organic anions (acetate, formate, propionate)	2019	Concentration range: Sub µg/L Online measurement to improve the analytical performance	(85)	Documents & Support page (29 results)[86]
ASTM D8234-19	Standard Test Method for Anions in High Ionic Water by Ion Chromatography using Tandem Suppressed Conductivity and UV Detection	Fluoride, chloride, nitrite, bromide, nitrate, o phosphate, sulfate	2019	Detection: suppressed conductivity, UV absorption. Concentration range: up to 20% sodium chloride	(87)	AppsLab anions (31 results)[81]
ASTM D6581-18	Standard Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography	Bromate, bromide, chlorate, chlorite	2019	Detection: suppressed conductivity. Carbonate and hydrogen carbonate, hydroxide eluents. Matrices: Raw, finished drinking and bottled (non-carbonated) water	(33)	AppsLab bromate, bromide, chlorate, chlorite (6 results)[80]
ASTM D5085-21	Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Suppressed Ion Chromatography	Chloride, nitrate, and sulfate	2017	Atmospheric wet deposition	(88)	AppsLab rain (4 results)[89]
ASTM D516-16	Standard Test Method for Sulfate Ion in Water	Sulfate	2017	Detection: suppressed conductivity. Concentration range: 250 mg/L At high concentrations, sulfate causes a cathartic action (especially in children) in the presence of sodium and magnesium.	(90)	AppsLab anions (31 results)[81]
ASTM D6919-17	Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography	Alkali and alkaline earth cations and ammonium	2017	Detection: suppressed and non-suppressed conductivity	(23)	AppsLab cations (7 results)[79]
ASTM D4327-17	Standard Test Method for Anions in Water by Suppressed Ion Chromatography	Fluoride, chloride, nitride, hydrogen phosphate, bromide, nitrate, and sulfate	2017	Detection: suppressed conductivity, both chemically and electrolytically regenerated suppressors. Carbonate and hydrogen carbonate, hydroxide eluents	(15)	AppsLab anions (31 results)[81]

* Publishing year or year of the last update

Examining the historical progress, ASTM and ISO initially specified different methods of IC based on the complexity of the sample matrix. For example, the approaches for testing drinking water differed from those for wastewater because only low-capacity separation phases and mainly isocratic separation methods were available or applied, at the early stages of IC standard development.

The introduction of highly efficient, high-capacity analytical ion exchangers ushered in a new era of chromatographic analysis. These columns boast increased loadability and improved chromatographic separation, particularly for early-eluting analytes. This has enabled the development of streamlined methods, allowing for examining samples of varying complexities using a single analytical setup.[12, 13] For example, in its newest edition, ISO 10304-1 outlines an IC method for determining the amount of dissolved fluoride, chloride, nitrite, bromide, nitrate, o-phosphate, and sulfate in drinking water, groundwater, surface water, wastewater, leachate, and seawater.[14]

The international standardization bodies describe suppressed conductivity detection utilizing chemically and electrolytically regenerated suppressors.[14, 15] Both standardization bodies accept hydroxide and carbonate/hydrogen carbonate eluents for anion analysis. A thorough assessment of ISO 10304-1 shows that hydroxide eluents can be generated in situ.[14] Thermo Scientific eluent generation (reagent-free IC, i.e., IC without manual handling of reagents) is thus a viable option. The Statistical and Analytical Support Branch (SASB) and the Office of Groundwater and Drinking Water's Technical Support Center (OGWDW/TSC) of the U.S. EPA established in 2002 that the use of hydroxide eluents (either manually prepared or electrolytically generated) was in line with U.S. EPA Methods 300.0 and 300.1 for determining inorganic anions. Consequently, hydroxide eluents in U.S. EPA Methods 300.0 and 300.1 are authorized for compliance monitoring under the Clean Water Act and Safe Drinking Water Act.[16]

It is essential to acknowledge the distinction between ASTM D 4327[15] and ISO 10304-1[14], which are standards for determining anions in water of various origins. ISO 10304-1 offers the choice between first- and second-order calibration functions based on empirical evidence and calibration data validation, while the former describes linear calibrations only. This choice can be beneficial when calibrating across a wide concentration range or with carbonate-based eluents (as discussed below).

For the investigation of complex matrices, the recommendation is to use gradient elution with hydroxide eluents for a higher peak capacity or "better separation." In addition, the eluent's suppression product is water, meaning the baseline increase during gradient elution is minimal, and most calibration functions will follow the linear model. On the other hand, if a carbonate-eluent is used without additional hardware for post-suppressor CO_2 removal, the anions of strong acids (chloride, bromide, nitrate, o-phosphate, sulfate) show a second-order calibration function.

Some national and international standards require linear calibration or limit the calibration range.[17, 18] Other standard procedures permit the choice of the calibration model and do not limit the concentration range.[14, 19] Regardless, the dynamic detector range of a modern digital detector—not necessarily the same as its linear dynamic range—allows for calibration and quantification across various orders of magnitude. Merging the technological elements of a digital detector output with the demand for linear calibration within a limited concentration range can be successfully achieved. Severoni et al. employed the capabilities of Chromeleon CDS to address this challenge, splitting larger concentration ranges into smaller parts. Subsequently, Chromeleon CDS selects the appropriate calibration segment for the amount calculation and reporting.[20] This method appropriately acknowledges the user's automation needs and the standards' requirements.

When using IC in water analysis, the ISO standards call for a minimum chromatographic resolution (R_s) of 1.3 between neighboring peaks, one of which must be an analyte. The evaluation of chromatographic resolution applies to both isocratic and gradient applications, and the calculation formula for both is the same. This approach provides users with a reliable way to assure the quality and validity of chromatographic separations. Leveraging Chromeleon CDS system suitability tests is essential in continuously monitoring column and separation performance, preventing out-of-control scenarios, and maximizing the accuracy of laboratory planning and the instruments' operational availability.[21, 22]

IC is the go-to technique for analyzing anions due to its simultaneous analyte detection capability. However, several other rapid and sensitive spectrometric methods, such as AAS, ICP-OES, ICP-MS, polarography, and stripping voltammetry, are available when analyzing cations. The significant advantage of IC is its ability to measure alkali and alkaline earth cations and, additionally, to determine ammonium and amines in complex samples. The ISO[19] and ASTM[23] methods for cation chromatography differ from the anion methods in that they document both suppressed and non-suppressed conductivity detection, thus allowing the analyst to choose. Suppressed conductivity detection reduces the background conductivity of the eluent, converts the analytes to a more conductive form, increases the signal-to-noise ratio, and facilitates the use of cation exchange chromatography with gradient elution, if relevant.

Its compatibility with eluents of high ionic strength allows for the use of sophisticated, high-capacity columns, thus enabling separations that were previously impossible due to column overload.

Non-suppressed conductivity detection is an indirect method. It measures the decrease in eluent background conductivity caused by eluting cations rather than the properties of the analytes. This method is more dependent on environmental parameters, has higher noise levels, and is compatible with isocratic conditions only. With non-suppressed conductivity detection, the dynamic working range is limited to the background conductivity of the eluent, and the analyte peaks are recorded as negative signals. Modern software for chromatographic data systems can process negative signals. However, chromatography is commonly expected to yield positive peaks. Hence, with non-suppressed conductivity detection the detector's polarity often is inverted to simulate the presence of positive peaks.

In discussions, the linearity of the calibration function of ammonium and amines, a consequence of indirect detection, can often be cited as an advantage for non-suppressed conductivity detection. With suppressed conductivity detection, converting these components into their corresponding hydroxide forms results in their presence as weaker bases. Their dissociation behavior consequently results in a second-order calibration function. For those users who seek the higher sensitivity and selectivity of suppressed conductivity detection yet are bound to the requirement of a linear calibration function for amines, the approach presented by Severoni et al.[20] offers a practical solution.

In conclusion, suppressed conductivity detection has become almost universally accepted in IC, enabling gradient elution and high-capacity ion exchangers for anion and cation determination. The performance of modern IC is due mainly to the variety of chromatographic separation materials available.[6] Combining these materials with flexible, selective, and sensitive suppressed conductivity detection offers IC as an analytical tool in routine and research and development environments. Generally, in most current IC publications, suppressed conductivity detection is described.

When a particular analytical task demands workflow alternatives that are too expensive or labor-intensive (e.g., derivatization or specific detectors for individual components), or if no suppressor is available, direct conductivity measurements (non-suppressed) are employed. This technique is mainly used to determine cations in an isocratic manner with low-capacity cation exchangers.[24, 25, 26]

Dionex ICS ion chromatographs offer both modes of conductivity detection, allowing the analyst to determine which approach

best meets their lab's requirements, detection limits, matrix composition, separation column, and application.

For most IC standards, the standardization committees established workflows that supply users with options rather than restrictions, granting some analytical choice. It is critical to remember that these options should only be used by those adequately trained and instructed in the corresponding analysis procedures.

Analytes

Adopting the type of analyte as an organizational tool, instead of presenting the individual standards in succession, will enable a more straightforward presentation of standardized IC methods below.

All international standards apply to various matrices. To avoid displaying the same or similar separations for different matrices, we will refer to the options in the appropriate section of the document.
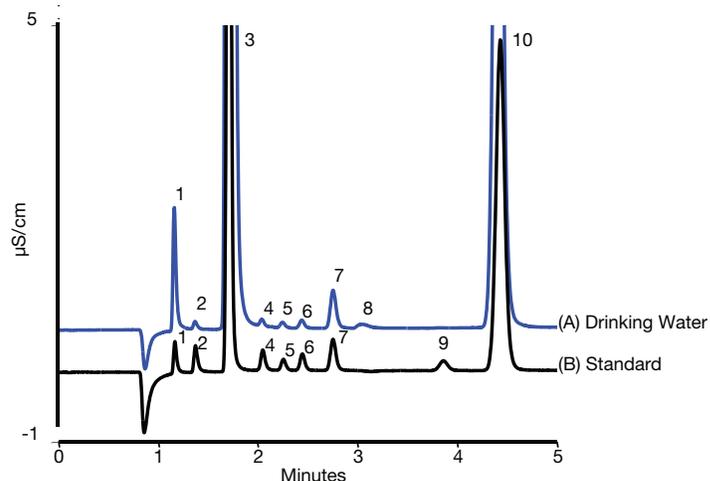

Figure 1. Fast anion separation in municipal drinking water. Column: Thermo Scientific™ Dionex™ IonPac™ AS22-Fast-4µm (4 × 150 mm) with guard column; eluent: 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$; flow rate: 2.0 mL/min; injection volume: 40 µL; temperature: 30 °C; detection: suppressed conductivity, Thermo Scientific™ Dionex™ AERS™ 500 Supressor (4 mm), AutoSuppression, recycle mode. Trace (A): drinking water, trace (B): reference standard with a standard concentration (mg/L): 1. fluoride (0.25), 2. formate (1.0), 3. chloride (12.5), 4. nitrite (0.5), 5. chlorate (0.5), 6. bromide (0.5), 7. nitrate (1.0), 8. carbonate (Not quantified (n.q.)), 9. phosphate (1.0), 10. sulfate (12.5).

ISO 10304-1[14] and ASTM D4327[15] recommend isocratic elution with carbonate/hydrogen carbonate eluents for the anion analysis of drinking water and wastewater samples with moderate complexity. Gradient elution with hydroxide eluents is often applied when analyzing challenging matrices, like complex wastewaters, and quantifying disinfection by-products (DBPs) in high ionic strength samples. To achieve accurate results, suppressed conductivity detection is essential. Membrane suppressors that are continuously regenerated are advantageous for consistent detection conditions, traceability, and for operational simplicity.

Figure 1 illustrates a representative isocratic fast anion separation on a Dionex IonPac AS22-Fast-4µm column, exhibiting the excellent chromatographic efficiency of the stationary phase. Combined with an increased flow rate, this facilitates the successful separation of major and minor components in less than five minutes.

Suppose the ionic strength of the sample is very high. In that case, the standards permit dilution, smaller injection volumes, higher capacity columns, and gradient elution. However, due to the comparatively high ion-exchange capacity of the Dionex IonPac AS22-Fast-4µm column, samples of high ionic strength, even wastewaters, can often be injected with minimal dilution or even directly. Conversely, larger injection volumes can be chosen to raise the mass injected into the column, thus enhancing the detectability of low concentrations.
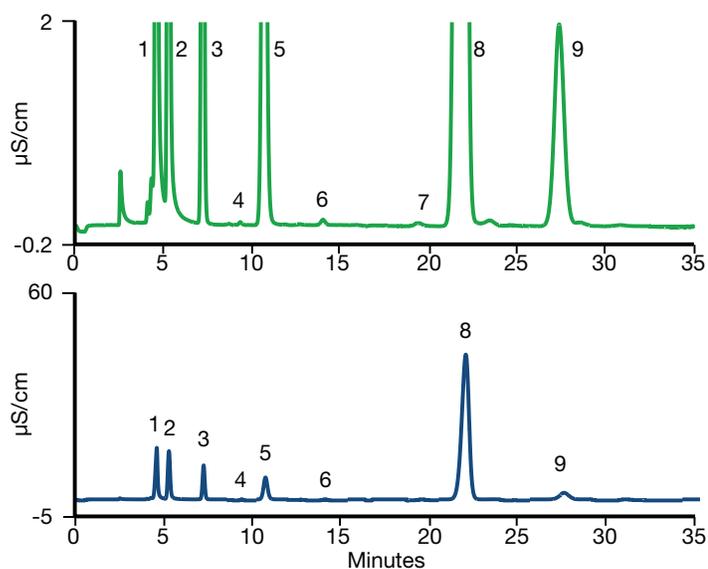
Figure 2. Anion separation in industrial wastewater. Column: Thermo Scientific™ Dionex™ IonPac™ AS23 (4 × 250 mm) with guard column; eluent: 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$; flow rate: 1.0 mL/min; injection volume: 2.5 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex AERS 500 suppressor (4 mm), AutoSuppression, recycle mode. Concentration (mg/L): 1. acetate (878), 2. formate (183), 3. chloride (61.8), 4. nitrite (0.6), 5. chlorate (214), 6. nitrate (1.5), 7. phosphate (1.4), 8. sulfate (1211), 9. unknown (n.q.). The green trace is an enlargement of the blue.

If standard anions need to be determined in wastewater, the complexity of the matrix largely dictates the selection of application and elution conditions. In the case of less complex wastewater, a high-capacity column with isocratic conditions may be employed to separate the standard anions (Figure 2). Furthermore, sample dilution can be avoided by using a small injection volume (2.5 µL). This example illustrates the use of a Dionex IonPac AS23 column with carbonate/hydrogen carbonate eluent. In this scenario, the determination of fluoride was not the immediate aim.
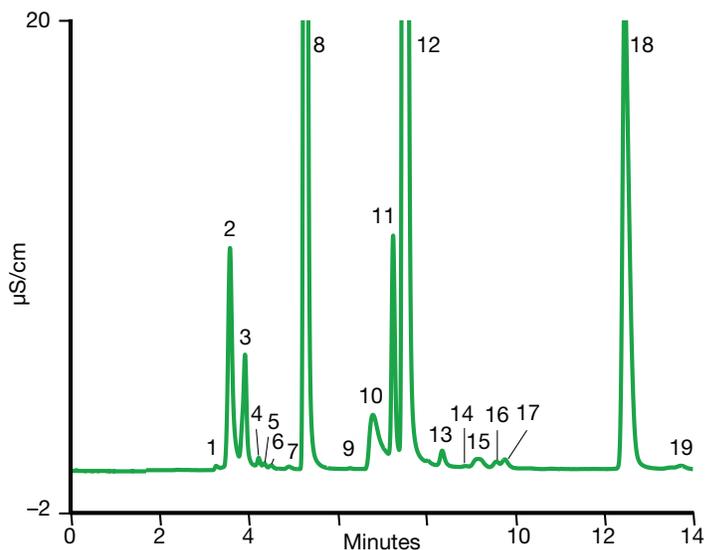

Figure 3. Fast anion separation in complex industrial wastewater. Column: Thermo Scientific™ Dionex™ IonPac™ IonPac AS18 (4 × 250 mm) with guard column; eluent: 12–44 mM KOH from 0–5 min and 44–52 mM KOH from 8–10 min; eluent source: Thermo Scientific™ Dionex™ EGC 500 KOH cartridge, flow rate: 1.0 mL/min; injection volume: 100 µL; temperature: 30 °C; detection: suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ ULTRA Suppressor (4 mm), AutoSuppression, recycle mode. Peaks: 1. fluoride, 2. acetate, 3. formate, 4. unknown, 5. unknown, 6. unknown, 7. unknown, 8. chloride, 9. nitrite, 10. carbonate (n.q.), 11. sulfite, 12. sulfate, 13. bromide, 14. unknown, 15. nitrate, 16. unknown, 17. unknown, 18. thiosulfate, 19. unknown. Sample preparation: dilution with DI water (1 to 100).

However, if the accurate measurement of fluoride in a complex matrix is necessary, gradient elution with a KOH eluent generated electrolytically has proven effective (Figure 3).

This case study concerns the determination of standard anions, including fluoride, in complex industrial wastewater. Organic acids in the matrix prevented trace fluoride measurements under isocratic conditions, so gradient conditions were employed to accomplish the analytical task (peak #1, Figure 3). The chromatogram legend in Figure 3 reflects a typical situation in a water analysis laboratory, where only the analytes are identified and quantified.

The noteworthy aspect of the chromatogram is its short runtime of 14 min. With the reconditioning steps taken into consideration, the total cycle time is around 22-23 min, comparable to an isocratic application. However, gradient separation offers improved performance, as evidenced by Figure 3.
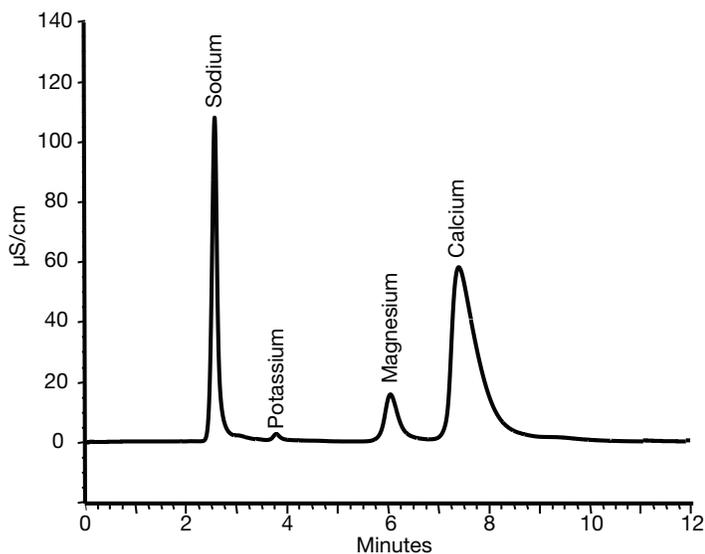
Figure 4. Fast cation separation in municipal drinking water. Column: Thermo Scientific™ Dionex™ IonPac™ CS12A-5µm (3 × 150 mm) with guard column; eluent: 18 mM methane sulfonic acid (MSA); flow rate 0.5 mL/min; injection volume: 10 µL; detection: suppressed conductivity, Thermo Scientific™ Dionex™ CERS™ 500 Suppressor, 2 mm, AutoSuppression, recycle mode. Concentration (mg/L): sodium (61.1), potassium (2.23), magnesium (10.1), calcium (115).

Figure 5. Cation separation in municipal drinking water. Application of non-suppressed and suppressed conductivity detection. Column: Dionex IonPac CS12A (4 × 250 mm) with guard column; eluent: 20 mM MSA; flow rate 1 mL/min; injection volume: 25 µL; detection: (A) non-suppressed conductivity detection with inverted detector polarity, (B) suppressed conductivity, Dionex CERS 500 suppressor (4 mm), AutoSuppression, recycle mode. Concentration (mg/L): (A) lithium (not detected), sodium (8.30), potassium (2.24), magnesium (5.43), calcium (93.7); (B) lithium (0.01), sodium (8.19), potassium (2.36), magnesium (5.27), calcium (93.2). Background conductivity: (A) 6011 µS/cm, (B) < 0.3 µS/cm. Signal offset: 25%.

Standard isocratic separations of alkali and alkaline earth metals and ammonium, are detailed in ASTM D6919 and ISO 14911.[23, 19] These separations typically employ acidic eluents of mM-range methanesulfonic acid and stationary phases of carboxylate cation exchangers. Polymeric and silica gel-based carboxylate phases are the two main categories of these columns, with the former boasting higher exchange capacities for standard columns (> 2000 eq/column) than the latter (< 320 µeq/column).[6] To prevent the masking formation of carbonates for, e.g., calcium and magnesium, the samples must be acidified to a pH of about 3-4, ideally during sampling. Thermo Scientific Dionex IonPac carboxylate functionalities used on polymeric resins have a pK_a value between 2.5 and 4.3 and demonstrate strong acidity[27], unlike the often-used misnomer "weakly acidic cation exchanger" suggests. This property permits the injection of more acidic samples (1 ≤ pH < 2) while maintaining excellent chromatographic performance.[28, 29] Figure 4 displays a compliant isocratic separation of alkali and alkaline earth metals from municipal drinking water, completed in less than 10 min. Detection was by suppressed conductivity.

ASTM and ISO outlined their procedures for suppressed conductivity and non-suppressed conductivity detection.[19, 23] Figure 5 illustrates two chromatograms of the same sample, using both forms of conductivity detection. Trace (A) represents the non-suppressed, and trace (B) displays suppressed
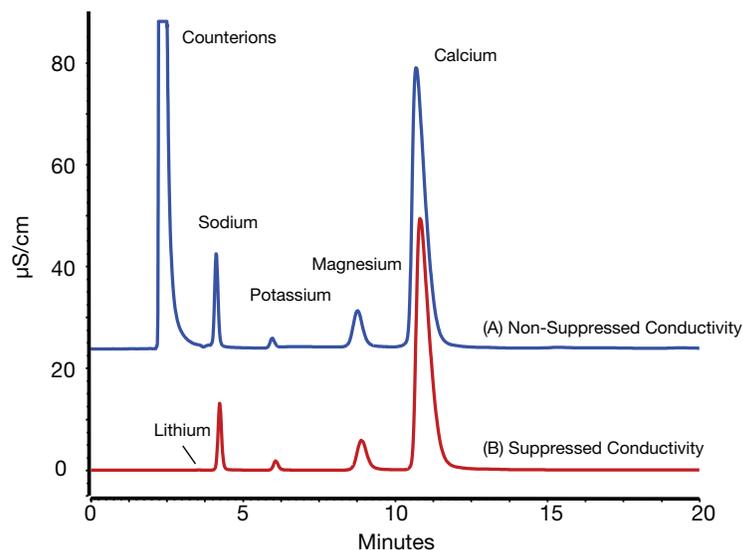
conductivity detection. With suppressed conductivity detection (background conductivity < 1 µS/cm, Figure 5(B)), counter-ions are eliminated, providing a higher detection selectivity and sensitivity. Non-suppressed conductivity detection (background conductivity > 6000 µS/cm, Figure 5(A)) is associated with increased noise, reduced detection sensitivity and selectivity, and difficulty detecting low-abundance components such as lithium. Suppressed conductivity detection yields higher sensitivity and selectivity and allows for gradient elution. Nevertheless, the results for the main components are comparable with both forms of conductivity detection. Therefore, Dionex ICS instruments offer the analyst the option to choose the method best suited to the analytical needs.

The chromatographic conditions in ASTM D6919 and ISO 14911 apply to drinking water and wastewater samples. Typically, the Dionex IonPac CS12A column is used. It has a capacity of 2800 µeq/column (4 × 250 mm). However, for a high ionic strength sample, high matrix load, or the need to analyze low ammonium content in high sodium amounts, the higher capacity Thermo Scientific™ Dionex™ IonPac™ CS16-4µm column, with 5400 µeq/column (4 × 250 mm), is recommended.[30]
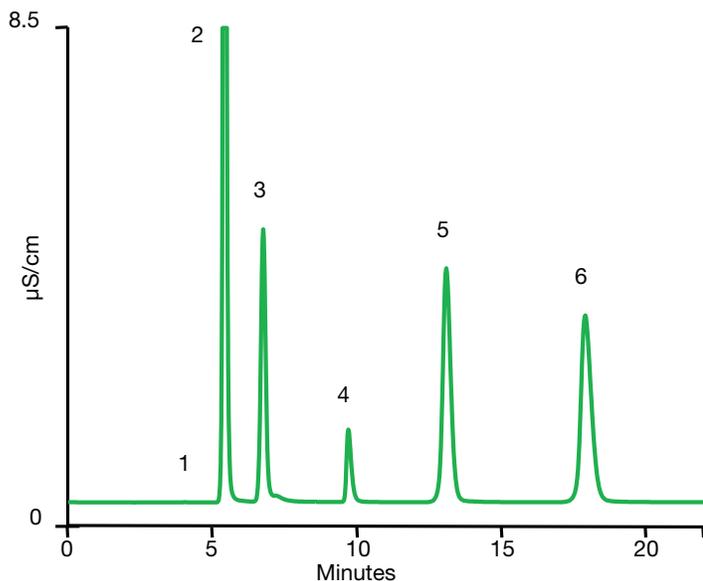
Figure 6. Cation separation in municipal wastewater.
Column: Dionex IonPac CS16-4μm (4 × 250 mm) with guard column; eluent: 30 mM MSA; flow rate: 0.9 mL/min; injection volume: 10 μL; detection: suppressed conductivity, Dionex CERS 500 suppressor (4 mm), AutoSuppression, recycle mode, temperature: 40 °C. Concentration (mg/L): 1. lithium (< 0.05), 2. sodium (34), 3. ammonium (9.6), 4. potassium (3.6), 5. magnesium (6.5), 6. calcium (11). Sample preparation: dilution (1 to 5) and filtration.

Figure 6 illustrates the separation of alkali and alkaline earth metals and ammonium in municipal wastewater. Owing to the higher ion exchange capacity of the resin and the 4 μm particles of the stationary phase, a baseline separation of sodium and ammonium is observed with improved chromatographic efficiency compared to older columns. However, the user should anticipate longer run times given the increased cation-exchange capacity of the Dionex IonPac CS16-4μm column.

Disinfection by-products
Bromate[31, 32, 33]

Consuming safe and reliable drinking water from a local municipality or a commercial bottle is essential for maintaining a healthy lifestyle. Ozone is a popular choice of water disinfectant. It is highly effective and does not leave a taste or residual disinfectant in the drinking water. However, reactions between disinfectants and inorganic and organic matter in the source water can create undesirable, potentially hazardous disinfection by-products such as bromate, chlorite, and trihalomethanes.[34, 35, 36] Bromate can result from ozonating water with naturally occurring bromide. It also can be introduced as an impurity in sodium hypochlorite used for water treatment.[37] Bromate is classified as a potential carcinogen by the International Agency for Research on Cancer.[38] Therefore, the U.S. EPA, European

Commission, and the WHO have set a maximum permissible limit of 10 μg/L bromate in tap water,[39, 40, 41] which the U.S. FDA has followed for bottled water.[42] In Europe, the maximum limit of bromate in natural mineral and spring waters treated by ozonation is 3 μg/L.[43]
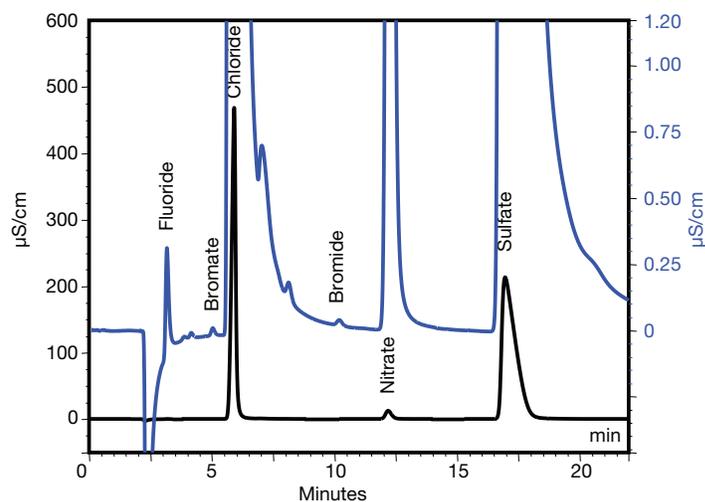

Figure 7. Bromate determination in a high ionic strength drinking water. Column: Thermo Scientific™ Dionex™ IonPac™ AS9-HC (2 × 250 mm) with guard column; eluent: 8 mM Na_2CO_3 and 1.5 mM NaOH; flow rate: 0.28 mL/min; injection volume: 35 μL; temperature: 30 °C; detection: suppressed conductivity, Thermo Scientific™ Dionex™ AMMS™-III Suppressor, 2 mm, displacement chemical regeneration mode (DCR). Concentration (mg/L): bromate (0.003), chloride, and sulfate: double-digit mg/L range. The blue trace is an enlargement of the black.

ISO 15061[31] and ASTM D6581[33] describe bromate determination methods based on anion exchange chromatography in conjunction with suppressed conductivity detection. A typical example of bromate determination (3 μg/L) in the presence of higher concentrations of other anions is shown in Figure 7. The Dionex IonPac AS9-HC column offers excellent anion-exchange capacity, enabling it to separate bromate in higher chloride and sulfate concentrations. The separation succeeds under isocratic conditions with a carbonate-based eluent in less than 25 min. Additionally, the chromatographic properties of this separation phase allow for accurate quantification of fluoride, bromide, nitrate, and other inorganic anions. Fulfilling the normative requirements for determining standard anions and bromate, a combination of ISO 10304-1 with ISO 15061 and ASTM D4327 with ASTM D6581, respectively, to determine bromate and standard anions simultaneously while complying with the standards is possible.
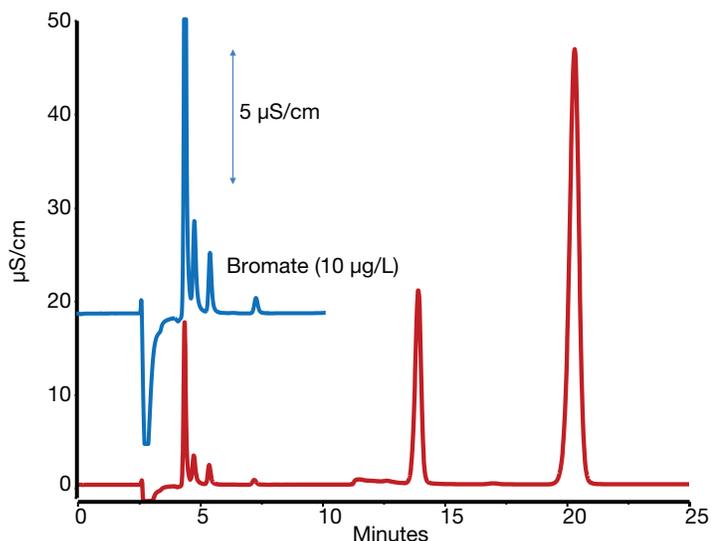
Figure 8. Bromate determination in higher concentrations of other anions using suppressed conductivity. Column: Dionex IonPac AS23 (4 × 250 mm) with guard column; eluent: 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$; flow rate: 1.0 mL/min; injection volume: 250 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex AERS 500 suppressor (4 mm), AutoSuppression, recycle mode. Concentration (mg/L): bromate (0.01), all other anions double digit mg/L range. Sample preparation: SPE with Thermo Scientific™ Dionex™ OnGuard™ Ag cartridge.[31] The blue trace is an enlargement of the red.

Figure 9. Chlorite, bromate, and chlorate determination in simulated drinking water. Column: Thermo Scientific™ Dionex™ IonPac™ AS19-4µm (4 × 250 mm) with guard column; eluent: 10 mM KOH from 0 to 10 min, 10-45 mM KOH from 10 to 25 min; eluent source: Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge, flow rate: 1.0 mL/min; injection volume: 250 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex AERS 500 suppressor (4 mm), AutoSuppression, recycle mode. Concentration (mg/L): 1. fluoride (1.0), 2. chlorite (0.005), 3. bromate (0.005), 4. chloride (50.0), 5. nitrite (0.005), 6. chlorate (0.005), 7. bromide (0.005), 8. nitrate (10.0), 9. carbonate (25.0), 10. sulfate (50.0), 11. phosphate (0.20). The blue trace is an enlargement of the red.

Direct sample analysis of trace bromate under those conditions may not always be feasible. For instance, if the chloride concentration in drinking water is higher than shown in Figure 7, the bromate eluting before the chloride may be obscured. In this case, there are several compliant solutions available.

According to ISO, such situations can be addressed by suitable sample preparation. The standards describe solid phase extraction (SPE) cartridges packed with metal-loaded cation exchangers.[44] Silver-loaded cation exchangers are used to remove chloride, and barium-loaded cation exchangers to lower the sulfate concentration. In the following example (Figure 8), chloride and bromide were precipitated using an OnGuard Ag cartridge, allowing the trace bromate determination in high chloride water matrices. Such sample preparations, however, come into use when the sample throughput is low, or no alternatives are available in the laboratory.

Figure 9 illustrates how chromatographic interferences can be effectively avoided without sample preparation. A high-capacity separation phase is used with an electrolytically generated hydroxide eluent. The chromatogram begins with an eluent with 10 mM KOH for 10 min under isocratic conditions, leading to a significantly improved chromatographic separation of chlorite and bromate from chloride. Subsequently, the ionic strength of the mobile phase is increased to elute additional anions.
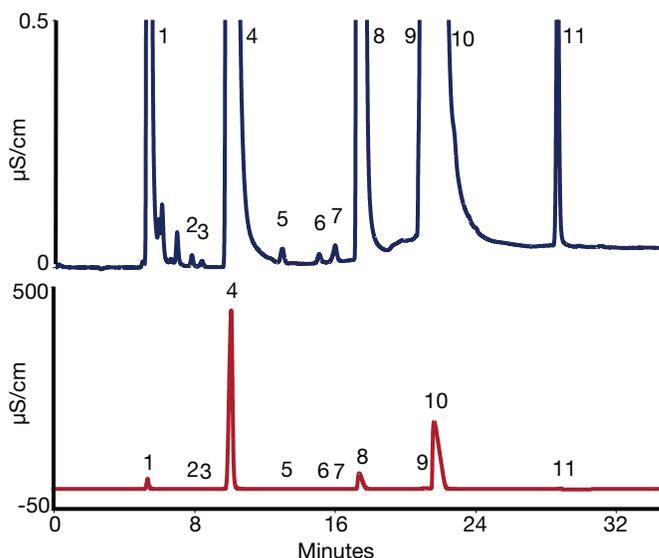
Using a hydroxide eluent significantly reduces background conductivity, permits gradient elution, and enhances detection sensitivity, as the suppression product of the eluent is water.

After ISO 15061[31] and ASTM D6581[33] were published, it was reported that ethylenediamine (EDA)-carbamate is formed in the presence of carbonate after sample stabilization with EDA. This component appears as a fluoride-interfering signal at the beginning of the chromatogram on most stationary phases.[45] The Thermo Scientific™ Dionex™ IonPac™ AS30, a newer, highly efficient, high-capacity column, addresses this issue and allows for the interference-free determination of fluoride and oxyhalides using suppressed conductivity detection (Figure 10). Moreover, this column improves the separation of early-eluting organic acid anions compared to other columns.[46]

Notably, electrolytically generated hydroxide eluents and continuously regenerated membrane suppressors facilitate coupling IC with mass spectrometry. To date, neither ISO nor ASTM has developed a corresponding standard for determining oxyhalides using IC-MS. However, U.S. EPA Method 557[47] outlines the conditions for identifying and quantifying bromate, nine haloacetic acids (HAA9), and 2,2-dichloropropionic acid (dalapon) with IC-ESI-MS/MS.
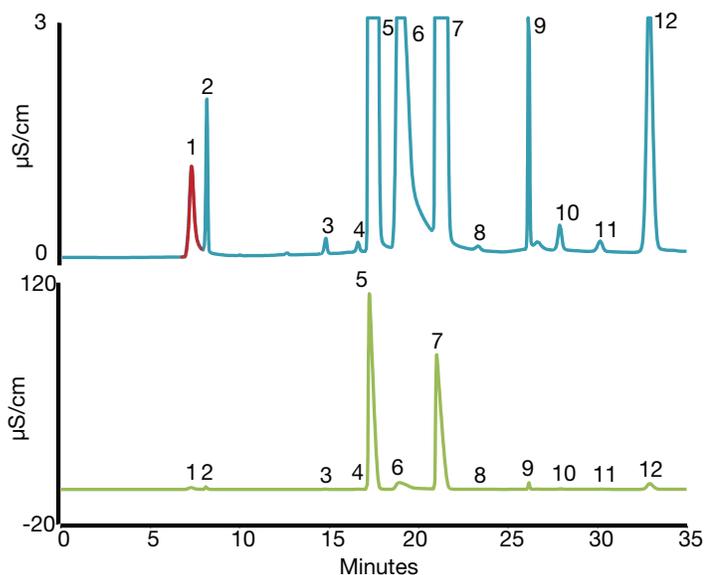
Figure 10. Gradient separation of simulated drinking water spiked with 50 mg/L ethylenediamine (EDA). Column: Dionex IonPac AS30 (2 × 250 mm) with guard column; eluent: 1 mM KOH from 0 to 0.10 min, 0.1-8 mM KOH from 0.10 to 8 min; to 25 mM in 8 min, to 30 mM in 6 min, to 60 mM in 2 min, keep for 11 min; equilibrate at 1 mM for 7 min. Eluent source: Dionex EGC 500 KOH cartridge, flow rate: 0.38 mL/min; injection volume: 50 µL; temperature: 30 °C; detection: suppressed conductivity, Thermo Scientific™ Dionex™ ADRS 500 suppressor, 2 mm, AutoSuppression, recycle mode. Concentration (mg/L): 1. EDA carbamate (50), 2. fluoride (0.08), 3. chlorite (0.06), 4. bromate (0.06), 5. chloride (20), 6. carbonate (20), 7. sulfate (20), 8. nitrite (0.004), 9. phosphate (1), 10. bromide (0.1), 11. chlorate (0.06), 12. nitrate (1.0). The blue trace is an enlargement of the green.

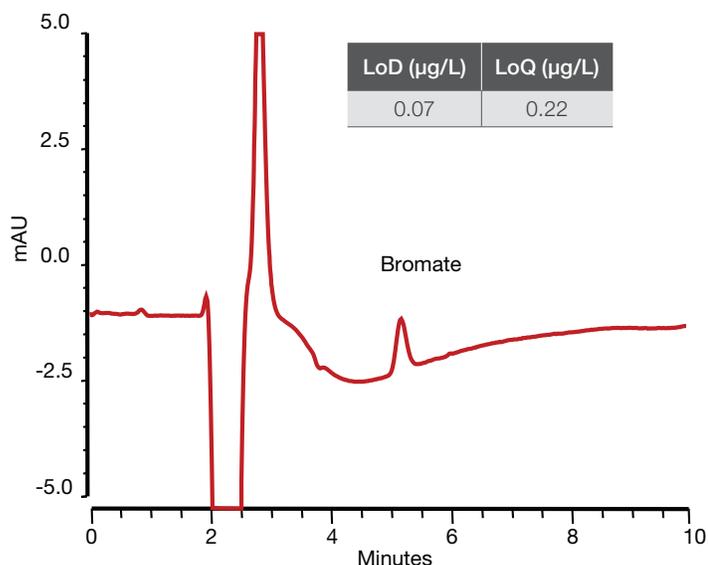| LoD (µg/L)	LoQ (µg/L)
0.07	0.22

Figure 11. Bromate separation using a Thermo Scientific™ Dionex™ CarboPac™ Column, post-column reaction, and UV-absorption detection. Column: Dionex CarboPac PA1 (4 × 250 mm) with guard column; eluent: 200 mM MSA; flow rate: 1.0 mL/min; injection volume: 500 µL; temperature: 30 °C; detection: UV, $\lambda_{abs} = 352$ nm (after post-column derivatization to triiodide), post-column reagent: 0.27 M KI, 0.05 mM $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, post-column reagent flow rate: 0.3 mL/min, reaction coil: 375 µL, reaction temperature: ambient to 30 °C. Concentration (µg/L): Bromate (1.2); (48).

ISO 11206[32] for detecting bromate via UV absorption supplements the ASTM and ISO procedures utilizing suppressed conductivity detection. This application is based on a redox reaction of bromate with iodide resulting in triiodide. Recorded at 352 nm, the triiodide detection permits trace determinations in the low µg/L range and below. ISO 11206 outlines two possible elution patterns; an alkaline eluent as proposed in U.S. EPA Method 326.0[49] and an acidic mobile phase suggested by the ISO working group.

The reaction with acidic eluents is often carried out at an ambient temperature and progresses quickly and quantitatively, thus reducing the workload and simplifying the instrument configuration.

In contrast, neutralization via suppression is needed when using alkaline eluents, and additional heating of the reaction loop to 80 °C is necessary. After the publication of the ISO method, user feedback indicated that the initially proposed sulfuric acid eluent severely limited the selection of separation columns.

We were inspired to re-evaluate the method and provide analysts with a more flexible yet standard-compliant choice among the commercially available stationary phases.

Figure 11 demonstrates bromate's successful separation on a Thermo Scientific™ Dionex™ CarboPac™ PA1 Column and trace detection (1.2 µg/L) using a 200 mM MSA eluent instead of the 100 mM H_2SO_4 used in ISO 11206.[32] Typical detection and quantification limits (LoD and LoQ) are presented in Figure 11, and are in the sub-µg/L-range.[48] This application has since been transferred to other columns, including the Thermo Scientific™ Dionex™ IonPac™ AS15 Column and the Dionex IonPac AS23 column, even with column diameters as small as 2 mm.[50] To ensure standard compliance, it is essential to maintain the mix of eluent and the post-column derivatization reagent and keep the pH in the reaction coil below 1. ISO 11206 provides an easy calculation formula to adjust the procedural parameters accordingly.[32]

ASTM D 6581[33] and ISO 10304-4[18] are standard methods used to determine three anionic chlorine species, chlorite, chloride, and chlorate, in drinking and low-polluted water. Bromate is also included in the list of analytes. The requirements for the chromatographic method are like those described for the standard anions (see above).

The importance of having reliable standards to determine oxychlorides has grown in the European Union. In the revised EU Directive on the quality of drinking water, chlorite and chlorate were added as parameters to be monitored if water disinfection processes are employed that could potentially generate these oxychlorides.[40]
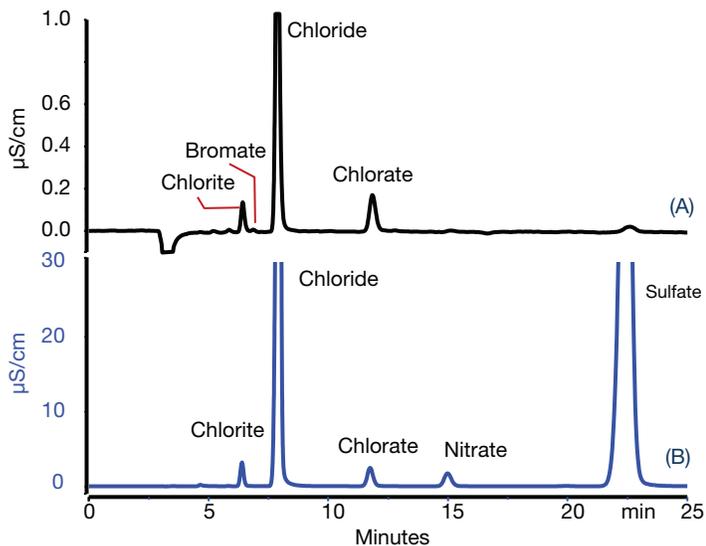
Figure 12. Chlorine speciation in swimming pool water.
Column: Dionex IonPac AS23 (2 × 250 mm) with guard column; eluent: 4.5 mM Na$_2$CO$_3$ and 0.8 mM NaHCO$_3$; flow rate: 0.25 mL/min; injection volume: 5 µL; temperature: 30 °C; detection: suppressed conductivity, Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Suppressor, 2 mm, AutoSuppression, recycle mode. Trace(A): reference standard, trace(B): public swimming pool water. Concentration (mg/L): chlorite (21), chloride (129), chlorate (13). Sample preparation: none.

Swimming pool water is also a matrix of focus, with disinfection processes using chlorine dioxide or sodium hypochlorite to produce chlorite and chlorate.[53] Figure 12(B) presents an analysis of an untreated swimming pool water with a run time of 25 min on a Dionex IonPac AS23 column under isocratic conditions. The eluent consisted of an aqueous carbonate/hydrogen carbonate solution; trace(A) shows a standard solution for comparison. Detection is achieved through suppressed conductivity detection, with the Dionex AERS 500 carbonate suppressor providing a low baseline noise for carbonate/hydrogen carbonate eluents and enhanced sensitivity of conductivity detection.

The conditions used for separating and determining oxychlorides (Figure 12) and those used for the standard anions and bromate (Figures 2 and 8) are identical. Additionally, the normative requirements are consistent. In other words, the standard anions, oxychlorides, and bromate can be determined simultaneously in one run in compliance with the standard. The result is a highly facilitated analytical workflow, significantly improving the analytical laboratory's efficiency.

Perchlorate[52, 54]

Perchlorate is known to contaminate drinking, ground, and surface waters both naturally and through anthropogenic sources.[55, 56] Natural sources include atmospheric deposition in the presence of ozone, chloride aerosols, and natural impurities in Chile saltpeter.[57,58] Anthropogenic sources comprise its use in solid propellants, rockets, missiles, fireworks, pyrotechnics,

flares, matches, and explosives.[59] Perchlorate is toxicologically relevant as it interferes with the uptake of iodine by the thyroid gland and the production of hormones necessary for early childhood development.[60, 61, 62] Disruption of the endocrine system, where the thyroid gland does not produce enough thyroid hormone in early pregnancy, may impair the fetus' physical and mental development.[63] This underscores the importance of determining perchlorate levels in matrices such as food and drinking water, for which national standardization organizations and ISO have developed methods.

ISO 19340 details a method to determine the perchlorate concentration using anion exchange chromatography and suppressed conductivity detection in drinking water, mineral water, raw water, surface water, partially treated water, swimming pool water, and wastewater from drinking and swimming-pool-water treatment plants. This method permits measuring perchlorate concentrations of at least 1 µg/L, provided the sample is pre-treated, such as through matrix elimination. However, it should be noted that the ion exchange capacity of the separator column defines the method's working range. In other words, the higher the anion-exchange capacity of the separation column, the larger the working range and the lower the matrix influences.

High chloride, sulfate, nitrate, and carbonate levels can impact the perchlorate determination (co-elution), retention time, peak shape (distortion), or recovery of perchlorate. The use of sample dilution, solid phase extraction with metal-loaded cation exchangers (e.g., Dionex OnGuard Ag, Dionex OnGuard Ba)[44], or advanced inline heart-cutting or re-injection techniques as outlined in the standard's informative annexes can reduce such interferences.

Perchlorate biodegradation can occur either in the absence of nitrate or with the help of anaerobic bacteria. Hence, it is advisable to filter the water through a 0.2 µm membrane at the sampling location.[52]

Annex D of the standard contains supplementary information on the successful implementation of IC hyphenated with triple quadrupole mass spectrometers (IC-MS/MS) during the compulsory round-robin test. Though the data was not formally included in the final evaluation, the standard explicitly states that the chosen instrument and analytical conditions adhere to the quality parameters specified.

Figure 13 illustrates the perchlorate determination in a high ionic strength river water sample. The untreated water sample was used for the injection in Figure 13(A). A larger sample aliquot of 750 µL was necessary to reliably detect the low perchlorate content. As the sample was untreated, the main anionic components (chloride, nitrate, carbonate, sulfate) were co-injected, resulting in sizable peaks between 6 and 12 min. Despite the column's high ion exchange capacity and

chromatographic efficiency, the prominent peaks' residual signals challenged the integration of the perchlorate peak area. It is beneficial to reduce the concentration of the interfering anions selectively. Figure 13(B) displays the chromatogram of the same sample treated with Dionex OnGuard Ag, Dionex OnGuard Ba, and Dionex OnGuard H. Matrix elimination decreased the peak size for chloride, carbonate, and sulfate, allowing for the interference-free determination of the perchlorate traces.
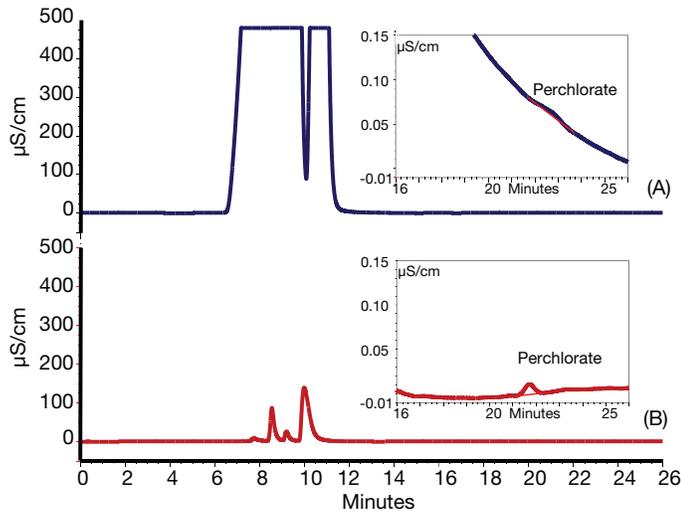

Figure 13. Perchlorate determination in a high ionic strength river water. Column: Dionex IonPac AS20 (2 × 250 mm) with guard column; eluent: 35 mM KOH; eluent source: EGC-III-KOH; flow rate: 0.25 mL/min; injection volume: 750 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex AERS 500 suppressor, 2 mm, AutoSuppression, recycle mode. trace (A): river water untreated, trace (B): river water treated with OnGuard Ba, Ag, H cartridges. Concentration (mg/L): perchlorate (3).
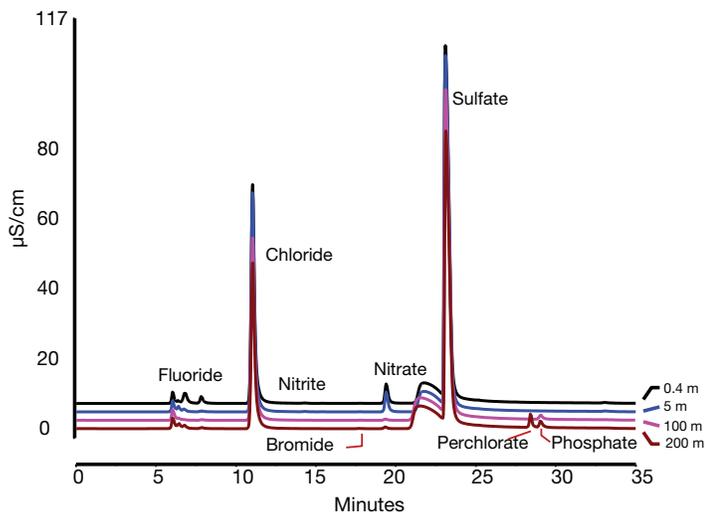

Figure 14. Perchlorate and anion determination in an alpine lake at different depths. Column: Dionex IonPac AS19-4µm (2 × 250 mm) with guard column; eluent: 10 mM KOH for 10 min, to 50 mM in 15 min, keep for 3 min, to 10 mM in 0.5 min, equilibrate for 7.5 min; eluent source: EGC KOH, flow rate: 0.25 mL/min; injection volume: 100 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex ADRS 600 suppressor, 2 mm, AutoSuppression, recycle mode. Concentration (µg/L) at 200 m water depth: fluoride (70), chloride (3000), nitrite (1), bromide (20), nitrate (< 1000), sulfate (10,000), perchlorate (< 120), phosphate (300). Sample preparation: None.

The perchlorate determination is not always as complex as in the previous example. Anion exchange chromatography was applied to determine standard anions and perchlorate in alpine lake water, as shown in Figure 14. This study explored the nutrient parameters (nitrite, nitrate, o-phosphate) at different lake depths and unexpectedly detected perchlorate at 200 meters and below. The separation was performed on a high-capacity Dionex IonPac AS19-4µm column, with an electrolytically generated KOH eluent in gradient mode, and suppressed conductivity detection was applied. The results complied with ISO 10304-1 and ISO 19340 acceptance criteria. Hence Figure 12 shows the compliant combination of both methods. The peak shapes remained undisturbed despite a 100 µL injection volume onto a 2 mm column. Perchlorate is attributed to an anthropogenic source, likely due to dumped World War II munitions.
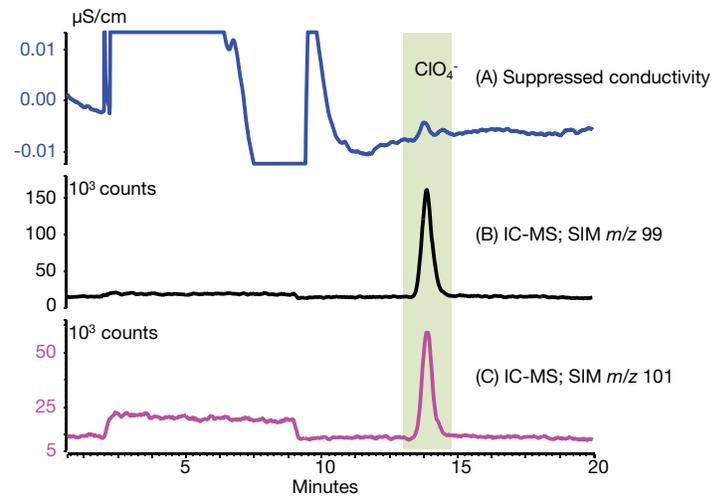

Figure 15. Perchlorate determination using IC-MS.
Column: Dionex IonPac AS20 (2 × 250 mm) with guard column; eluent: 50 mM KOH; eluent source: EGC-III-KOH; flow rate: 0.25 mL/min; injection volume: 100 µL; temperature: 30 °C; detection: suppressed conductivity, Dionex AERS 500 suppressor, 2 mm, AutoSuppression, external water mode; MS-detection: ESI (-), make-up solvent: acetonitrile: water (Φ = 0.5). Trace (A): suppressed conductivity

Of the two international standardization authorities, ISO describes an IC method combined with mass spectrometry (MS) for perchlorate determination, but only in the informative annex to ISO 19340. Because MS has undeniable advantages in sensitivity and selectivity compared to conductivity detection, a representative example is shown in Figure 15. A high-capacity Dionex IonPac AS20 column in the 2 mm format is used, and the eluent is an electrolytically generated potassium hydroxide solution. On the one hand, the suppressor is required for conductivity detection. On the other hand, in combination with MS, it assumes the function of a continuously regenerated desalter. Comparing Figure 15(A) – suppressed conductivity -

with Figure 15 (B) and Figure 15(C) (selected ion monitoring (SIM) channels of m/z 99 and m/z 101), mass spectrometry's higher sensitivity and detection selectivity for perchlorate becomes apparent.

In contrast, the United States Environmental Protection Agency has concentrated more on identifying perchlorate in water, as evidenced by numerous entries on its homepage.[64] The entries include methods with inline matrix elimination[65, 66], two-dimensional IC[67], LC-MS/MS utilizing volatile amine eluents[68], and U.S. EPA Method 332.0.[54]

U.S. EPA Method 332.0 outlines the instrumentation and processes for determining low levels of perchlorate in drinking water with IC combined with electrospray ionization and MS detection (IC-ESI-MS). The drinking water samples are collected after sterile filtration and injected into an ion chromatograph. An anion exchange column separates perchlorate from other sample ions with a KOH-eluent. A suppressor replaces the mobile phase's potassium ions and the samples' counter cations before they enter the MS interface with oxonium ions. Finally, an ^{18}O-enriched $^{35}Cl^{18}O_4^-$ internal standard (m/z 107) helps improve accuracy and stability. Identification is verified by comparing the relative retention times of the two predominant natural ClO_4^- isotopologues to the internal standard. Qualitative confirmation of ClO_4^- is determined by confirming that the m/z 99/101 area count ratio is within a specific range, after which the concentration – based on the m/z 101 evaluation — is reported. This procedure and approach have already successfully served as a template for Thermo Scientific application development.[69]

Chromium(VI), chromate[70, 71]

It is essential to monitor chromates - oxyanions (e.g., CrO_4^{2-}, $Cr_2O_7^{2-}$) of chromium in the oxidation state of +6 - in water samples to safeguard public health. As potent oxidizing agents, they are toxic to biological systems and may cause cancer. Hence, chromates are strictly regulated in the environment and are considered primary drinking water contaminants.

Potential sources of Cr(VI) in water include industrial activities such as metal plating, leather tanning, and stainless-steel manufacturing, as well as natural events such as volcanic activity and rock erosion. As it can remain in the water for long and travel long distances, continuous monitoring is necessary to confirm whether chromate concentrations are below the permissible levels.

ASTM and ISO describe IC methods based on ion exchange chromatography for chromate determination. Both papers propose similar eluents based on ammonium sulfate and ammonium hydroxide and UV/VIS detection. ISO 10304-3[70] describes the direct measurement of the chromate UV absorbance at 365 nm, while ASTM D5257[71] uses a post-column derivatization reaction with 1,5 diphenylcarbazide (DPC)

and the measurement of the VIS absorbance of the reaction product at 530 nm. ISO 10304-4 documents the working range between 0.05 mg/L and 50 mg/L chromate. ASTM D5257 has been assessed for accuracy and bias in reagent water and industrial wastewater, with satisfactory results from 0.001 to 1 mg/L.

The ASTM method is more selective and sensitive due to the bathochromic shift of the optimum analytical absorption wavelength, the higher molar extinction coefficient of the post-column reaction product, and a larger injection volume.

Large amounts of reducing species (e.g., sulfide, sulfite) may cause the reduction of Cr(VI) to Cr(III) regardless of the analytical method employed. To prevent this, the sample should be buffered to a pH of 9.0 - 9.5, filtered, and stored below 6 °C.

The European Union Directive on water intended for human consumption[40] stipulates a maximum limit value of 50 µg/L for total chromium at present and a limit of 25 µg/L by 2036. ICP-OES and ICP MS are usually employed in the EU to establish the total chromium content of drinking water. Hazard assessment, e.g., for wastewater from industrial dischargers, requires the differentiation between Cr(III) and Cr(VI). In this regard, both international IC standard methods provide this selective determination of chromate.
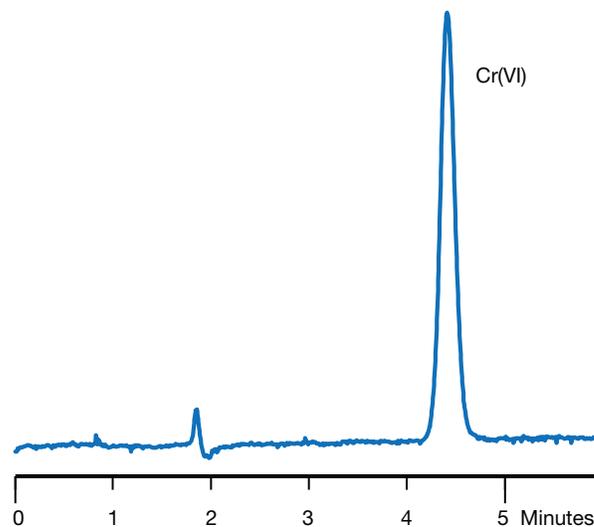

Figure 16. Chromate determination in wastewater from the plating industry. Column: Thermo Scientific™ Dionex™ CarboPac™ PA100 (4 × 250 mm) with guard column; eluent: 250 mM Na_2SO_4 and 100 mM NaOH; flow rate: 1.0 mL/min; injection volume: 100 µL; temperature: Ambient; detection: UV, λ_{abs} = 365 nm.
Concentration (µg/L): chromate (7.5).

Figure 16 displays chromate detection in wastewater from the electroplating industry. The wastewater contained chromate at a concentration of 7.5 µg/L. The conditions followed the specifications of ISO 10304-3, and the normative framework conditions ($R_s \geq 1.3$) were met. Though the ISO standard's working range starts at higher concentrations, this method permits detection limits in the lower µg/L range and, when combined with larger injection volumes, even in the middle ng/L range. Unlike the ASTM method, no post-column derivatization unit was needed, leading to a simplified instrument setup. Controlling the sample's pH value for IC separation is effective in practice. If feasible, the pH of the injected solution should be between 9 and 9.5 to shift the pH-dependent equilibrium between chromate and dichromate to the side of chromate. As chromate is the weaker oxidant, this step avoids additional chemical stress on the separation column.
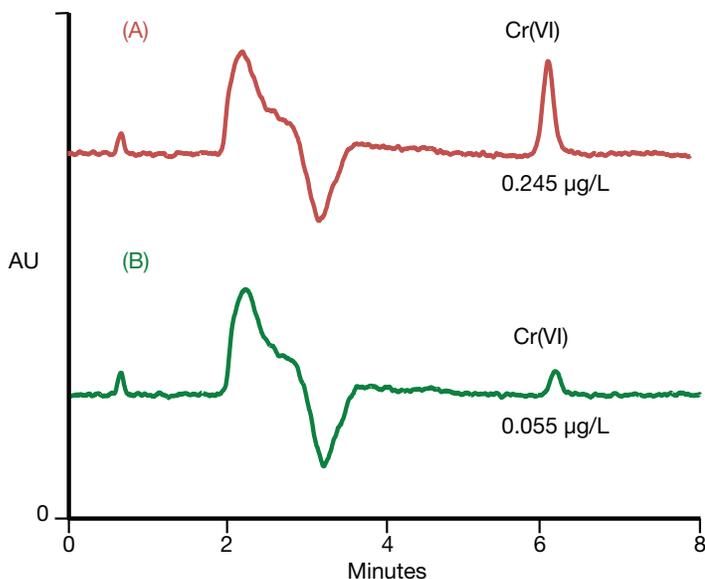

Figure 17. Chromate determination in drinking water.
Column: Thermo Scientific™ Dionex™ IonPac™ AS7 with Thermo Scientific™ Dionex™ IonPac™ NG1 Guard Column, eluent: 250 mM $(NH_4)_2SO_4$ and 100 mM NH4OH, flow rate: 1 mL/min, injection volume: 1000 µL, post-column reagent: 2 mM 1,5-diphenylcarbazide + 10% CH_3OH, 0.5 M H_2SO_4, post-column flow rate: 0.33 mL/min, reaction coil: 750 µL, detection: VIS, λ_{abs} = 530 nm. Sample: tap water, trace(A): tap water spiked with 0.2 µg/L Cr(VI), trace(B): original tap water.

Figure 17 displays the optimized performance of the ASTM method. The two chromatograms of drinking water have a run time of less than eight minutes. Upon injection into a Dionex IonPac AS7 column, separation, derivatization with 1,5-diphenylcarbazide, and VIS detection at 530 nm, the concentration of the original drinking water (Trace(B)) was determined to be 0.055 µg/L. In this example, 1000 µL were injected, as opposed to 250 µL mentioned in the ASTM standard. When the drinking water was spiked with 0.2 µg/L of chromate, the determination yielded 0.245 µg/L (Trace(A)), resulting in a quantitative recovery of 96%.

DIN's development of a remarkable "combination standard" is highly commendable. A team of specialists has devoted their efforts to crafting a single document (DIN 38405-52[72]) that unites and harmonizes different experimental conditions and methods for Cr(VI) determination. This standardization facilitates comparing analytical data obtained with various approaches, like IC, discrete analyzers, flow analysis, and manual static photometric methods.

Conclusion

This document offers an overview of the leading international standards for IC water analysis methods, particularly on applying Thermo Fisher Scientific products according to these standards. It concentrates on ISO and ASTM procedures and mentions applicable national standards if an international one is unavailable. This summary does not claim to be exhaustive. Therefore, we suggest consulting the ISO and ASTM literature for more information, for example, regarding test conditions and sample preparation requirements. The copyright-protected documents are commercially available from the respective homepages.[73, 74]

The Thermo Scientific AppsLab Library is an excellent and accessible online application database. It has entries on IC, HPLC, GC, discrete analyzers applications, and element-specific methods such as ICP-OES and ICP-MS. Advanced search functions enable the refinement of results based on the matrix, analytes, and market segments. Additionally, this database offers experimental conditions, application notes, eWorkflows for Chromeleon CDS, and other related literature, if available.[75]

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