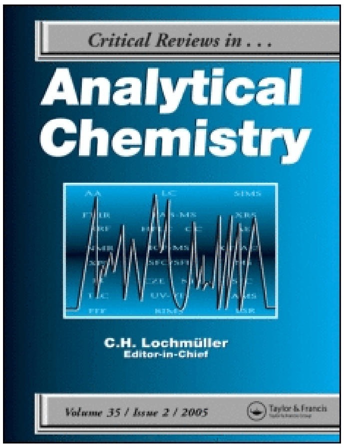

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Ion Chromatography as a Reference Method for Determination of Inorganic Ions in Water and Wastewater

Rajmund Michalski[a]
[a] Institute of Environmental Engineering of Polish Academy of Science, Zabrze, Poland

To cite this Article Michalski, Rajmund(2006) 'Ion Chromatography as a Reference Method for Determination of Inorganic Ions in Water and Wastewater', Critical Reviews in Analytical Chemistry, 36: 2, 107 — 127
To link to this Article: DOI: 10.1080/10408340600713678
URL: http://dx.doi.org/10.1080/10408340600713678

Critical Reviews in Analytical Chemistry, 36:107–127, 2006
Copyright © Taylor and Francis Group, LLC
ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408340600713678

Ion Chromatography as a Reference Method for Determination of Inorganic Ions in Water and Wastewater

Rajmund Michalski
Institute of Environmental Engineering of Polish Academy of Science, Zabrze, Poland

Water analysis is an important part of the chemical analysis of environmental samples. The development of new methods of water analysis and improvement of existing ones is a major task for analytical chemists. Analysis of common inorganic anions and cations in water is mandatory. Ion chromatography has almost replaced most of the wet chemical methods used in water analysis. The demands from regulators for justifiable analytical results and from laboratories for validated methods have led to necessity to standardize ion chromatography methods. The paper is a review of application of ion chromatography for the determination of inorganic anions (F^-, Cl^-, NO_2^-, NO_3^-, BrO_3^-, ClO_2^-, ClO_3^-, PO_4^{3-}, SO_3^{2-}, SO_4^{2-}, CrO_4^{2-}, I^-, SCN^-, and $S_2O_3^{2-}$) and cations (Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}) in water and wastewater.

Keywords ion chromatography, water analysis, anions, cations

INTRODUCTION

Water can be considered as one of the basic substances supporting life and the natural environment, a primary component for industry, a consumer item for humans and animals and a vector for domestic and industrial pollution. Various directives provide a framework for the control of aquatic substances, the quality of bathing, surface and drinking water and effluent control. Such regulatory measures are closely related to analytical measurements.

The number of chemicals determined in water has grown exponentially in the past 30 years. However, for the hundreds of them, very few have been studied or have documented proof of their health effects. Nearly half of the monitored parameters are being measured for operational reasons (e.g., iron, ammonium, pH, chloride, dissolved organic carbon) and for reasons of customer satisfaction (e.g., colour, taste, total hardness).

Of the health-related compounds, a number of metals and small groups of organic compounds and pesticides are being measured on a regular base in the majority of countries. It concerns such metals as antimony, arsenic aluminium, chromium, magnesium, manganium, cadmium, copper, nickel, lead, mercury, iron as well as inorganic ions (ammonium, fluoride, nitrite, nitrate, cyanide) and organic compounds (e.g., benzo(a)pyrene, trihalomethanes, chlorobenzenes, pesticides). Recently inorganic oxyhalide disinfection by-products such as bromate, chlorite and chlorate are also measured.

The identification of new and possibly hazardous compounds in drinking water has become an important task for water suppliers. In an ideal situation, where standards for different intake routes of exposure are fully adjusted to each other, regular monitoring of such compounds should only be necessary when these are carcinogens, or if the relative contribution of drinking water to the total exposure or to the tolerable daily intake is high (1).

The determination of common inorganic anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate) and cations (sodium, potassium, magnesium and calcium) usually was carried out using chemical wet methods such as: gravimetry, titration, photometry, turbidimetry and colorimetry.

Many of these methods suffer from interferences and limited sensitivity; they can be labour intensive and are often difficult to automate. Although performance criteria (trueness, precision and limit of detection) can be specified for analytical methods, it is still difficult to obtain similar results in different laboratories.

Standards specify, a maximum contaminant level (MCL) for a number of inorganic anions and cations. These limits are set to minimize potential health effects arising from ingestion of these ions in drinking water. For instance, high level of fluoride causes skeletal and dental fluorosis, while nitrite and nitrate can cause methemoglobulinemia, which can be fatal to infants.

Address correspondence to Rajmund Michalski, Institute of Environmental Engineering of Polish Academy of Science, 34 Sklodowska-Curie Street, Zabrze 41-819, Poland. E-mail: michalski@ipis.zabrze.pl

TABLE 1
The milestones in the development of ion chromatography

Year	Event
1971	Hamish Small and his colleagues proposed and tested an ion chromatographic method that used ion exchange as the separation mode and conductivity detection for lithium, sodium and potassium determination
1975	Publication in *Analytical Chemistry* by Small et al. (4) a novel ion-exchange chromatographic method for the separation and conductometric detection of ionic species
1975	The public exposure of first commercial ion chromatograph in 1975, during the fall meeting of the American Chemical Society in Chicago
1980	Developed by Gjerde et al. (6, 7) a variety of ion chromatography—a non-suppressed ion chromatography
1981	Introduction to the market an ion chromatographs with all parts contacted with eluents made of non-metallic materials
1981	Introduction on new generation of membrane suppressors
1984	Introduction of first software for ion chromatography
1984	U.S. EPA, and ASTM established a several methods with ion chromatography as reference methods for water and waste water analysis
1986	Introduction of micromembrane suppressors and gradient elution in ion chromatography
1992	Introduction of autosuppressors by Dionex Co.
1998	Introduction of automatic eluent generator ("*Just Add Water*")
1992–2000	Introduction by ISO six ion chromatography standards for water and waste water analysis
Currently	Introduction of new generation suppressors, modern high-selectivity and high-capacity columns, new sample treatment methods, miniaturisation of apparatus

Other common inorganic anions, like chloride and sulfate, are considered as secondary contaminants and are responsible for water taste, odor, color and certain esthetic effects.

Until 1975, only a small range of analytical parameters could be measured automatically, it was therefore necessary to develop and validate new methods to extend the list of such parameters.

Regulators and clients expect to receive "true," and comparable results from the laboratory. Legislators generally define which of the different validated methods should be applied to analyze environmental water samples. In general, standard methods can be chosen to serve as a reference method, but the laboratory serving a public client should apply reference methods.

THE PRINCIPLES OF ION CHROMATOGRAPHY

Ion chromatography (IC) is an innovative analytical technique that has significantly improved analysis of ions in water and wastewater. In the late 1950s, a few researchers at the Dow Physical Research Laboratory (Midland, MI, USA) have foreseen the benefits of inorganic ion analysis by replacing many wet chemical methods with a single chromatographic technique (2). The first breakthrough came in the late 1971, when Hamish Small and his colleagues proposed and tested a chromatographic method that used ion exchange as the separation mode and conductivity detection (3). Dow Chemicals patented suppressed conductivity and subsequently licensed it to Durrum Instruments, which later became Dionex for commercialization of ion chromatography.

In 1975 Small et al. (4) described a novel ion-exchange chromatographic method for the separation and conductometric detection of ionic species. They employed a low-capacity ion-exchange stationary phase for the separation of analyte ions, in conjunction with the second ion-exchange column and conductivity detector, which allowed for continuous monitoring of eluent.

In September 1975 IC has got its first public presentation at the meeting of the American Chemical Society, where Dionex showed the first commercially available instrument (5). In 1979 Gjerde et al. (6, 7) developed variety of ion chromatography—a non-suppressed ion chromatography technique. They showed that suppression was not essential to sensitive conductivity detection, provided that appropriate low-capacity stationary phases and low-conductance eluents were used.

Ion chromatography can be used for the determination of ionic solutes such as: inorganic anions, inorganic cations (including alkali metals, alkaline earth metals, transition metals and rare earth metals), carboxylic, phosphonic and sulfonic acids, detergents, carbohydrates, low-molecular-weight organic bases and ionic metal complexes (8).

Ion-exchange remains the primary separation mode used in modern ion chromatography, although other approaches used for separation of inorganic anions and cations include ion interaction, ion exclusion and chelation chromatography.

Ion chromatography with suppressed conductivity detection is used most widely and generally offers the best performance. In suppressed ion chromatography an eluent containing a suitable electrolyte is passed through a high-performance ion-exchange resin in a device called suppressor (formerly suppressor column) and then to conductivity detector.

Bicarbonate eluents have been used as the mainstay eluent in suppressed ion chromatography. Anyway, the ideal eluent seems to be hydroxide, since after suppression it forms water that has virtually zero conductance, and therefore provides the perfect conductivity baseline. However hydroxide eluent is difficult to

TABLE 2
The characteristics of ISO standard 10304-1 and 10304-2

Method number	ISO 10304-1		ISO 10304-2	
Published	1992		1995	
Method name	Water quality—Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions using liquid chromatography of ions. Part 1: Method for water with low contamination		Water quality—Determination of dissolved anions by liquid chromatography of ions. Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in wastewaters	
Sample matrix	Drinking water, rain water, ground water, surface water		Wastewater	
	Ions	Range	Ions	Range
Working range of determined ions [mg L^{-1}]	Fluoride (F^-)	0.01–10	—	—
	Chloride (Cl^-)	0.1–50	Chloride (Cl^-)	0.1–50
	Nitrite (NO_2^-)	0.05–20	Nitrite (NO_2^-)	0.05–20
	Orthophosphate (PO_4^{3-})	0.1–20	Orthophosphate (PO_4^{3-})	0.1–20
	Bromide (Br^-)	0.05–20	Bromide (Br^-)	0.05–20
	Nitrate (NO_3^-)	0.1–50	Nitrate (NO_3^-)	0.1–50
	Sulfate (SO_4^{2-})	0.1–100	Sulfate (SO_4^{2-})	0.1–100
Detection mode	Suppressed conductivity			

use because it readily absorbs carbon dioxide and forms carbonate (9).

The most popular eluents used in cations analysis are low concentration mineral acids such as: HCl, HNO_3, H_2SO_4 containing also organic modificators (e.g., ethylenediamine, 2,3-diaminopropionic acid) (10). Analyte ions are separated on the ion-exchange column and these ions together with the eluent move to the suppressor. In the suppressor, the conductance of the eluent is lowered (so-called "suppressed") and the conductance of the sample ions is increased, leading to a large increase in the signal-to-noise ratio of the detection signal.

The conceptualization of suppressed conductivity by Small et al. (4) was the seminal idea in the development of ion chromatography. Suppressor columns were used in the beginning of ion chromatography; however, there were a number of limitations associated with the original solutions. These included: the column's limited suppression capacity with necessitated frequent off-line regeneration; and a large extra-volume, which became increasingly important as the efficiency of analytical columns improved (11).

These problems were largely eliminated in 1981 by the introduction of membrane based suppressors by Stevens et al. (12). A development and use of suppression devices for the conductometric detection of inorganic ions by ion chromatography was described by Haddad et al. (13).

Developments in membrane suppressor technology have enabled suppression to be conducted in a continuous and unattended manner have enhanced separation and detection by reducing the system band broadening and have increased the concentration of eluent that can be suppressed. Over the past years, a large variety of stationary phases with different selectivities and capacity have been developed for both anion- and cation-exchange chromatography. The stationary phases used in ion chromatography have been usually polystyrene-divinylbenzene (PS-DVB), polymethacrylate and polyvinyl resins.

Ion-exchange materials used in IC are described by Weiss and Jensen (14). Recently there is an increasing interest in using porous monolithic stationary phases for high-performance separation of inorganic and organic ions (15).

Previously, suppressed and nonsuppressed IC required low column capacities. These columns were easily overloaded by high sample concentrations. Increasing suppression capacity has enabled ever-increasing eluent concentrations and in turn, increasing column capacities.

At the beginning of ion chromatography column materials utilized particles greater than 40 μm and generated only about 120 and 300 theoretical plates efficiency, respectively. In the first commercial column used in IC (Dionex AS-1), the particle size was reduced to 25 μm and efficiencies increased to 700 theoretical plates. Modern high-capacity columns have efficiencies over 5000 plates (for 4 × 250 mm column dimensions) and 5 μm particle size (16). Through the choice of stationary phase and eluent composition the selectivity can be modulated but the eluent must meets requirements of the detection system. Although the conductivity detector is still the most popular, other types of detection can be applied for different analytes.

These include the following methods: electrochemical (amperometric, pulsed and integrated amperometric, potentiometric), photometric (UV/VIS, indirect photometric following post column derivatisation, chemiluminescence, refractive index)

TABLE 3
The characteristics of ISO standard 10304-3 and 10304-4

Method number	ISO 10304-3			ISO 10304-4		
Published	1997			1997		
Method name	Water quality—Determination of dissolved anions by liquid chromatography of ions. Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate			Water quality—Determination of dissolved anions by liquid chromatography of ions. Part 4: Determination of chlorate, chloride and chlorite in water with low contamination		
Sample matrix	Waste water			Drinking water, raw water, swimming pool water		
	Ion	Range	Detection	Ion	Range	Detection
Working range of determined ions [mg L^{-1}]	Chromate (CrO_4^{2-})	0.05–50	UV ($\lambda = 365$ nm)	Chlorate (ClO_3^-)	0.03–10	Suppressed conductivity
	Iodide (I^-)	0.1–50	CD or UV ($\lambda = 205$ nm to 236 nm); AD (0.7 V to 1.1 V)	Chloride (Cl^-)	0.1–50	Suppressed conductivity
	Sulfite (SO_3^{2-})	0.1–50	CD	Chlorite (ClO_2^-)	0.05–1	Suppressed conductivity
	Thiocyanate (SCN^-)	0.5–50	UV ($\lambda = 205$ nm to 220 nm)		0.1–1	UV ($\lambda = 207$ nm to 220 nm)
	Thiosulfate ($S_2O_3^{2-}$)	0.1–50	CD or UV ($\lambda = 205$ nm to 236 nm); AD (0.7 V to 1.1 V)		0.01–1	AD (0.4 V to 1.0 V)

TABLE 4
The characteristics of ISO standard 15061 and 14911

Method number	ISO 15061		ISO 14911	
Published	2001		1998	
Method name	Water quality—Determination of dissolved bromate. Method by liquid chromatography of ions		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. Method for water and wastewater	
Sample matrix	Drinking water, raw water, surface water, partially treated water and swimming pool water		Wastewater	
Working range of determined ions [mg L^{-1}]	Bromate (BrO_3^-)	0.0005–1	Lithium (Li^+)	0.01–1
			Sodium (Na^+)	0.1–10
			Ammonium (NH_4^+)	0.1–10
			Potassium (K^+)	0.1–10
			Manganese (Mn^{2+})	0.5–50
			Calcium (Ca^{2+})	0.5–50
			Magnesium (Mg^{2+})	0.5–50
			Strontium (Sr^{2+})	0.5–50
			Barium (Ba^{2+})	1–100
Detection mode	Suppressed conductivity. UV detector ($\lambda = 190$–205 nm) is suitable to confirm the conductivity results only.		Suppressed conductivity	

and fluorescence. Coupling techniques represent the link of IC system with an independent analytical detection method, usually spectroscopic (AAS—Atomic Absorption Spectroscopy, ICP-AES—Inductively Coupled Plasma Atomic Emission Spectroscopy, ICP-MS—Inductively Coupled Plasma—Mass Spectrometry (17, 18)).

Ion chromatography offers several advantages over conventional methods:

- short analysis time;
- sensitivity on the ppb level (19, 20);
- high selectivity (even in samples with complex matrix) (21–23);
- simple water sample pretreatment (24);
- small sample volume;
- simultaneous determination of anions and cations, or inorganic and organic ions (25, 26);

TABLE 5
The characteristics of U.S. EPA Methods 300 and 300.1

Method number	300.0		300.1	
Published	1993		1997	
Method name	The determination of inorganic anions in water by ion chromatography		The determination of inorganic anions in water by ion chromatography	
Sample matrix	Drinking water, surface water, wastewater			
Limit of detection [mg L^{-1}]	Fluoride (F^-)	0.009	Fluoride (F^-)	0.009
	Chloride (Cl^-)	0.004	Chloride (Cl^-)	0.004
	Nitrite (NO_2^-)	0.001	Nitrite (NO_2^-)	0.001
	Bromide (Br^-)	0.014	Bromide (Br^-)	0.014
	Nitrate (NO_3^-)	0.011	Nitrate (NO_3^-)	0.008
	Phosphate (PO_4^{3-})	0.019	Phosphate (PO_4^{3-})	0.019
	Sulfate (SO_4^{2-})	0.019	Sulfate (SO_4^{2-})	0.019
	Bromate (BrO_3^-)	0.020	Bromate (BrO_3^-)	0.00144
	Chlorite (ClO_2^-)	0.010	Chlorite (ClO_2^-)	0.00089
	Chlorate (ClO_3^-)	0.003	Chlorate (ClO_3^-)	0.00131
Detection mode	Suppressed conductivity			

TABLE 6

The characteristics of U.S. EPA Methods: 314.1; 317.0; 321.8; 326.0 and 332.0

Method number Published	314.1 Revised in 2005	317.0 2001	321.8 1997	326.0 2002	332.0 Revised 2005
Method name	Determination of perchlorate in drinking water using inline column concentration/ matrix elimination ion chromatography with suppressed conductivity detection	Determination of inorganic oxyhalide disinfection by-products in drinking water using ion chromatography with the addition of a post-column reagent for trace bromate analysis	Determination of bromate ions in waters using ion chromatography with inductively coupled plasma mass spectrometry	Determination of inorganic oxyhalide disinfection by-products in drinking water using ion chromatography incorporating the addition of a suppressor acidified post-column reagent for trace bromate analysis	Determination of perchlorate in drinking water by ion chromatography with suppressed conductivity and electrospray ionization mass spectrometry
Sample matrix	Raw and drinking water	Drinking water			
Limit of detection [mgL^{-1}]	ClO_4^- 0.00003	Conductivity detection ClO_2^- 0.00045 ClO_3^- 0.00092 BrO_3^- 0.00098 Uv/Vis detection ClO_2^- 0.00089 $ClO_3{}^-$ 0.00062 BrO_3^- 0.00012	BrO_3^- 0.0003	Conductivity detection ClO_2^- 0.002 ClO_3^- 0.0017 $BrO_3{}^-$ 0.0012 Uv/Vis detection BrO_3^- 0.00017 — — — —	ClO_3^- 0.00002
Detection mode	Suppressed conductivity	Suppressed conductivity followed in series with UV post column derivatisation with *o*-dianisidine	ICP-MS	Suppressed conductivity or UV/Vis	ESI/MS

TABLE 7
The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part I

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Dionex Fast Run Anion	2.3 mM Na_2CO_3 + 4.8 mM $NaHCO_3$	Suppressed conductivity	Surface water, drinking water, rain water	(65)
Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	Dionex Fast Cation I, Fast Cation II	17 mM HCl + 0.26 mM 2,3-diaminopropionic acid	Suppressed conductivity	Drinking water, wastewater, surface water	(66)
Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^+, Pb^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}	TSK_{gel} IC cation SW	3.5 mM EDTA + 10 mM citric acid	Non-suppressed conductivity	Waste water, drinking water	(67)
Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}	Dionex CS 1	0.028 mM $Ce(NO_3)_3$	Indirect fluorescence	Rain water, fog, clouds, aerosols	(68)
F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Dionex AS 4	1.2 mM Na_2CO_3 + 1.5 mM $NaHCO_3$	Suppressed conductivity and amperometric		
NO_2^-	Dionex IonPac AS 4A	$H_3BO_4 + Na_2CO_3$, Na_2CO_3 + $NaHCO_3$, NaCl	Suppressed conductivity, UV ($\lambda = 210$ nm), amperometric	Waters with a large excess of chloride	(69)
BrO_3^-, ClO_2^-, ClO_3^-	Dionex IonPac AS9-SC	30 mM NaOH + 120 mM boric acid	Suppressed conductivity	Drinking water	(70)
Cl^-, NO_2^-, Br^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}, $(COO)_2^{2-}$	Dionex IonPac AS4A	1,8 mM Na_2CO_3 + 1,7 mM $NaHCO_3$	Suppressed conductivity	Organic rich natural waters from peatlands	(71)

TABLE 8
The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part II

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS10	40 mM HCl + 12 mM 2,3-diaminopropionic acid	Suppressed conductivity	Organic rich natural water from peatlands	(72)
Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, $(COO)_2^{2-}$	Dionex IonPac AS4A	1,7 mM Na_2CO_3 + 1,8 mM $NaHCO_3$	Suppressed conductivity	Rain water	(73)
F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, $HCOO^-$, CH_3COO^-	Dionex IonPac AS5A	NaOH (gradient elution)			
Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	Dionex IonPac CS 10	40 mM HCl + 20 mM 2,3-diaminopropionic acid			
F^-, Cl^-, Br^-, NO_2^-, PO_4^{3-}, SO_4^{2-}	Waters IC Pak A HC	1.3 mM gluconic acid + 1.3 mM boric acid	Non-suppressed conductivity	Rain water	(74)
Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}	Waters IC Pak C M/D	3.0 mM HNO_3 + 0.1 mM EDTA			
BrO_3^-	Dionex IonPac AS9-SC	40 mM boric acid + 20 mM NaOH	Suppressed conductivity	Ozonated drinking water	(75)
Cl^-, NO_3^-, SO_4^{2-}	Dionex IonPac AS4A-SC	1,8 mM Na_2CO_3 + 1,7 mM $NaHCO_3$	Suppressed conductivity	Rain water, snow	(76)
Na^+, K^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS12	20 mM CH_3SO_3H			

TABLE 9
The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part III

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}	Dionex IonPac CS 12	20 mM methanesulphonic acid	Suppressed conductivity	Mineral water	(77)
Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Sr^{2+}, Ca^{2+}	Dionex IonPac CS 12	20 mM 2,3-diaminopropionic acid	Suppressed conductivity	Mineral water	(78)
F^-, Cl^-, BrO_3^-, ClO_2^-, ClO_3^-, NO_2^-, Br^-, PO_4^{3-}, SO_4^{2-}	Dionex IonPac AS 12A	0.3 mM Na_2CO_3 + 2.7 mM $NaHCO_3$	Suppressed conductivity	Drinking water	(79)
K^+, Na^+, Mg^{2+}, Ca^{-2+}	Waters IC-PAK CM/D	7.5 mM citric acid + 1.0 mM PDCA	Suppressed conductivity	Drinking water	(80)
Cl^-, NO_3^-, SO_4^{2-}, Br^-	Dionex IonPac AS 4A-HC	Na_2CO_3 + $NaHCO_3$	Suppressed conductivity and UV ($\lambda = 210$ nm)	Sea water	(81)
Cr(III)/Cr(VI)	Dionex IonPac CS5	2 mM PDCA + 2 mM $NaHPO_4$ + 1 mM NaI + 5 mM CH_3COONH_4	On-line thermal lens spectrometric	Drinking water	(82)
Cr(III)/Cr(VI)	Excelpak ICS-A23	1 mM EDTA-$2NH_4$ + 10 mM oxalic acid	ICP-MS	Drinking water, wastewater	(83)
F^-	Dionex IonPac AS 10	13 mM NaOH	Suppressed conductivity	Rain water	(84)

TABLE 10

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part IV

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
BrO_3^-	Dionex IonPac AS 10, Dionex IonPac A Dionex IonPac AG 10	100 mM NaOH	ICP-MS	Drinking water	(85)
F^-, $HCOO^-$, CH_3COO^-, Cl^-, SO_4^{2-}, $(COO)_2^2$,	Dionex IonPac AS11 or IonPac AS 10	NaOH (gradient elution) or 85 mM NaOH (isocratic elution)	Suppressed conductivity	High purity water, drinking water	(86)
Li^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS 12A	11 mM H_2SO_4			
Cr(III)/Cr(VI)	Dionex IonPac CG5 + AS7	55 mM K_2SO_4 + 95 mM KNO_3	Chemiluminescence	Waste water	(87)
F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}	Allsep. Anion	Na_2CO_3 + $NaHCO_3$, p-hydroxybenzoic acid, phthalic acid	Suppressed or non-suppressed conductivity	Drinking water	(88)
BrO_3^-	Excelpak ICS-A1 + ICS A-13	5 mM Na_2CO_3 + 1 mM $NaHCO_3$	PCR with Br_3^- ($\lambda = 267$ nm)	Drinking water, ozonated drinking water	(89)
Cr(III)/Cr(VI), As(III)/As(V)	Waters IC-Pak A HC	NaOH (gradient elution) or KNO_3 (isocratic elution)	ICP-MS	Drinking water, wastewater	(90)
Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Waters IC-PAK CM/D	5 mM HNO_3 + 0.1 mM EDTA	Suppressed conductivity	Mineral waters	(91)

TABLE 11

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part V

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
BrO_3^-	Anion-exchanger PA-100	10 mM NaOH or 5 mM HNO_3	ICP-MS	Drinking water, ozonated drinking water	(92)
Cl^-, NO_2^-, SO_4^{2-}, F^-, $(COO)_2^{2-}$	Dionex IonPac AS 10	85 mM NaOH	Suppressed conductivity	Power plant water	(93)
Fe^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}	Dionex IonPac CS5A	7.0 mM PDCA + 66 mM KOH + 74 mM formie acid	PCR with PAR UV ($\lambda = 530$ nm)	Industrial waste water	(94)
Cl^-, ClO_2^-, ClO_3^-, ClO_4^-	Vydac 302 IC	1 mM potassium hydrogen phthalate	Non-suppressed conductivity or UV ($\lambda = 254$ nm)	Drinking water, waste water, swimming pool water	(95)
BrO_3^-, Br^-	Teflon-PFA anion exchanger	NH_4NO_3 + NH_3	NTI-IMDS, ICP-MS	Drinking water	(96)
Cl^-, NO_2^-, SO_4^{2-}, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Laboratory-made silica-based chimica-bonded	0.5 mM sodium benzoate + 0.1 mM sodium citrate	Suppressed conductivity	Oil field water	(97)
Mg^{2+}, Ca^{-2+}, Sr^{2+}, Ba^{-2+}		1.5 mM HNO_3			

- species analysis (e.g., $NO_2^-/NO_3^-/NH_4^+$, $SO_3^{2-}/SO_4^{2-}/S^{2-}$, $H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$ Br^-/BrO_3^-, $Cl^-/ClO_2^-/ClO_3^-/ClO_4^-$, Cr(III)/Cr(VI), Fe(II)/Fe(III)) (27–29);
- use of cheap, safe and environment friendly chemicals.

Acceptance of ion chromatography for the analysis of anionic solutes was very rapid, primarily due to the lack of alternative methods that could determine multiple anions in a single analysis. However, the situation regarding the analysis of cations in environmental samples was quite different, due to many rapid and sensitive spectroscopic methods such as AAS, ICP-AES, ICP-MS, polarography and stripping voltammetry.

Ion chromatography provides a straightforward method for the simultaneous determination of alkali and alkaline earth cations and ammonia. A key benefit of this approach is the ability to determine ammonia in complex samples which contain both inorganic cations and organic amines, as the latter compounds can interfere with the conventional colorimetric or ion selective electrode methods used for ammonia analysis.

Until recently analytical methods allowed analysts to determine total content of analytes only, but it was soon realized that this analytical information was insufficient. Biochemical and toxicological investigation has shown that for living organisms the chemical form of a specific element or the oxidation state in which that element is introduced into the environment is as important as its quantities.

Speciation of an element is the determination of the individual physicochemical forms of that element that, together, make up its total concentration in a sample (Florence and Batley (30)). According to Kot and Namiesnik (31) the main types of speciation of chemical compounds are: screening, group, distribution and individual speciation. Speciation plays a unique role in: the studies of biogeochemical cycles of chemical compounds, determination of toxicity and ecotoxicity of selected elements, quality control of food products, control of medicines and pharmaceutical products, technological process control, research on the impact of technological installation on the environment, examination of occupational exposure and clinical analysis.

IC plays an important role in hyphenated techniques used in species analysis, as an effective and reliable separation method (32–34). More than 15 years ago, capillary electrophoresis appeared as a promising substitute for the IC mainly because of its higher speed of separation. Determination of inorganic anions and cations by capillary electrophoresis can be considered as an emerging technique, in which current research carries an emphasis on fundamentals rather than applications.

Comparison of IC and capillary electrophoresis has shown that these techniques can be considered as complementary rather than competitive (35, 36). Nevertheless until now there are no

TABLE 12

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part VI

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
BrO_3^-, ClO_2^-, ClO_3^-, IO_3^-	Dionex IonPac AG9	H_2O + methanol + NH_4NO_4 + Na_2CO_3 + $NaHCO_3$	ESI-MS-MS	Drinking water	(98)
BrO_3^-, ClO_2^-, ClO_3^-	Dionex IonPac AS12	2.7 mM Na_2CO_3 + 0.3 mM $NaHCO_3$	PCR with Br_3^- ($\lambda = 267$ nm)	Drinking water, ozonated drinking water, mineral water	(99)
F^-, Cl^-, NO_3^-, SO_4^{2-}, $HCOO^-$, CH_3COO^-	Dionex IonPac AS11	21 mM NaOH or 0.5 mM NaOH	Suppressed conductivity	Rain water	(100)
Cl^-, ClO_2^-, ClO_3^-, ClO_4^-, I^- IO_3^-	Waters IC-Pak Anion HR	KNO_3	ICP-MS	Drinking water	(101)
BrO_3^-	Self-made high-capacity anion-exchange	NH_4NO_3	ICP-MS	Drinking water, swimming pool water	(102)
BrO_3^-, Br^-, ClO_2^-, ClO_3^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3	Suppressed conductivity	Drinking water	(103)
BrO_3^-, ClO_2^-, IO_3^-	Dionex IonPac AS12	2.7 mM Na_2CO_3 + 0.3 mM $NaHCO_3$	PCR with Br_3^- ($\lambda = 267$ nm)	Drinking water	(104)
CH_3COO^-, BrO_3^-, ClO_3^-, Br^-, SO_4^{2-}, trifluoroacetate, methansulfate	Dionex IonPac AS 11	NaOH (gradient elution)	Suppressed conductivity	Dinking water	(105)

TABLE 13

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part VII

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
ClO_4^-	Dionex IonPac AS11	100 mM NaOH	Suppressed conductivity	Drinking water, ground water	(106)
BrO_3^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3	PCR with Br_3^- ($\lambda = 268$ nm)	Drinking water	(107)
NO_2^-	Denki Kagaku Keiki, LIC-10SA1	1.5 mM phthalate	PCR with I_3^- ($\lambda = 350$ nm)	River water, lake water, sewage works water	(108)
IO_3^-, BrO_3^-, Br^-, SO_4^{2-}, $S_2O_3^{2-}$, I^-	Waters IC-Pak Anion HR	0.5 M ammonium citrate + 10% acetonitrile	API-MS	Drinking water	(109)
BrO_3^-, Br^-, IO_3^-, I^-	Dionex IonPac AS9-HC	25 mM $Na_2B_4O_7$	PCR with fuchsine ($\lambda = 520$ nm)	Drinking water	(110)
BrO_3^-, Br^-, ClO_3^-, $S_2O_3^{2-}$, IO_3^-, SO_4^{2-}	Waters IC-Pak Anion HR	Na_2CO_3	Suppressed conductivity and API-MS	Drinking water	(111)
BrO_3^-, Br^-, Cl^-, ClO_2^-, IO_3^-, NO_2^-, SO_4^{2-}, NO_3^-, PO_4^{3-}	Dionex IonPac AS9-HC	9 mM Na_2CO_3	Suppressed conductivity and PCR with KI + ($NH_4Mo_7O_{24}$ $\lambda = 352$ nm)	Drinking water, ozonated drinking water	(112)
BrO_3^-, Br^-, Cl^-, SeO_3^{2-}, PO_4^{2-}, AsO_4^{2-}, SeO_4^{2-}, ClO_3^-,ClO_2^-, SO_4^{2-}	Dionex IonPac AS12A	11 mM $(NH_4)_2CO_3$	ICP-MS	Drinking water	(113)

TABLE 14

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part VIII

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
BrO_3^-, Br^-, ClO_2^-, ClO_3^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3 or 12 mM Na_2CO_3 + 5 mM $NaHCO_3$	PCR with o-dianisidine ($\lambda = 450$ nm)	Drinking water, ozonated drinking water	(114)
BrO_3^-, ClO_2^-, ClO_3^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3	PCR with o-dianisidine ($\lambda = 450$ nm)	Drinking water, ozonated drinking water	(115)
BrO_3^-	Waters IC-Pak Anion HR or self-made PS/DVB anion-exchanger	5 mM Na_2CO_3 or 75 mM NH_4NO_3	API-MS or ICP-MS	Surface water, Drinking water	(116)
BrO_3^-, Br^-, ClO_2^-, ClO_3^-, F^-, Cl^-, $NO_2^-$$SO_4^{2-}$, NO_3^-, PO_4^{3-}	Self-made PS-DVB anion-exchanger	70 mM NaOH + 0.5 mM $HClO_4$ or 5 mM Na_2CO_3	Suppressed conductivity or PCR with chlorpromazine ($\lambda = 530$ nm)	Drinking water, table water, swimming pool water, mineral water	(117)
Br^-, Cl^-, NO_2^-, NO_3^-, F^-, HPO_4^-, SO_4^{2-}	Dionex IonPac AS4A-SC Dionex IonPac AS14	3.15 mM Na_2CO_3 + 0.9 mM $NaHCO_3$ 20 mM NaOH	Suppressed conductivity and UV ($\lambda = 215$ nm)	High purity water, drinking water	(118)
Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}	TSK_{gel} OA-PAK-A	Sulfosalicylic acid + methanol + water	Non-suppressed conductivity	Drinking water	(119)

international standards applied for capillary electrophoresis methods but rapid development of capillary electrophoresis can be expected.

The milestones in the ion chromatography development are given in Table 1. Determination of inorganic anions and cations in environmental waters, such as drinking water, surface water and wastewater, is the most widely used application of IC worldwide (37). Application of IC in environmental analysis including sample handling and preparation, analytical performances and quality assurance has been described by Jackson (38).

STANDARDIZATIONS OF ION CHROMATOGRAPHIC METHODS

The most routine IC methods have been standardized in the past 30 years. Advances in IC provided analytical chemists with the new reliable tools for environmental analysis.

The best methods for inorganic anions and cations determinations should meet the following requirements:

- determination of target ions with limit of determination on 25% of maximum acceptable concentration;
- simple sample treatment;
- short time of analysis;
- low cost of single analysis;
- method availability.

IC methods meet these requirements and can be used for routine applications in environmental laboratories. Laboratories benefit from applying ion chromatography, because of simplified sample preparation, renunciation of hazardous reagents (e.g. acids, organics solvents) and robustness against matrix interferences.

International Standard Organization (ISO) standards can remove trade barriers and promote business across national frontiers. Standardization on the European level is the responsibility of European Committee of Standardization (CEN), whereas on the international level, the ISO is responsible.

Around 120 national standardization bodies cooperate in activities that aim to stimulate cooperation in the scientific, technical and economics spheres across national frontiers. Standardization is based on consensus, on scientific findings, on technical progress, and has to bear in mind economical consequences.

CEN and ISO standards are elaborated in Technical Committees (TC), installed for a distinct field of action. ISO TC 147, founded in 1971, is responsible for the standardization in the field of water quality. The correspondent European committee is CEN TC 230 "Water Quality," founded in 1990.

Recently both standardization institutions cooperate according to the Vienna Agreement established in 1991. It means that standards can be transferred between ISO and CEN if necessity arises. Experts work on the standardization of IC methods due to:

TABLE 15

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part IX

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
Fe^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}	Dionex IonPac CS2	10 mM oxalic acid + 7.5 mM citric acid or 40 mM tartaric acid + 12 mM citric acid	UV ($\lambda = 520$ nm)	Groundwater	(120)
	Dionex IonPac CS5	6 mM PDCA or 50 mM oxalic acid + 95 mM LiOH			
F^-, CH_3COO^-, $HCOO^-$, NO_3^-, NO_2^-, Br^-, ClO_3^-, SO_4^{2-}, $(COO)_2^{2-}$, PO_4^{2-}	Dionex IonPac AS 17	KOH (gradient elution)	Suppressed conductivity	Drinking water	(121)
BrO_3^-, SeO_3^{2-}, SeO_4^{2-}, AsO_4^{2-}, MnO_4^{2-}, CrO_4^{2-}	Dionex IonPac AS9-HC	3.5 mM $NaHCO_3$	Suppressed conductivity	River water	(122)
CN^-	Dionex IonPac AS11	5 mM NaOH	Suppressed conductivity (Ion Exchange Reaction)	Wastewater	(123)
F^-, Cl^-, Br^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, NO_3^-	Dionex IonPac AS11	21 mM NaOH	Suppressed conductivity	Groundwater	(124)
Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Laboratory-made aluminium-adsorbing silica Gel Al-silica	1.2 mM tyramine + 0.2 mM oxalic acid + 5 mM 15-crown-5 or 5 mM 18-crown-6	UV ($\lambda = 265$ nm)	Wastewater	(125)

- profit from the technical advantages;
- the request from laboratories to have validated methods for accreditation procedures according to ISO 17025;
- the demand from administrative authorities to have reference methods for water analysis and regulations.

One of the most important IC methods is US EPA (US Environmental Protection Agency) Method 300.0 recommended for the determination of common inorganic anions (fluoride, chloride, nitrate and sulfate) using standard low capacity anion-exchange column and conductivity detection, introduced in 1993 (39). Soon this method was updated to include part B for the determination of bromate and other inorganic disinfection by-products using modern high capacity anion exchange column with carbonate/bicarbonate eluent (40).

Many countries have similar to the USA health and environmental standards and a considerable number of regulatory IC methods. Most of methods for determination of inorganic anions and cations in environmental waters are similar to the U.S. EPA Method 300.0, and have been published worldwide. For example, German Methods DIN 38 405, DIN 55609 and DIN 38405-7, French Method AFNOR T90-042, Italian Method UNICHIM 926, and Japanese K0101 are similar to the U.S. EPA Method 300.0 (41).

THE REVIEW OF ISO AND U.S. EPA ION CHROMATOGRAPHY METHODS

IC can be considered a well-established, mature technique for the analysis of anions and cations and many organizations, such as ISO (42–47), U.S. EPA (39, 40, 48–52), ASTM (American Society for Testing and Materials) (53–59), or AOAC (Association of Official Analytical Chemists) (60) have standards or regulatory methods of analysis based upon it.

The review of ISO and U.S. EPA methods for the determination of inorganic anions and cations in water and wastewater is given in Tables 2–4 (ISO Standards), and Tables 5 and 6 (U.S. EPA Methods). This review includes: method number, title, limit

TABLE 16

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part X

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
BrO_3^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3	PCR with Br_3^- ($\lambda = 267$ nm)	Drinking water, ozonated dinking water	(126)
BrO_3^-, NO_2^-	Dionex IonPac AS9-HC	9 mM Na_2CO_3	PCR with Br_3^- ($\lambda = 267$ nm) or PCR with o-dianisidine ($\lambda = 450$ nm) or PCR with KI + ($NH_4Mo_7O_{24}$, $\lambda = 352$ nm)	Drinking water	(127)
F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}	Metrohm Metrosupp IC Anion	Phthalic acid	Non-suppressed conductivity	Drinking water	(128)
F^-, Cl^-, Br^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, NO_3^-	Dionex IonPac AS4A-SC, IonPac AS14, IonPac AS14A	Na_2CO_3 + $NaHCO_3$	Suppressed conductivity	Drinking water, industrial wastewater, domestic wastewater, surface water	(129)
Cl^-, Br^-, NO_3^-, SO_4^{2-}	Dionex IonPac AS9-HC	3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$	Suppressed conductivity	Rain water	(130)
Na^+, K^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS12	20 mM CH_3SO_3H			
F^-, Cl^-, Br^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, NO_3^-, BrO_3^-	Phenomenex Kingsorb	5 mM Phthalate	UV ($\lambda = 279$ nm)	Drinking water, sea water, river water	(131)
Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS16	26 mM methanesulfonic acid	Suppressed conductivity	Surface water, drinking water, wastewater	(132)

of determination or range of determined ions, sample matrix, and detection mode.

These methods have been developed especially for drinking and waste water analyses, however other applications (e.g., rain water, swimming pool water) are acceptable. During the standardization process the draft standard methods had to go through a validation procedure, including checks for trueness, precision, recovery, and finally an interlaboratory trial before they were published as a standard method.

The normative part of an analytical standard method in ISO includes at least the following clauses: scope, normative references, interferences, principle, essential minimum requirements, reagents, apparatus, quality requirements for the separator column, sampling and sample pretreatment, procedure, calculation, expression of results and test report.

Methods can be deleted from the standards system if they do not pass the approval stage successfully, or a confirmation after 5 years is refused, or a replacement of an existing standard by a new one takes place (61).

SUMMARY

Since its introduction in 1975, ion chromatography has been used in most areas of analytical chemistry and has become a versatile and powerful technique for the analysis of a vast number of ions present in the environment.

One of the premier analytical chemists of the 20th century, Professor Harvey Diehl of Iowa State University proposed that any scientist who could develop a better method for sulphur analysis than gravimetry or nephelometry should be given the Nobel Prize. Today, we can say that ion chromatography has met this challenge.

The most important advantages of IC are: broad range of applications, well-developed hardware, many detection options, reliability (good accuracy and precision), high selectivity, high speed, high separation efficiency, good tolerance to sample matrices, low cost of consumables, accepted as standard methodology.

It is an attractive technique especially for laboratories which need to determine numerous anions and cations in several thousand samples, but do not have the throughput to justify the purchase of large automatic analysers, usually based on colorimetric procedures. IC eliminates the need to use hazardous reagents, which are often integral to colorimetric procedures.

Considering that several individual wet chemistry methods for common inorganic anions or cations could be replaced by one quick (e.g., 15 minutes) and reliable chromatographic

TABLE 17
The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part XI

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
ClO_4^-, BrO_3^-, SeO_3^{2-}, SeO_4^{2-}	Dionex IonPac AS9-HC and IonPac AS16	Na_2CO_3 + $NaHCO_3$ or NaOH	ESI-MS	Drinking water, surface water	(133)
F^-, Cl^-, Br^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, NO_3^-, $HCOO^-$, CH_3COO^-	Dionex IonPac AS15	KOH	Suppressed conductivity	Power plant water	(134)
$[Ag(CN)_2]^-$, $[Au(CN)_2]^-$ $[Cu(CN)_3]^{2-}$, $Ni(CN)_4]^{2-}$ $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$	Transgenomic QS-A1, QS-A2	20 mM NaOH + 150 mM NaCN, 20 mM NaOH + 100 mM $NaClO_4$	UV ($\lambda = 215$ nm)	Wastewater	(135)
NO_2^-, SO_3^{2-}, $(COO)_2^{2-}$, I^-, $S_2O_3^{2-}$, ascorbic acid,	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Fluorescence detection	River water, drinking water	(136)
BrO_3^-, NO_2^-, NO_3^-, F^-, Cl^-, CH_3COO^-, $HCOO^-$, Br^-, PO_4^{3-}, SO_4^{2-}	Dionex IonPac AS 9-HC	11.5 mM Na_2CO_3	Suppressed conductivity	Drinking water, bottled water	(137)
NO_2^-, NO_3^-, Cl^-, PO_4^{3-}, SO_4^{2-}	Dionex IonPac AS 9-HC	9.0 mM Na_2CO_3	Suppressed conductivity and UV ($\lambda = 225$ nm)	Sea water, wastewater	(138)
NO_2^-, NO_3^-, NH_4^+	TSK_{gel} IC Anion SW + TSK_{gel} IC Cation	5 mM Na_2SO_4	UV ($\lambda = 206$ nm) or fluorescence (410/470 nm)	Rain water	(139)
NO_2^-, NO_3^-, SO_4^{2-}, Br^-	TSK_{gel} IC Anion SW + TSK_{gel} IC Cation	1 mM H_2SO_4	UV ($\lambda = 210$ nm)	Rain water, drinking water, pond water	(140)

separation, it is not surprising that ion chromatography quickly became accepted by regulatory bodies worldwide for the analysis of anions in drinking and wastewaters. However, there are relatively few regulatory methods for cations analysis which use ion chromatography.

The laboratories need validated methods for performing a variety of required characteristics, e.g., robust against possible matrix interferences or matrix changes, specific and selective for contaminant of interest, suitable working range, applicable for the control of maximum contaminant level. Additional desirable characteristics are that method should, for example, allow simplified sample preparation, rapid analyses, economical benefits, avoidance of hazardous reagents, robust apparatus, compatible with the requirements of an analytical quality control system.

Quality control is essential part of environment analysis when it comes to generating reliable results using ion chromatography, or any analytical method. Well-qualified strategies are the use of certified reference materials (CRM) (62, 63) or the participation in interlaboratory trials.

Standard methods (e.g., from ISO, CEN, and the U.S. EPA) can be adopted as recommendation on a voluntary basis by any laboratory around the world. Governments can decide to incorporate existing standards into their national standards.

After the publications of the U.S. EPA, ASTM and particularly ISO standards concerning with ion chromatography the number of laboratories applying this technique have increased dramatically. For those laboratories ion chromatography is a reliable and economic supplement for an existing wet chemical methods.

In 1992–2005, five IC standards concerning anion determination in water and wastewaters have been published. Only one standard concerns cation determination (Tables 2–4). Many different regulatory agencies use the same methodology as U.S. EPA Method 300.0 (39), however, each agency has a unique method format and style. Also, differences exist between the methods in the area of quality control.

The U.S. EPA published 7 methods, for among, 3 (Methods: 317.0, 321.8, and 326.0) concern determination of oxyhalide disinfection by-products (bromate, chlorite, and chlorate). It is noteworthy, that two U.S. EPA Methods (314.1, and 332.0) described the analysis of perchlorate, which is a new challenge in analytical chemistry.

In contrast to ISO standards, some U.S. EPA methods recommend use modern columns, new sample preparation and hyphenated detection scheme (e.g., ICP-MS (50) and ESI/MS (52)).

All ISO ion chromatography standards are based on suppressed conductivity detection, although two of them (ISO 10304 part 3, and part 4 allow using UV/Vis and amperometry detection mode (Table 3).

TABLE 18

The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part XII

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
Cl^-, NO_3^-, SO_4^{2-}	Metrohm Metrosepp A SUPP 5	3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$	Suppressed conductivity	Rain water	(141)
Na^+, K^+, Mg^{2+}, Ca^{2+}	Metrohm Cation 1–2	4 mM tartaric amid + 0,75 mM dipicolinic acid			
F^-, Cl^-, NO_3^-, SO_4^{2-}	Metrohm Metrosepp 3	1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$	Suppressed conductivity	Rain water	(142)
Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Metrohm Metrosepp Cation 1–2	10 mM tartaric acid	Non-suppressed conductivity		
Cl^-, Br^-, NO_3^-, SO_4^{2-}	Dionex IonPac AS9-HC	3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$	Suppressed conductivity	Rain water	(143)
Na^+, K^+, Mg^{2+}, Ca^{2+}	Dionex IonPac CS12	20 mM CH_3SO_3H			
F^-, Cl^-, Br^-, NO_2^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}	Phenomenex Star-Ion A 300	3.75 mM Na_2CO_3 + 3.6 mM $NaHCO_3$	Suppressed conductivity	High purity water	(144)
F^-, CH_3COO^-, $ClO_3^{-'}$, $HCOO^-$, BrO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}, NO_2^-	Dionex IonPac AS9-HC	11.5 mM Na_2CO_3	Suppressed conductivity	Drinking water, bottled water	(145)
F^-, Cl^-, Br^-, ClO_2^-, NO_3^-, BrO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Mg^{2+}, Ca^{2+}	Dionex IonPac AS9-HC	8 mM (or 10 mM) Na_2CO_3 + 0.2 mM EDTA	Suppressed conductivity	Drinking water, wastewater	(146)

TABLE 19
The examples of applications of IC for the determination of inorganic anions and cations in different types of water—part XIII

Analytes	Columns	Eluent	Detection mode	Sample matrix	References
F^-, Cl^-, Br^-, ClO_2^-, NO_2^-, BrO_3^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Mg^{2+}, Ca^{2+}	Dionex IonPac AS9-HC	8 mM (or 10 mM) Na_2CO_3 + 0.2 mM EDTA	Suppressed conductivity		(147)
Cl^-, NO_3^-, SO_4^{2-},	Metrohm Metrosepp A SUPP 5	3.2 mM Na_2CO_3 + 1.0 mM $NaHCO_3$	Suppressed conductivity	Rain water	(148)
Na^+, K^+, Mg^{2+}, Ca^{2+}	Metrohm Cation 1-2	4 mM tartaric amid + 0,75 mM dipicolinic acid			
Cr(III)/Cr(VI)	Dionex IonPac CS5A	40 mM L^{-1} $MgSO_4$ + 30 mM L^{-1} $HClO_4$	PCR with 15 mM $Na_2S_2O_8$+ 0.23 mM $AgNO_3$ UV ($\lambda = 365$ nm)	Drinking water, wastewater	(149)
BrO_3^-	Dionex IonPac AS9-HC	9.0 mM Na_2CO_3	Suppressed conductivity and PCR with Br_3^- ($\lambda = 267$ nm)	Drinking water, ozonated drinking water	(150)
F^-, Cl^-, Br^-, PO_4^{3-}, NO_2^-, SO_4^{2-}, NO_3^-	Metrohm Metrosepp A SUPP 4	1.0 mM Na_2CO_3 + 4.0 mM $NaHCO_3$	Suppressed conductivity and electrochemical	High purity water	(151)

The philosophy of setting standards in CEN and ISO on the one hand and the U.S. EPA on the other hand is different. CEN and ISO prefer documents that do not specify trademarks or equipment produced by a single manufacturer (monopolies).

The examples of applications of ion chromatography (literature data encompasses years 1980–2005) for the determination of inorganic anions and cations in different types of waters (drinking water, wastewater, rain water, river water etc.) including: analyzed ions, separation column, eluent, detection mode and sample matrix are given in Tables 7–19. On the basis of these data we may say, that in comparison to ISO standards that recommend using well-established, older procedures, regarding applied sample treatment methods, columns, eluents, detection scheme—the range of application of ion chromatography in real water analysis is broaden significantly.

In recent years, the separation of less common anions and cations as well as the analysis of ionic species in complicated matrices required the development of stationary phases with widely different selectivities and much higher resolution power. Extreme concentration differences between analyte ions, typically the case of environmental samples initiated development of high-capacity columns with high chromatographic efficiencies. Moreover, those columns can tolerate large volume injections, thereby facilitating trace analysis. Thus, the diversity of columns available today allows the ion chromatography user to individually select a stationary phase that is best suited for the respective application. This, in turn, allows the determination of inorganic contaminants at lower detection limits and expands the range of analytes that can be measured in water and wastewaters. Ion chromatography appears certain to remain an important technique for drinking water analysis and new method based on ion chromatography separation will continue to be developed as more and more inorganic contaminants (e.g., perchlorate, chromate, cyanide) become regulated at lower and lower limits in the future.

IC is applicable to the determination of ions in many sample types, although the determination of inorganic ions in water continues to be the most widely used application. Nevertheless IC is use in many others fields such as: pharmaceutical, petrochemical, semiconductor, and power industry; as well as analysis of: food, beverages, fertilizers, explosives, detergents, cosmetics, etc. (8, 37).

Currently ISO/TC 147 WG 33 (responsible for ion chromatography methods) work on several new methods concerning with: determination of bromate in drinking water (post-column derivatisation method with triiodide), determination of common anions in water (Draft ISO/DIS 10304) and new method of cyanide determination using amperometric detection (64).

At present, ion chromatography accounts for over $165 million of the $3 billion worldwide liquid chromatography market, with over 2,500 ion chromatographs sold in 2002. Approximately 4,000 applications of ion chromatography have been published over the past 30 years (35).

ABBREVIATIONS

AAS	atomic absorption spectroscopy
AD	amperometric detection
AFNOR	French Standardization Association
AOAC	Association of Official Analytical Chemists
API-MS	atmospheric pressure ionization tandem mass spectrometry
ASTM	American Society for Testing and Materials
CD	conductivity detection
CEN	European Committee of Standardization
CRM	certified reference materials
DIN	German Institute for Standardization
ESI/MS	electrospray ionization mass spectrometry
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectrometry
ISO	International Standard Organization
MCL	maximum contaminant level
NTI-IMDS	negative thermal ionization isotope dilution mass spectrometry
PAR	4-(2-pyridylazo)-resorcinol
PCR	post-column reaction (post-column derivatisation)
PS-DVB	polystyrene-divinylbenzene
TC	technical committees
U.S. EPA	United States of Environmental Protection Agency

REFERENCES

1. A. M. Dijk-Looijaard and J. Genderen, Levels of exposure from drinking water. *Food Chemical Toxicology* 38 (2000):37–42.
2. C. A. Lucy, Evolution of ion-exchange: From Moses to the Manhattan Project to Modern Times. *Journal of Chromatography A* 1000 (2003):711–724.
3. H. Small, Twenty years of ion chromatography. *Journal of Chromatography A* 546, (1991):3–15.
4. H. Small, T. S. Stevens, and W. C. Bauman, Novel ion exchange chromatographic method using conductometric detection. *Analytical Chemistry* 47 (1975):1801–1886.
5. H. Small and B. Bowman, Ion chromatography: A historical perspective. *American Laboratory* 10 (1998):1–8.
6. D. T. Gjerde, J. S. Fritz, and G. Schmuckler, Anion chromatography with low-conductivity eluents. *Journal of Chromatography A* 186 (1979):509–519.
7. D. T. Gjerde, J. S. Fritz, and G. Schmuckler, Anion chromatography with low-conductivity eluents II. *Journal of Chromatography A* 187 (1980):35–45.
8. P. R. Haddad, and P. E. Jackson, *Ion Chromatography* (New York: Elsevier, 1990).
9. Y. Liu, E. Kaiser, and N. Avdalovic, Determination of trace-level anions in high-purity water samples by ion chromatography with an automated on-line eluent generation system. *Microchemical Journal* 62 (1999):164–173.
10. D. T. Gjerde, Eluent selection for determination of cations in ion chromatography. *Journal of Chromatography A* 439 (1988):49–61.
11. Y. Liu, K. Srinivasan, Ch. Pohl, and N. Avdalovic, Recent developments in electrolytic devices for ion chromatography. *Journal of Biochemical and Biophysical Methods* 60 (2004):205–232.
12. T. S. Stevens, J. C. Davis, and H. Small, Hollow fibber ion-exchange suppressor for ion chromatography. *Analytical Chemistry* 53 (1981):1488–1492.
13. P. R. Haddad, P. E. Jackson, and M. J. Shaw, Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection. *Journal of Chromatography A* 1000 (2003):725–742
14. J. Weiss and D. Jensen, Modern stationary phases for ion chromatography. *Analytical Bioanalytical Chemistry* 375 (2003):81–98.
15. B. Paull and P. N. Nesterenko, New possibilities in ion chromatography using porous monolithic stationary-phase media. *Trends in Analytical Chemistry* 24 (2005):295–303.
16. C. Sarzanini and M. C., Bruzzoniti, New materials: analytical and environmental applications in ion chromatography. *Analytical Chimica Acta* 540 (2005):45–53.
17. W. W. Buchberger and P. R. Haddad, Advances in detection techniques for ion chromatography. *Journal of Chromatography A* 789 (1997):67–83.
18. W. W. Buchberger, Detection techniques in ion chromatography of inorganic ions. *Trends in Analytical Chemistry* 20 (2001):296–303.
19. A. Marchetto, R. Mosello, G. A. Tartari, H. Muntau, M. Bianchi, H. Geiss, G. Serrini, and G. S. Lanza, Precision of ion chromatographic analyses compared with that of other analytical techniques through intercomparison exercises. *Journal of Chromatography A* 706 (1995):13–19.
20. G. A. Tartari, A. Marchetto, and R. Mosello, Precision and linearity of inorganic analyses by ion chromatography. *Journal of Chromatography A* 706 (1995):21–29.
21. R. P. Singh, N. M. Abbas, and S. A. Smesko, Suppressed ion chromatography analysis of anions in environmental waters containing high salt concentration. *Journal of Chromatography A* 733 (1996):73–91.
22. P. R. Haddad, P. Doble, and M. Macka, Developments in sample preparation and separation techniques for the determination of inorganic ions by ion chromatography and capillary electrophoresis (Review). *Journal of Chromatography A* 856 (1999):145–177.
23. L. M. Thienpont, J. E. Van Nuwenborg, and D. Stöckl, Ion chromatography as reference method for serum cations. *Journal of Chromatography A* 789 (1997):557–568.
24. R. Slingby, and R. Kiser, Sample treatment techniques and methodologies for ion chromatography. *Trends in Analytical Chemistry* 20 (2001):288–295.
25. P. N. Nesterenko, Simultaneous separation and detection of anions and cations in ion chromatography. *Trends in Analytical Chemistry* 20 (2001):311–319.
26. R. Saari-Nordhaus, L. Nair, and J. M. Anderson, Dual-column techniques for the simultaneous analysis of anions and cations. *Journal of Chromatography A* 602 (1992):127–133.
27. C. Sarzanini and M. C. Bruzzoniti, Metal species determination by ion chromatography. *Trends in Analytical Chemistry* 20 (2001):304–310.
28. Y. Kitamaki, J. Y. Jin, and T. Takeuchi, Simultaneous determination of inorganic nitrogen species by microcolumn ion chromatography. *Journal of Chromatography A* 1003 (2003):197–202.

29. V. Ruiz-Calero and M. T. Galceran, Ion chromatographic separations of phosphorus species. A review. *Talanta* 66 (2005):376–410.
30. T. M. Florence and G. E. Batley, Speciation trace elements in natural water. *Analytical Letters* 9 (1976):329–338.
31. A. Kot and J. Namiesnik, The role of speciation in analytical chemistry. *Trends in Analytical Chemistry* 19 (2000):69–79.
32. R. J. C. Brown and M. T. J. Milton, Analytical techniques for trace element analysis: An overview. *Trends in Analytical Chemistry*, 24 (2005):226–274.
33. S. D. Richardson, Water analysis: Emerging contaminants and current issues (Review). *Analytical Chemistry* 75 (2003):2831–2857.
34. A. K. Das, M. Guardia, and M. L. Cervera, Literature survey of on-line elemental speciation in aqueous solutions (Review). *Talanta*, 55, (2001): 1–28.
35. P. R. Haddad, Comparison of ion chromatography and capillary electrophoresis for the determination of inorganic anions. *Journal of Chromatography A* 770 (1997):281–290.
36. V. Pacakova, P. Coufal, K. Stulik, and B. Gas, The importance of capillary electrophoresis, capillary electrochromatography, and ion chromatography in separations of inorganic ions. *Electrophoresis* 24 (2003):1883–1891.
37. J. Weiss, *Handbook of Ion Chromatography* (Weinheim: Wiley-VCH, 2004).
38. P. Jackson, Ion chromatography in environmental analysis, in *Encyclopedia of Analytical Chemistry,* ed. R. A. Meyers (Chichester: Wiley & Sons, 2000).
39. U.S. EPA Method 300.0, *The determination of inorganic anions in water by ion chromatography*, U.S. EPA, Cincinnati, OH, 1993.
40. U.S. EPA Method 300.1, *The determination of inorganic anions in water by ion chromatography*, U.S. EPA, Cincinnati, OH, 1997.
41. P. E. Jackson, Determination of inorganic ions in drinking water by ion chromatography, *Trends in Analytical Chemistry* 20 (2001):320–329.
42. ISO 10304–1:1992, *Water quality—Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions using liquid chromatography of ions-Part 1: Method for water with low contamination.*
43. ISO 10304-2:1995, *Water quality—Determination of dissolved anions by liquid chromatography of ions-Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste waters.*
44. 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.*
45. ISO 10304-4:1997, *Water quality—Determination of dissolved anions by liquid chromatography of ions-Part 4: Determination of chlorate, chloride and chlorite in water with low contamination.*
46. ISO 15061:2002, *Water quality—Determination of dissolved bromate-Method by liquid chromatography of ions.*
47. 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.*
48. U.S. EPA Method 314.1, *Determination of perchlorate in drinking water using inline column concentration/matrix elimination ion chromatography with suppressed conductivity detection.*
49. U.S. EPA Method 317.0, *Determination of inorganic oxyhalide disinfection by-products in drinking water using ion chromatography with the addition of a postcolumn reagent for trace bromate analysis.*
50. U.S. EPA Method, 321.8, *Determination of bromate ions in waters using ion chromatography with inductively coupled plasma mass spectrometry.*
51. U.S. EPA Method 326.0, *Determination of inorganic oxyhalide disinfection by-products in drinking water using ion chromatography incorporating the addition of a suppressor acidified postcolumn reagent for trace bromate analysis.*
52. U.S. EPA Method 332.0, *Determination of perchlorate in drinking water by ion chromatography with suppressed conductivity and electrospray ionization mass spectrometry.*
53. ASTM D 4327-03, *Standard test method for anions in water by chemically suppressed ion chromatography.*
54. ASTM D 5085-02, *Standard test method for determination of chloride, nitrate, and sulfate in atmospheric wet deposition by chemically suppressed ion chromatography.*
55. ASTM D 5257-03, *Standard test method for dissolved hexavalent chromium in water by ion chromatography.*
56. ASTM D 5827-95, *Standard test method for analysis of engine coolant for chloride and other anions by ion chromatography.*
57. ASTM D 5996-05, *Standard test method for measuring anionic contaminants in high-purity water by on-line ion chromatography.*
58. ASTM D 6581-00, *Standard test method for bromate, bromide, chlorate, and chlorite in drinking water by chemically suppressed ion chromatography.*
59. ASTM D 6919-03, *Standard test method for determination of dissolved alkali and alkaline earth cations and ammonium in water and wastewater by ion chromatography.*
60. AOAC Method 993.30, *The determination of inorganic anions in water using ion chromatography.*
61. P. Hecq, A. Hulsmann, F. S. Hauchman, J. L. McLain, and F. Schmitz, Drinking water regulations, in *Analytical Methods for Drinking Water. Advances in Sampling and Analysis,* ed. P. Quevauviller and K. C. Thompson (Wiley & Sons, Chichester, England, 2006), ch. 4, 16–35.
62. F. Koch, Ion chromatography and the certification of standard reference materials. *Journal of Chromatography Science* 27 (1989):418–421.
63. H. Lee, J. S. Kim, B. H. Min, S. T. Kim, and J. H. Kim, Determination of anions in certified reference material by ion chromatography. *Journal of Chromatography A* 813 (1998):85–90.
64. Personal information from Franz Schmitz, Convenor of ISO/TC 147/SC 2, WG 33, November 2005.
65. R. Schwabe, T. Darimont, T. Möhlmann, E. Pabel, and M. Sonneborn, Determination of inorganic compounds and organic acids in different types of water by ion chromatography. *International Journal of Environmental Analytical Chemistry* 14, (1983):169–179.
66. R. D. Rockln, M. A. Rey, J. R. Stillian, and D. L. Campbell, Ion chromatography of monovalent and divalent cations. *Journal of Chromatography Science* 27 (1989): 474–479.
67. S. Reifenstuhl and G. Bonn, Determination of mono-, bi- and trivalent cations using non-suppressed ion chromatography. *Journal of Chromatography A* 482 (1989):289–296.
68. K. Bächmann, K. H. Blaskovitz, H. Bukatsch, S. Pohl, and U. Sprenger, New development in ion chromatographic methods for atmospheric analysis. *Journal of Chromatography A* 482 (1989):307–316.

69. P. Pastore, I. Lavagnini, A. Boaretto, and F. Magno, Ion chromatographic determination of nitrite in the presence of a large amount of chloride. *Journal of Chromatography A* 475 (1989):331–341.

70. D. P. Hautmann and M. Bolyyard, Analysis of oxyhalide disinfection by-products and other anions of interest in drinking water by ion chromatography. *Journal of Chromatography A* 602 (1992):65–74.

71. W. Shotyk, Ion chromatography of organic-rich natural waters from peatlands, Cl^-, $NO_2{}^-$, Br^-, $NO_3{}^-$, $HPO_4{}^{2-}$, $SO_4{}^{2-}$ and oxalate. *Journal of Chromatography A* 640 (1993):309–316.

72. W. Shotyk, Ion chromatography of organic-rich natural waters from peatlands, II Na^+, $NH_4{}^+$, K^+, Mg^{2+} and Ca^{2+}. *Journal of Chromatography A* 640 (1993):317–322.

73. E. Dabek-Zlotorzynska and J. Dlouhy, Automatic simultaneous determination of anions and cations in atmospheris aerosols by ion chromatography. *Journal of Chromatography A* 640 (1993):217–226.

74. H. Schumann and M. Ernst, Monitoring of ionic concentrations in airborne particles and rain water in an urban area of central Germany. *Journal of Chromatography A* 640 (1993):241–249.

75. R. J. Joyce and H. S. Dhillon, Trace level determination of bromate in ozonated drinking water using ion chromatography. *Journal of Chromatography A* 671 (1994):165–171.

76. K. Oikawa, K. Murano, Y. Enomoto, K. Wada, and T. Inomata, Automatic monitoring system for acid rain and snow based on ion chromatography. *Journal of Chromatography A* 671 (1994):211–215.

77. N. Gros and B. Gorenc, Ion chromatographic determination of alkali and alkaline earth metals in mineral waters. *Chromatographia* 39 (1994):448–452.

78. N. Gros and B. Gorenc, Expert system for the ion chromatographic determination of alkali and alkaline earth metals in mineral waters. *Journal of Chromatography A* 697 (1995):31–43.

79. J. Weiss, S. Reinhard, Ch. Pohl, Ch. Saini, and L. Narayaran, Stationary phase for the determination of fluoride and other inorganic anions. *Journal of Chromatography A* 706 (1995):81–92.

80. M. Pantsar-Kallio, K. Pentti, and K. G. Manninen, Determination of sodium, potassium, calcium and magnesium cations by capillary electrophoresis compared with ion chromatography. *Analytica Chimica Acta* 314 (1995):67–75.

81. S. Carrozzino and F. Righini, Ion chromatographic determination of nutrients in sea water. *Journal of Chromatography A* 706 (1995):277–280.

82. M. Sikovec, M. Novic, V. Hudnik, and M. Franko, On-line thermal lens spectrometric detection of Cr(III) and Cr(VI) after separation by ion chromatography. *Journal of Chromatography A* 706 (1995):121–126.

83. Y. Inoue, T. Sakai, and H. Kumagai, Simultaneous determination of chromium(III) and chromium(VI) by ion chromatography with inductively coupled plasma mass spectrometry. *Journal of Chromatography A* 706 (1995):127–136.

84. M. A. G. T. den Hoop, R. F. M. J. Cleven, J. J. von Staden, and J. Neele, Analysis of fluoride in rain water. Comparison of capillary electrophoresis with ion chromatography and ion-selective electrode potentiometry. *Journal of Chromatography A* 739 (1996):241–248

85. J. T. Creed, M. L. Magnuon, J. D. Pfaff, and C. Brockhoff, Determination of bromate in drinking waters by ion chromatography with inductively coupled plasma mass spectrometric detection. *Journal of Chromatography A* 753 (1996):261–267

86. E. Kaiser, J. Riviello, M. Rey, J. Statler, and S. Heberling, Determination of trace level ions by high-volume direct-injection ion chromatography. *Journal of Chromatography A* 739 (1996):71–79.

87. C. R. Warner and D. H. Daniels, Measurement of bromate in bottled water by high-performance liquid chromatography with post-column flow reactor detection. *Food Additives and Contaminations* 13 (1996):633–638.

88. L. Nair, R. Saari-Nordhaus, and R. M. Montgomery, Applications of a new methacrylane-based aion stationary phase for the separation of inorganic anions. *Journal of Chromatography A* 789 (1997):127–134.

89. Y. Inoue, T. Sakai, H. Kumagai, and Y. Hanaoka, High selective determination of bromate in ozonized water by using ion chromatography with postcolumn derivatization equipped with reagent preparation device. *Analytical Chimica Acta* 346 (1997):299–305.

90. M. Pantsar-Kallio, K. Pentti, and M. G. Manninen, Simultaneous determination of toxic arsenic and chromium species in water samples by ion chromatography-inductively coupled plasma mass spectrometry. *Journal of Chromatography A* 779 (1997):139–146.

91. J.-H. Kim and J.-Hae Lee, Simultaneous determination of six cations in mineral water by single-column ion chromatography. *Journal of Chromatography A* 782 (1997):140–146.

92. J. Creed, T. Magnuson, L. Matthew, L. Brockhoff, and A. Carol, Determination of bromate in the presence of brominated haloacetic acids by ion chromatography with inductively coupled plasma mass spectrometric detection. *Environmental Science and Technology* 31 (1997):2059–2063.

93. M. Toofan, J. R. Stillian, Ch. A. Pohl, and P. E. Jackson, Preconcentration determination of inorganic anions and organic acids in power plant waters separation optimization through control of column capacity and selectivity. *Journal of Chromatography A* 761 (1997):163–168.

94. N. Cardellicchio, P. Ragone, S. Cavalli, and J. Riviello, Use of ion chromatography for the determination of transition metals in the control of sewage-treatment-plant and related waters. *Journal of Chromatography A* 770 (1997):185–193.

95. M. Biesaga, M. Kwiatkowska, and M. Trojanowicz, Separation of chlorine-containing anions by ion chromatography and capillary electrophoresis. *Journal of Chromatography A* 777 (1997):375–381.

96. J. Diemer and K. G. Heumann, Bromide-bromate speciation speciation by NTI-IDMS and ICP-MS coupled with ion exchange chromatography. *Fresenius Journal Analytical Chemistry* 357 (1997):72–74.

97. X. Liu, S. X. Jiang, L. R. Chen, Y. Q. Xu, and P. Ma, Determination of inorganic ions in oil field waters by single-column ion chromatography. *Journal of Chromatography A* 789 (1997):569–573.

98. L. Charles and D. Pepin**,** Analysis of oxyhalides in water by ion chromatography-ionspray mass spectrometry. *Journal of Chromatography A* 804 (1998):105–111.

99. H. Weinberg, H. Yamada, and R. J. Joyce, New, sensitive and selective method for determining sub-μg/l levels of bromate in

drinking water. *Journal of Chromatography A* 804 (1998):137–142.

100. J. A. Morales, L. S. de Graterol, H. Velasquez, M. G. de Nava, and B. S. de Borrego, Determination by ion chromatography of selected organic and inorganic acids in rainwater at Maracaibo, Venezuela. *Journal of Chromatography A* 804 (1998):289–294.
101. M. Pantsar-Kallio and P. K. G. Manninen, Speciation of halogenides and oxyhalogens by ion chromatography-inductively coupled plasma mass spectrometry. *Analityca Chimica Acta* 360 (1998):161–166.
102. M. Nowak and A. Seubert, Ultra-trace determination of bromate in drinking water by means of microbore column ion chromatography and on-line coupling with inductively coupled plasma mass spectrometry. *Analityca Chimica Acta* 359 (1998):193–204.
103. L. K. Jackson, R. J. Joyce, M. Laikhtman, and P. E. Jackson, Determination of trace level bromate in drinking water by direct injection ion chromatography. *Journal of Chromatography A* 829 (1998):187–192.
104. H. S. Weinberg and H. Yamada, Post-column chromatography derivatization for the determination of oxyhalides at sub-ppb levels in drinking water. *Analytical Chemistry* 70 (1998):1–6.
105. C. B. Boring, P. K. Dasgupta, and A. Sjogren, Compact, field-portable capillary ion chromatograph. *Journal of Chromatography A* 804 (1998):45–54.
106. P. E. Jackson, M. Laikhtmann, and J. S., Rohrer, Determination of trace level perchlorate in drinking water and ground water by ion chromatography. *Journal of Chromatography A* 850 (1999):131–136.
107. H. P. Wagner, B. V. Pepich, D. P. Hautman, and D. J. Munch, Analysis of 500-ng/l levels of bromate in drinking water by direct-injection suppressed ion chromatography coupled with a single pneumatically delivered post-column reagent. *Journal of Chromatography A* 850 (1999):119–129.
108. Y. Miura and H. Hamada, Ion chromatography of nitrite at the ppb level with photometric measurement of iodide formed by post-column reaction of nitrite with iodide. *Journal of Chromatography A* 850 (1999):153–160.
109. W. Buchenberger and W. Ahrer, Combination of suppressed and non-suppressed ion chromatography with atmospheric pressure ionization mass spectrometry for the dteremination of anions. *Journal of Chromatography A* 850 (1999):99–106.
110. S. Valsecchi, A. Isernia, S. Polesello, and S. Cavalli, Ion chromatography determination of trace level bromate by large volume injection with conductivity and spectrometric detection after post column derivatisation. *Journal of Chromatography A* 864 (1999):263–270.
111. W. Ahrer and W. Buchenberger, Analysis of low-molecular-mass inorganic and organic anions by ion-chromatography—atmospheric pressure ionisation mass spectrometry. *Journal of Chromatography A* 854 (1999):257–287.
112. E. Salhi and U. Gunten, Simultaneous determination of bromide, bromate and nitrite in low μg/l levels by ion chromatography without sample treatment. *Water Research* 33 (1999):3239–3244.
113. B. Divjak, M. Novic, and W. Goessler, Determination of bromide, bromate and other anions with ion chromatography and an inductively coupled plasma mass spectrometer as element-specific detector. *Journal of Chromatography A* 862 (1999):39–47.
114. H. P. Wagner, B. V. Pepich, D. P. Hautman, and D. J. Munch, Performance evaluation of a method for the determination of bromate in drinking water by ion chromatography (EPA Method 317.0) and validation of EPA Method 324.0. *Journal of Chromatography A* 884 (2000):201–210.
115. H. P. Wagner, B. V. Pepich, D. P. Hautman, and D. J. Munch, Elimination the chlorite interference in US Environmental Protection Agency Method 317.0 permits analysis of trace bromate levels in drinking water matrices. *Journal of Chromatography A* 884 (2000):309–319.
116. A. Seubert, G. Schminke, M. Nowak, W. Ahrer, and W. Buchenberger, Comparison of on-line coupling of ion-chromatography with atmosphere pressure ionisation mass spectrometry and with inductively coupled plasma mass spectrometry as tools for the ultra-trace analysis of bromate in surface water samples. *Journal of Chromatography A* 884 (2000):191–199.
117. G. Schminke and A. Seubert, Simultaneous determination of inorganic disinfection by-products and the seven standard anions by ion chromatography. *Journal of Chromatography A*, 890 (2000): 295–301.
118. H. Lu, S. Mou, R. Deng, and J. M. Riviello, Studies of trace anions analysis by ion chromatography. *Microchemical Journal* 64 (2000):1–7.
119. K. Tanaka, K. Ohta, P. R. Haddad, J. S. Fritz, A. Miyanaga, W. Hu, and K. Hasebe, Simultaneous ion-exclusion/cation-exchange chromatography of anions and cations in acid rain waters on a weakly acidic cation-exchange resin by elution with sulfosalicylic acid. *Journal of Chromatography A* 884 (2000):167–174.
120. E. Santoyo, S. Santoyo-Gutiérrez, and S. P. Verma, Trace analysis of heavy metals in groundwater samples by ion chromatography with post-column reaction and ultraviolet-visible detection. *Journal of Chromatography A* 884 (2000):229–241.
121. P. E. Jackson, C. Weigert, Ch. A. Pohl, and C. Saini, Determination of inorganic anions in environmental waters with a hydroxide-selective column. *Journal of Chromatography A* 884 (2000):175–184.
122. V. F. Saverwyns, G. Wannemacker, L. Moens, and R. Dams, Comparison of the application of higher mass resolution and cool plasma conditions to avoid spectral interferences in Cr(III)/Cr(VI) speciation by means of high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Analytical Chemical Acta* 419 (2000):55–64.
123. A. Caliamanis, J. McCornick, and P. D. Carpenter, Enhanced conductometric detection of cyanide in suppressed ion chromatography. *Journal of Chromatography A* 884 (2000):75–80.
124. J. A. Morales, L. S. de Graterol, and J. Mesa, Determination of chloride, sulfate and nitrate in groundwater samples by ion chromatography. *Journal of Chromatography A* 884 (2000):185–190.
125. K. Ohta, Indirect ultraviolet spectrophotometric detection in the ion chromatography of common mono- and divalent cations on an aluminium adsorbing silica gel column with tyramine-containing crown ethers as eluent. *Journal of Chromatography A* 884 (2000):113–122.
126. C. A. Delcomyn, H. S. Weinberg, and P. C. Singer, Use of ion chromatography with post-column reaction for the measurement of tribromide to evaluate bromate levels in drinking water. *Journal of Chromatography A* 920 (2001):213–219.

127. S. Echigo, R. A. Minear, H. Yamada, and P. E. Jackson, Comparison of three post-column reaction methods for the analysis of bromate and nitrite in drinking water. *Journal of Chromatography A* 920 (2001):205–211.
128. S. C. Stefanovic, T. Bolanca, and L. Curkovic, Simultaneous determination of six inorganic anions in drinking water by non-suppressed ion chromatography. *Journal of Chromatography A* 918 (2001):325–334
129. P. E. Jackson, D. H. Thomas, B. Donovan, Ch. A. Pohl, and R. E. Kiser, New block-grafted anion exchanger for environmental water analysis by ion chromatography. *Journal of Chromatography A* 920 (2001):51–60.
130. Z. Polkowska, T. Górecki, and J. Namieśnik, Quality of roof runoff waters from an urban region (Gdansk, Poland). *Chemosphere* 49 (2002):1275–1283.
131. D. Connolly and B. Paull, Fast ion chromatography of common inorganic anions on a short ODS column permanently coated with didodecyldimethylammonium bromide. *Journal of Chromatography A* 953 (2002):299–303.
132. D. H. Thomas, M. Rey, and P. E. Jackson, Determination of inorganic cations and ammonium in environmental waters by ion chromatography with a high-capacity cation-exchange column. *Journal of Chromatography A* 956 (2002):181–186.
133. R. Roehl, R. Slingsby, N. Avdalovic, and P. E. Jackson, Applications of ion chromatography with electrospray mass spectrometric detection to the determination of environmental contaminants in water. *Journal of Chromatography A* 956 (2002):245–254.
134. Z. Q. Lu, Y. Liu, V. Barreto, Ch. Pohl, N. Avdalovic, R. Joyce, and B. Newton, Determination of anions at trace levels in power plant water samples by ion chromatography with electrolytic eluent generation and suppression. *Journal of Chromatography A* 956 (2002):129–138.
135. S. V. Karmarkar, Anion-exchange chromatography of metal cyanide complexes with gradient separation and direct UV detection. *Journal of Chromatography A* 956 (2002):229–235.
136. Y. Miura, M. Hatakeyama, T. Hosino, and P. R. Haddad, Rapid ion chromatography of L-ascorbic acid, nitrite, sulfite, oxalate, iodide and thiosulfate by isocratic elution utilizing a postcolumn reaction with cerium(IV) and fluorescence detection. *Journal of Chromatography A* 956 (2002):77–84.
137. Y. Liu and S. Mou, Simultaneous determination of trace level bromate and chlorinated haloacetic acids in bottled drinking water by ion chromatography. *Microchemical Journal* 75 (2003):79–86.
138. P. Bruno, M. Caselli, G. de Gennaro, B. de Tommaso, G. Lasetta, and S. Mastrolitti, Determination of nutrients in the presence of high chloride concentrations by column-switching ion chromatography. *Journal of Chromatography A* 1003 (2003):133–141.
139. Y. Kitamaki, J. Y. Jin, and T. Takeuchi, Simultaneous determination of inorganic nitrogen species by microcolumn ion chromatography. *Journal of Chromatography A* 1003 (2003):197–202.
140. K. J. B. Abd Karim, J. Y. Jin, and T. Takeuchi T., Simultaneous separation of inorganic anions and cations by using anion-exchange and cation-exchange columns connected in tandem in ion chromatography. *Journal of Chromatography A* 995 (2003):153–160.
141. W. E. Krawczyk, B. Lefauconnier, and L. E. Pettersson, Chemical denutiation rates in the Bayelva catchment, Svalbard, in the Fall of 2000. *Physics and Chemistry of the Earth* 28 (2003):1257–1271.
142. P. C. Mouli, S. V. Mohan, and S. J. Reddy, A study on major inorganic ion composition of atmospheric aerosols at Tirupati. *Journal of Hazardous Materials* 96 (2003):217–228.
143. A. Astel, J. Mazerski, Z. Polkowska, and J. Namieśnik, Application of PCA and time series analysis in studies of precipitation in Tricity (Poland). *Advances in Environmental Research*, 8 (2004):337–349.
144. N. Kapinus, L. A. Revelsky, V. O. Ulogov, and Y. A. Lyalikov, Simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate in aqueous solutions at 10^{-9} to 10^{-8} level by ion chromatography. *Journal of Chromatography A* 800 (2004):321–323.
145. Y. J. Liu and S. Mou, Determination of bromate and chlorinated haloacetic acids in bottled drinking water with chromatographic methods. *Chemosphere* 55 (2004):1253–1258.
146. R. Garcia-Fernandez, J. I. Garcia-Alonso, and A. Sanz-Medel, Simultaneous determination of inorganic anions, calcium and magnesium by suppressed ion chromatography. *Journal of Chromatography A* 1033 (2004):127–133.
147. J. R. E. Thabano, D. Abong'o, and G. M. Sawula, Determination of nitrate by suppressed ion chromatography after copperised-cadmium column reduction. *Journal of Chromatography A* 1045 (2004):153–159.
148. W. E. Krawczyk and U. Skret, Organic compounds in rainfall at Hornsund SW Spitsbergen: Qualitative results. *Polish Polar Research* 26 (2005):65–76.
149. R. Michalski, Trace level determination of Cr(III)/Cr(VI) in water samples using ion chromatography with UV detection. *Journal of Liquid Chromatography and Related Technologies* 28 (2005):2849–2862.
150. R. Michalski, A comparison of direct and indirect ion chromatography methods for the determination of bromide/bromate ions in drinking water. *Chemical Analysis* 50 (2005):583–591.
151. R. Figi, C. Schreiner, and D. Bleiner, Systematic investigations of plastic vials concerning their suitability for ultratrace anion analysis in high-purity industrial applications. *Microchimica Acta* 150 (2005):199–209.