Review

Advances in the determination of inorganic anions by ion chromatography

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Abstract

The time period covered for this review includes articles published from 1997 to 1999, with the addition of a few classic references. The purpose of the review is to include the most relevant works from each topic area of the determination of inorganic anions by ion chromatography, including new sample pretreatments, new separation methods, new detection systems and the latest applications in the field of environmental, water, foods, etc. samples. Experimental conditions such as stationary phase, eluent, detection mode, as well as matrix are summarized in a table. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

When ion chromatography (IC) was introduced in 1975, it was basically a chromatographic method for the determination of inorganic ions, which consisted of a low ion-exchange capacity resin as the stationary phase and conductimeter as detector and a suppressor column to increase separation speed and detection sensitivity [1]. In 1979, Gjerde et al. [2] developed a non-suppressed IC technique by using a low conductivity eluent. This concept of IC was later successively widened so that it could also include organic ions, other separation methods (e.g., ion interaction and ion exclusion), simultaneous separation of anions and cations, and a great variety of detectors.

Even though IC has become a routine analytical method for the determination of inorganic ions, especially anions present in various matrices, many papers have been published during the last 2 years dealing with new modalities in sample pretreatment, separation, detection, etc., for improving the analysis of the samples.

For more immediate information and comparison of some of the cited methods, the experimental conditions are summarized in Table 1.

2. Importance of the determination of inorganic anions

Bromate is a disinfection by-product of the ozonation of drinking water derived from source water containing bromide. The bromide in the source water is oxidized to bromate by the ozone. It is a potential carcinogen to rats and mice at mg l^{-1} levels. New toxicological studies have led the International Agency for Research on Cancer (IARC) to classify bromate as a group 2B carcinogen to humans with renal tumour risks at concentrations >0.05 μg l^{-1}. At the moment the US Environmental Protection Agency (EPA) recommends a concentration limit of 10 μg l^{-1} for bromate in drinking water, while the World Health Organization (WHO) accepts a limit of 25 μg l^{-1}. The Commission of European Union proposes a concentration limit of 10 μg l^{-1}. For this reason trace analysis of bromate in water has received considerable attention in recent years.

Chlorine and bromine are considered to be conservative elements in ground-water systems and, therefore, their concentration in pore-waters can be a useful tool in constraining the origins of groundwater salinity. Whole rock determinations for chlorine and bromine are therefore important in helping to distinguish between, e.g., saline intrusions and palaeosalinity.

Iodine species in seawater exist as iodide and iodate. Iodide, which is thermodynamically unstable in oxygenated water, is usually a minor species in seawater compared to iodate. Iodine is an essential micronutrient for many organisms. Iodide in seawater is produced by biologically mediated reduction of iodate and is also produced under reducing conditions. Thus, the distribution of iodide and iodate gives clues to understanding the marine environment. In addition, the need to determine iodide and iodate in environmental samples has arisen because iodine may play a role in taste and odor problems in drinking water. Also, the importance from the clinical and epidemiological point of view of iodide determination in biological matrices, such as urine and serum, has led to a great interest in searching for rapid, simple and specific methods for the determination of iodide in those matrices.

The nitrogen, phosphorus and sulfur cycles are of particular significance to a number of biological and non-biological processes in the environment. Natural and anthropogenic effects can cause localized interrelated changes to the cycles. In order to assess the impact and extent of the changes, it is essential to develop analytical methods that allow the simultaneous determination of two or all three constituents in a wide variety of environmental samples. Phosphorus and nitrogen are released into environmental waters from many different sources, e.g. animal and chemical fertilizer run-off and sewage. Excessive amounts of these nutrients activate eutrophication, the process of rapid growth of phytoplankton, algae and plants. Subsequent decay of these materials causes dissolved oxygen to be removed from a water body and with it the ability to sustain life. A large number of studies have illustrated the dynamic nature of the nitrogen speciation and phosphorus fractionation balances in natural waters, and the significance of the organic nitrogen and particulate phosphorus fraction in contributing to the total

Table 1
Experimental conditions of the inorganic anions determination by ion chromatography

Species	Matrix	Column	Eluent	Detector	Ref.
Total organic carbon (TOC)	Deionized, mineral, tap and river water	Hamilton PRP-X100	KOH, KHP (pH 9.5)	Indirect UV at 272	[42]
o-Phosphate	Water samples	Dionex IonPak AS12A	NaOH, sodium tetraborate	Conductivity	[35]
NO_2^-, PO_3^{4-}	Sea water	Dionex AS4A	Na_2CO_3, $NaHCO_3$	Conductivity	[40]
NO_2^-, NO_3^-	Human plasma Rat blood	Exsil SAX Dionex IonPac AS12A	KH_2PO_4, H_3PO_4, acetonitrile Na_2Co_3, $NaHCO_3$	UV at 214 nm Coulometry	[38]
NO_2^-, NO_3^-	Meat products	Dionex IonPac AS11	NaOH	UV at 225 nm	[191]
PO_3^{4-}	Cola beverages	Waters IC-Pak A HR	Sodium gluconate, boric acid, sodium tetraborate in glycerine–water	Conductivity	[184]
BrO_3^-	Drinking waters	Microbore laboratory-packed packed PS–DVB functionalized with chloromethyloctylether and $AlCl_3$	NH_4NO_3 (pH 6.0)	ICP-MS	[55]
BrO_3^-	Ozonized water	Excelpak ACS-A1G/ICS-A13×2	Na_2CO_3, $NaHCO_3$	Conductivity	[108]
BrO_3^-	Drinking water	Dionex IonPac AS9-HC	Na_2CO_3, $NaHCO_3$ Na_2CO_3	Conductivity	[56]
BrO_3^-	Drinking water	Dionex IonPac AS9-HC	Na_2CO_3	Conductivity	[33]
BrO_3^-	Drinking water	Dionex IonPac AS4A-SC	Na_2CO_3, $NaHCO_3$	Spectrophotometric at 530 nm	[111]
BrO_3^-	Drinking water	Dionex IonPac AS12	NaOH	ICP-MS	[121]
BrO_3^-, IO_3^-	Ozonized water	Excelpak ICS-A23 Excelpak ICS-A13	$(NH_4)_2CO_3$	ICP-MS	[124]
BrO_3^-	Water	Dionex IonPac AG9-SC	Water–methanol, $(NH_4)_2SO_4$	MS–MS	[37]
I^-, IO_3^-	Mineral and drinking waters	Dionex IonPac AS11	NaBr, NaOH (for I^-) $B(OH)_3$, NaOH (for IO_3)	UV–Vis at 288 nm	[110]
I^-	Ground water and soil	Dionex IonPac AS11	NaOH, in methanol–water	Conductivity	[155]
I^-	Soil and water	Hamilton PRP-X100	NaCl, methanol	UV at 230 nm	[159]
I^-	Sea water	TSK-gel SAX (Tosoh)	$NaClO_4$ sodium phosphate buffer (pH 6.1)	UV at 226 nm	[32]
I^-	Urine and serum	Water Nova-Pak C_{18} reversed-phase coated with N-cetylpyridinium chloride	KNO_3	Laboratory-made iodide ion-selective electrode	[68]
$Cl_2(Cl^-)$, $Br_2(Br^-)$	Sedimentary and igneous rocks	Dionex IonPac AS12A	Na_2CO_3, $NaHCO_3$	UV at 210 nm	[52]
Total nitrogen (NO_3^-), phosphorus (PO_4^{3-}) and sulfur (SO_4^{2-})	Reference materials Oyster tissue Buffalo River sediments	Dionex IonPac AS4A	Na_2CO_3, $NaHCO_3$	Conductivity	[45]

Table 1 (*continued*)

Species	Matrix	Column	Eluent	Detector	Ref.
Total nitrogen (NO_3), and phosphorus (PO_4^{3-})	Wastewaters	Dionex IonPac AS4A	Na_2CO_3, $NaHCO_3$	Conductivity	[46]
Cyanate	Gold processing samples	Waters HC IC-Pak A	Anthranilic acid (pH 6.7)	Indirect UV–Vis at 355 nm	[39]
CN^-, SCN^-	Blood	TSK-gel IC-Anion-SW (Tosoh)	Phosphate buffer (pH 6.1)	UV at 210 nm Fluorimetric λ_{ex}=418 nm, λ_{em}=460 nm	[114]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SCN^-	Hot spring waters	TSK-gel IC-Anion-PW (Tosoh)	Na_2CO_3, acetonitrile	Photometric at 350 nm	[109]
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SCN^-	Samples with biological matrices	Dionex IonPac AS12A	NaOH	ICP- MS	[123]
SO_4^{2-}, $S_2O_3^{2-}$, SCN^- $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_3O_6^{2-}$ $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	Hot-spring waters	Kaseisorb LC ODS super (Tokyo Kasei)	Phthalate, TPAOH in acetonitrile–water	Conductivity	[99]
Selenite, selenate, SeCys, SeMet	Synthetic samples	Hamilton PRP X-100	Phosphate buffer (pH 7.0)	Hydride generation-quartz cell atomic absorption spectrometric	[120]
Selenite, selenate, Se–cystine, Se–methionine	Synthetic sea water	Dionex IonPac AS4A Dionex IonPac AS10 Dionex IonPac AS11	Na_2CO_3 or NaOH	ICP-AES	[117]
Selenite, selenate, Se–cystine, Se–methionine	Selenium-rich yeast	Hamilton PRP-1 reversed phase	Water–acetonitrile	ETAAS	[118]
Trimethylselenonium iodide, Se–methionine, selenious acid, selenic acid	Synthetic samples	ESA Anion III	Ammonium citrate	ICP-MS or FAAS	[126]
Arsenite, arsenate, phenyl arsonate, dimethyl arsinate, arsenobetaine, arsenocholine	Highly ferrous/ferric contaminated leachates of lignite spoil	Dionex IonPac AS4A	Na_2CO_3, NaOH, methanol	ICP-MS	[127]
F^-, NO_3^-, Cl^-, Br^-, NO_3^-, acetic, lactic, succinic, malic, citric, tartaric, Na^+, NH_4^+, K^+	Beverages	Mixed bed column packed with anion-exchange resin ICS-A23 and cation-exchange resin CH1	Oxalic acid	Conductivity	[87]
Cl^-, Br^-, NO_3^-	Synthetic samples	Two ODS-packed columns, the first coated with CHAPS micelles and the second with Zwittergent-3–14 micelles	Water	Conductivity Photodiode array UV	[78]
Cl^-, Br^-, NO_3^-, SO_4^-	Water	TSK-gel IC-Anion-PW (Tosoh)	KOH	Chemiluminiscence	[115]
Cl^-, NO_3^-, SO_4^-, acetate, lactate, succinate, malate, citrate, tartrate	Wines	Shimpack IC-Al (Shimadzu)	Phthalic acid (pH 4.15)	Conductivity	[186]
Cl^-, NO_3^-, SO_4^{2-}	Plant sap	Dionex IonPac AS9-SC Dionex IonPac AS11 Waters IC-PACK Anion HR	Na_2CO_3, $NaHCO_3$ NaOH Borate–gluconate (pH 8.5) Borate–tartrate (pH 4.0)	Conductivity	[201]
Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, lactate, acetate, propionate, butyrate, succinate, citrate	Milk	Dionex IonPac AS11	NaOH	Conductivity	[179]

Table 1 (*continued*)

Species	Matrix	Column	Eluent	Detector	Ref.
Cl^-, NO_3^-, SO_4^-	Conc. reagents	Hamilton PRP-X100	Phthalate (pH 5.5 or 4.7)	UV–Vis at 298 nm	[36]
Cl^-, NO_3^-, CO_3^{2-} SO_4^{2-}, PO_4^{3-}, lactate, acetate, propionate, butyrate, succinate, citrate	Milk	Dionex IonPacAS11	NaOH	Conductivity	[179]
Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, quinate, formate, malate, malonate, oxalate, citrate, isocitrate, aconitate	Beverages and citric acids fermenting-medium	Dionex IonPacAS11	NaOH, methanol	Conductivity	[182]
Cl^-, NO_3^-, SO_4^{2-}	Oil field waters	Laboratory packed	Sodium benzoate, sodium citrate	Conductivity	[57]
Cl^-, SO_4^{2-}, PO_4^{3-}	Edible vegetable oils	Dionex IonPac AS9	Na_2CO_3, $NaHCO_3$	Conductivity Photometric at 520 nm	[48]
Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, SCN^-,	Landfill leachates	Dionex IonPac AS11	NaOH	Conductivity	[156]
F^-, CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-}, acetate, formate, oxalate	Power plant waters	Dionex IonPac AS10	NaOH	Conductivity	[91]
$H_2PO_4^-$, Cl^-, NO_3^-, SO_4^{2-}, acetic, ascorbic, succinic, malic, malonic citric, tartaric	Tea	Shimpack IC-A1 (Shimadzu)	Potassium hydrogenphthalate, phthalic acid	Conductivity	[181]
Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CO_3^{2-}	Environmental water	TSK guardgel QAE-SW (Tosoh)	Trimellitic acid–EDTA	Indirect UV at 270 nm	[95]
Cl^-, NO_3^-, SO_4^{2-}	Polar ice core samples	Laboratory packed with resins synthesized	Potassium hydrogenphthalate,	Conductivity	[163]
F^-, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-}, HS^-, HPO_4^{2-}, HCO_3^-	Natural water	Dionex IonPac AS4A	$NaHCO_3$	Conductivity	[172]
F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, I^-	Pharmaceutical compounds	Carbon BI-01 (Bio-Tech Research)	TBA, Na_2CO_3, acetonitrile	Conductivity	[58]
Cl^-, NO_3^-, SO_4^{2-}	Beet sugar	Dionex IonPac AS11	NaOH	Conductivity	[193]
Cl^-, NO_3^-, SO_4^{2-}	Rainwater at Maracaibo, Venezuela	Dionex IonPac AS11	NaOH	Conductivity	[164]
Cl^-, NO_2^-, Br^-, NO_3^-	Synthetic samples	TSK-gel IC-anion-PWXL (Tosoh)	Sodium tetraborate, boric acid, potassium gluconate	Conductivity UV at 210 or 230 nm	[84]
BO_3H_3, AsO_3H_3	Synthetic samples	Dionex IonPac AS11	NaOH	Conductivity	[107]
NO_3^-, Cl^-, NO_2^-, $H_2PO_4^-$, SO_4^-	Vegetables	Shimpack IC-Al (Shimadzu)	Phthalic acid (pH 4.0)	Bulk acoustic wave sensor	[134]
Cl^-, NO_3^-, SO_4^{2-}	Synthetic samples	TSKguardgel QAE-SW (Tosoh)	Pyromellitate (pH 5.4)	Conductivity	[93]
ClO_4^-	Drinking water and groundwater	Dionex IonPac AS11	NaOH	Conductivity	[174]
SeO_3^{2-}, $HAsO_4^{2-}$, SeO_4^{2-}, WO_4^{2-}, MoO_4^{2-}, GeO_3^{2-}, CrO_4^{2-}, IO_3^-, $HAsO_3^-$, BrO_3^-, NO_2^-, NO_3^-	Synthetic samples	CS5A	Na_2HPO_4 (pH 9.3)	UV at 204 nm	[211]

nutrient loading in a water body. So a rapid method for the simultaneous determination of total nitrogen (TN) and total phosphorus (TP) is needed, both for environmental studies on natural waters and routine control of sewage and wastewater.

Total organic carbon (TOC) has been used successfully as a general indicator of organic pollutant in water for both volatile and nonvolatile organic compounds. Due to the need in semiconductor, computer, and other high technology industries for trace organic analysis in deionized water, and the concern about organic pollution of drinking water and various environmental waters, a sensitive method for the determination of trace amounts of TOC in water is needed. If TOC is completely oxidized to CO_2, the carbonate anion obtained can be determined.

Nitric oxide (NO) is a vital messenger in many cellular communication and control systems. Endothelium-derived relaxation factor (EDRF) was identified nearly 10 years ago as being the free radical species nitric oxide (NO). It is involved in many physiological and pathophysiological processes, and in cancer biology. NO has been shown to modify tumour vascular tone, metastasis, angiogenesis and tumour cell proliferation. The assessment of novel therapeutic approaches, which modulate NO levels within tumours therefore, relies on the accurate determination of NO within different sample matches. Because of the short half-life of NO in aqueous media, assay of NO is performed on its metabolites, nitrite and nitrate. The content of nitrite and nitrate in the urine is considered as an index of NO production in vivo.

Both nitrite and nitrate must also be monitored regularly because of their toxicity. Nitrite can be converted to carcinogenic nitrosamines in food products and within the human digestive system. Nitrate, although more stable and less toxic than nitrite, is also a concern because it can readily be converted to nitrite by microbial reduction in food products.

The endless list of natural and man-made water pollutants also contains inorganic sulfur-containing anions, such as S^{2-}, SO_3^{-2}, SO_4^{-2}, $S_2O_3^{-2}$. These anions have been shown to have a diverse impact on plants, animals and humans. They can react with one another and undergo decomposition or air oxidation. Sulfite and thiosulfate, are formed as intermediate

products by oxidation of sulfide and finally oxidized to sulfuric acid, which causes the acidification of natural waters in rivers and lakes. This has created a need for their determination.

The analysis of cyanide in biological fluids is of interest because cyanide acts not only as an acute toxicant, which binds to and inhibits the activity of cytochrome oxidase, but also as a chronic toxicant. Cyanide is usually metabolized in vivo to thiocyanate by rhodanese, which is a mitochondrial enzyme in liver and kidney. Therefore, an accurate and reliable method for simultaneous determination of cyanide and thiocyanate has long been sought after for studies in forensic science and clinical medicine.

Compounds and forms of arsenic in aquatic, terrestrial, and biological systems have been the target of increasing attention in recent years. Being able to determine different species and compounds of arsenic is important if their transport mechanism in the environment, toxicological risks, and inter-relationships are to be specified. IC with inductively coupled plasma MS detection was developed to separate either cationic, neutral, and anionic species or soluble and suspended arsenic species in water samples of environmental interest.

In recent years, the chemistry and biology of selenium and its various species has been the subject of increasing attention, due to the importance of selenium both as an essential and toxic element. However, the identification and determination of the many chemical forms of selenium in environmental and biological systems is still a major challenge for analytical chemists, a prerequisite to investigate its pathways in the environment and its mechanism of action in living organisms. The inorganic selenium species, selenious and selenic acid (selenite and selenate) are very important in the biochemical cycle of selenium. Because of the difference in their oxidation states, these two species exhibit quite different chemical and biological properties. Organic species of selenium, such as selenoamino acids, take part in the biological selenium cycle and are incorporated into proteins. The main selenoamino acid found in plants is selenomethionine, which is used as a selenium supplement in the diet of man and animals. Trimethylselenium ion has been identified in urine and is used as a tracer of selenium levels in humans.

Since the toxicity, bioavailability and transport of selenium depend on different selenium forms and their concentrations, it is essential to selectively determine selenium species present in the studied samples.

Phosphate is a nutrient that must usually be determined in different kinds of samples, such as food, environmental samples, etc.

3. General reviews

Numerous review articles on the subject of IC have appeared during this period in the literature. Some of the reviews cover the general aspects of IC techniques, such as those that include: the theory and methodology of liquid chromatography [3]; the general aspects of IC [4]; the basic principles of IC [5]; the theory and application of the chemical equilibria in IC [6]; the questions that remain unanswered and unasked in ion analysis [7]; the recent advances in IC [8], electrostatic IC [9]; the advances in detection techniques for IC [10,11]; the decomposition method as sample preparation for simultaneous multielement analysis [12]; the advances in stationary phase development in suppressed IC [13]; the separation and determination of inorganic anions by reversed-phase high-performance liquid chromatography [14]; the design and application of bulk acoustic wave-based detector for IC [15]; the development of suppressed conductivity detection in IC [16]; the comparison of IC and capillary electrophoresis for the determination of inorganic ions [17–19]; the mechanism and application of IC for simultaneous analysis [20]; the simultaneous determination of anions and cations by IC [21]. Other more narrowly focused reviews on practical aspects of IC include the chromatographic and electrophoretic methods for inorganic phosphate analysis [22]; the applications of IC to the determination of inorganic ions in food [23]; the use of IC in food and beverage analysis [24]; the development of automatic acid rain monitoring system by IC [25]; the applications of anion chromatography in terrestrial environmental research [26]; the quantification of sulfate and thiosulfate in clinical samples by IC [27]; the characterization of toxic solutions by IC in biological liquids [28]; the analysis of adhered

substances by IC [29]; the retention models in IC and their use in computer optimization of eluent composition [30]; the application to IC of knowledge discovery in databases [31].

4. Sample pretreatment

In most cases, sample pretreatment previous to determination of inorganic anions by IC techniques involves only simple operations, such as filtration, sample dilution, pH adjustment, protein precipitation, extraction of the analyte. However, the analyses of other kinds of samples require more complex sample preparation procedures. This occurs, e.g., when the concentration of anions in samples is very low, or the concentrations of sample matrix anions are high relative to the analytes, or when matrix constituents are a source of interferences in the IC separation.

Therefore, during the last 2 years papers have been published that describe new methods to resolve and simplify this decisive analytical step in sample preparation for IC anion determination.

Ito [32] used a high-capacity anion-exchange resin with styrene–divinylbenzene for both preconcentration and separation of iodide in seawater. Iodide was trapped quantitatively without broadening on a pre-concentrator column, (TSK gel SAX resin). The major anions in seawater, chloride and sulfate ions were partially trapped and did not interfere in the determination of I^-. Sodium perchlorate 0.35 M and phosphate buffer (pH 6.1) was selected as eluent with strong eluting power. Colombini et al. [33] supposed that by using a high-capacity anion-exchange column, it should be possible to determine bromate at μg l^{-1} levels by direct injection of a very large volume without any sample preconcentration and pretreatment, but experimental results showed that matrix effect, due to inorganic ions contained in drinking water, strongly influenced the chromatographic behavior of the bromate peak. Toofan et al. [34] studied the factors affecting the ion chromatographic preconcentration behavior of inorganic anions and organic acids.

Mattusch and Wennrich [35] developed a liquid–liquid extraction procedure for the elimination of high levels of sulfate to determine ppb concentrations of phosphate in the presence of a 20 000-fold

excess of sulfate. The determination of traces of inorganic contaminants in concentrated reagent by IC requires matrix elimination from the bulk solution in order to avoid the overloading of the analytical column. Roeder and Jardy [36] proposed the precipitation of the predominant anion by means of a cation preliminary fixed on a macroporous cation exchange. Charles et al. [37] proposed an IC–MS–MS method to determine bromate ions in water, which requires sample pretreatment to remove any major ions that displace bromate, consisting of eliminating SO_4^{2-}, Cl^- and HCO_3^- ions respectively with barium-form, silver-form, and acid (H^+-form) exchange resins. The three cartridges were successively connected in the order Ba–Ag–H and then installed on the vacuum manifold. Stratford et al. [38] reported a means to remove Cl^- ions from small volumes using an Ag^+ resin that facilitates quantification of both nitrite and nitrate in biological samples. Fagan et al. [39] proposed an ion chromatographic analysis of cyanate in gold processing samples containing large concentrations of metallo–cyanide complexes. In order to remove the metallo–cyanide complexes they developed two procedures: the first was a manual off-line method which used solid-phase extraction cartridges containing a strong anion-exchange resin to trap the complexes, while the second approach consisted of an automated on-line method, which used an anion-exchange guard column to trap the complexes and a column switching valve to allow back flushing of the cyanate from the guard column. Dahllöf et al. [40] used a second switching valve between the precolumn and the main column. Interference of a high chloride concentration could be reduced substantially and detection limits for nitrate and phosphate lowered five-fold. Montgomery et al. [41] described a new online sample preparation technique using electrochemical-regenerated ion suppression and sample neutralization.

Determination of total organic carbon (TOC) requires two steps. The first is the conversion of organically bounded carbon to a simple molecular form that can be measured quantitatively, and the second step is to detect the CO_2 evolved during the oxidation of the organic compounds. Fung et al. described [42] the applicability and reliability of the hyphenated technique of catalytic thermal combustion–ion chromatography for the determination of

TOC at the $\mu g \, l^{-1}$ level in industrial, environmental, and drinking water. Two years later, the same group developed a new analytical procedure based on thermal combustion–IC for an hourly determination of total carbon in air particulate matters using equipment readily available in the chemistry laboratory [43]. A pressurized alkaline decomposition with IC was applied for the determination of trace amounts of chloride in silica [44]. Colina and Gardiner [45] reported the use of hydrogen peroxide at low pH in combination with closed-vessel microwave assisted digestion for the oxidation of various nitrogen, phosphorus, and sulfur containing compounds. The nitrate, phosphate and sulfate ions formed were determined by IC. Colombini et al. [46] proposed the digestion of samples by alkaline persulfate solution in a microwave oven. A column switching was used for eliminating sulfate after microwave assisted persulfate digestion in order to get a fast simultaneous determination of total nitrogen and total phosphorus by suppressed ion chromatography without any sample preparation. A method for determining halogens (I, Br, Cl, F) in geological and biological materials with pyrohydrolysis as sample preparation was described [47]; by this process the halogens were separated from the matrix and then collected in a receiver solution. Buldini et al. [48] showed that saponification followed by oxidative UV photolysis is a good method to remove completely the organic matrix, which strongly interferes in the IC determination procedure of some inorganic species in edible vegetable oils and fats. Kock et al. [49] presented the use of membranes with a molecular-mass-cutoff of M_r 10 000 for the ultrafiltration of blood serum and synovial fluid samples previous to the determination of sulfates by HPLC. The viscosity of the synovial fluids was reduced by treatment with hyaluronate lyase before ultrafiltration. HPLC-grade water was evaluated as an alternative extraction reagent to acid extraction of plant tissue. Cations and anions were determined by IC, and in about 95% of occurrences concentration of ions in tissues extracted with HPLC-grade water were equal to, or greater than, those extracted with acids [50]. A diffusion scrubber system equipped with an ion chromatograph was used for collection and determination of low-concentration (ppb levels) of ammonia and nitric acid gas [51].

Blackwell et al. [52] described the use of alkaline fusion by sodium peroxide to dissolve chlorine and bromine in rocks to produce a solution, which is suitable for analysis by IC.

Sanders [53] proposed a procedure for determination of total iodine using automated sample preparation and IC. The protocol for sample preparation consists of sequentially hydrolyzing the sample, oxidizing any organic/inorganic iodo compounds to iodate, and reduction of iodate to iodide. After preparation, liberated iodide is analyzed by IC.

The detection of small quantities of nitrogen oxides in air in a quick and automated way was carried out by coupling chromatomembrane (CM) cells operating in computer-aided flow injection analysis systems with IC [54].

5. Separation

This subsection covers publications in the area of novel or modified stationary phases and also new eluents as well as concentrator pre-columns and suppressor columns and eluents, due to their implication in the separation process. At present, many research groups are working on this aspect of IC.

In the method of bromate determination in drinking waters proposed by Nowak and Seubert [55], the use of high-capacity ion exchangers (polystyrene–divinylbenzene copolymer functionalized by chloromethylation), allows both the analysis of water samples containing high ion strength (mineral or waste water) and the use of large injection volumes (>500 μl) without overloading the analytical column. For this reason, no matrix elimination step is required. Also proposed the use of microbore columns (2 mm I.D.) which allow flow-rates up to 500 μl min^{-1}. Jackson et al. [56] developed a new high-capacity column to improve the quantitation of bromate at the 10 μg l^{-1} maximum contaminant level currently being proposed by the US EPA. The production of high-capacity columns requires the use of latex with a large diameter, which ultimately results in band broadening and decreases chromatographic efficiency. They used a superporous resin, which allows a thin latex layer to be coated on both the exterior and interior surfaces of the resin. This approach provides a simple way to increase the resin capacity 5–10-fold using a standard diameter latex while maintaining the high chromatographic efficiency typically associated with pellicular materials.

New column packings have been investigated to improve the separation conditions of anions. Liu et al. [57] prepared an anion stationary phase to analyze inorganic anions in oil field waters, which make possible the use of a single-column IC. Micro silica beads, γ-chloropropyltriethoxysilane, hexamethyldisilazane and *N,N*-dimethylbenzylamine were used for the synthesis of the required phase. The eluent used was a mixture of sodium benzoate and sodium citrate. Okamoto et al. [58] developed a new graphitized carbon packing, which is sintered from carbonic material at a high temperature for an ion-interaction chromatographic method. They employed an ion-interaction reagent, tetrabutylammonium hydroxide, as the eluent instead of an anion-exchange group, and sodium carbonate as the eluting agent. Inorganic anions were successfully separated [59] on a non-modified porous graphitic carbon (PGC) column with an aqueous eluent containing an electronic modifier in the mobile phase such as carboxylic acid. The addition of organic modifier in the mobile phase was without effect in the retention of inorganic anions but the addition of pyridine improves the efficiency of the separation. The retention of inorganic anions on non-modified PGC is dominated by electronic interaction based purely on donor–acceptor interaction between the lone pair electrons of the solute and the π electrons of the PGC. A new metacrylate-based packing with quaternary amine functional groups was proposed for the analysis or inorganic anions by ion chromatography [60]. Columns packed with this new material work for both suppressor-based and single-column ion chromatographic methods. Monodisperse agglomerated pellicular anion-exchange resins for high-performance ion chromatography have been described. The resins are stable from pH 0 to 14 [61,62].

The development of novel stationary phases involves the use of a modified stationary phase. Retention behavior on anion exchangers modified with various ionic polymers has been studied; IC-Anion-SW columns modified with mucopolysaccharides such as chondroitin sulfate or heparin showed unusual retention behavior [63–65], reten-

tion of anions on the anion exchanger was remarkably reduced after the modification with heparin [66]. When silica-based anion exchangers were modified with heparin and dextran sulfate and under the appropriate conditions both anions and cations were simultaneously separated [67]. A C_{18} reversed-phase column was coated with *N*-cetylpyridinium chloride to prepare a low-exchange-capacity analytical column and with hexadecyltrimethyl-ammonium bromide to prepare a concentrator pre-column. Both columns were successfully used in the IC determination of iodide in urine and serum [68]. The surface of gel-type-anion exchange resin was modified by the adsorption of an anionic polyelectrolyte: polycondensation product of sodium naphthalenesulfonate and formaldehyde (trade name Demo N) was applied to inorganic anions separation [69]. Bohme et al. [70] described an IC method for trace analysis of bromate and bromide based on coating reversed-phase material with an ionogenic agent, tetrakisdecylammonium bromide, to obtain a pseudo ion-exchange column. Goessler et al. [71] studied the retention behavior of eight selenium compounds with aqueous solutions of pyridine in the pH range 2.0–5.7 on a silica-based strong-cation-exchange column with strongly acidic sulfonic acid groups as exchange sites. The surface of the functionalized silica particles is covered with siloxane groups, free silanol groups, geminal silanol groups, and associated silanol groups that may interact with the analyte. The sulfonate exchange sites will interact with the cationic selenium compounds, the hydrophobic backbore of the column material with uncharged lipophilic selenium compounds, and the compounds with carboxylic acid groups may be retained via hydrogen bonds to siloxane or silanol groups. A microcolumn ion chromatography of inorganic anions was proposed using bovine serum albumin immobilized on silica gel as a stationary phase [72,73]. The same group described how octadecylsilica immobilized with bovine serum albumin was capable of separating inorganic anions [74,75].

C_8 silica gel dynamically modified with cetyltrimethylammonium bromide has been used for the determination of inorganic anions by IC, and the time to separate dihydrogenphosphate, chloride, nitrite, bromide, nitrate, and sulfate ions was 7 min [76]. Tonelli et al. [77] proposed the separation of inorganic anions by ion-interaction chromatography. An octadecyl-bonded silica column was dynamically coated with crystal violet and acetonitrile–water buffered with phthalate as the counter-ion was used as the mobile phase. This technique employs a buffered or unbuffered mobile phase containing a hydrophobic positively charged ion. The major advantages of these techniques in comparison with conventional fixed-site ion exchangers are: (i) greater chromatographic efficiency and flexibility with regard to the choice of columns, mobile phases, and ion-pairing reagent for optimum separation, and (ii) the possibility of controlling the anion-exchange capacity of the column by varying the mobile phase composition.

Electrostatic ion chromatography is a new method of separating ions reported in 1995 by Hu et al., based on simultaneous electrostatic attraction and repulsion interactions between analyte ions and fixed positive/negative charges of a zwitterionic stationary phase, having the special advantage of using only water as the mobile phase [78]. The method uses a conventional reversed-phase ODS stationary phase modified with a zwitterionic surfactant. The chromatograms with the complicated peaks, derived from various 'ion pairs' appeared when the sample solution contained several kinds of cations and anions, were simplified by using a preconditioning cation-exchange column. In the preconditioning column, various kinds of countercations of the analyte anions were converted to a particular kind of common cation, and thus all analyte anions were separated as the common form cation. The more effective separation was achieved by converting to a divalent cation form than a monovalent cation form, because the anions paired with divalent cation provided longer elution times than those paired with monovalent cation [79–84]. Mixed micelles obtained by mixing sodium dodecylsulfate (SDS) with Zwittergent-3–14 were used as a dynamic stationary phase for the simultaneous IC of inorganic cations and anions [85]. A novel polymer-based zwitterionic separation material was synthesized; the resulting material carried strong/strong charge zwitterionic pendant groups, whose charge properties did not change over a wide pH range. It was capable of separating inorganic anions and cations both independently and simultaneously using aqueous solu-

tion of perchloric acid or perchlorate salts as eluent [86].

A mixed-bed column was packed with anion-exchange resin ICS-A23 and cation-exchange resin CH1. The ion chromatographic method developed with this mixed-bed column was used for the simultaneous determination of organic acids, inorganic anions and cations in different food samples without any special pretreatment procedure [87]. Mixtures of inorganic ions and neutral organics were simultaneously separated in several ion-exchange stationary phases that contained both exchange— as well as reversed-phase functionality. Mobile phases were a blend of those normally used for ion-exchange separation with those generally used for reversed-phase high-performance liquid chromatography [88]. A hyphenated IC–ion-exclusion chromatography technique has been reported for determining organic and inorganic anions [89].

Construction and preliminary characterization of an open tubular capillary column for ion chromatography has been proposed; increasing the column temperature resulted in a dramatic increase in the column efficiency [90].

Toofan et al. developed an anion-exchange column for the separation of anions in power plant waters. The column was optimized, in terms of capacity and selectivity, to allow the isocratic separation of weakly retained organic and inorganic anions, in addition to more strongly retained anions. This new moderate capacity anion-exchange column was utilized for the preconcentration ion chromatography determination of key anions, at low μg l^{-1} levels [91].

Different eluents have been studied including the use of vanillic acid–*N*-methyldiethanolamine eluents for suppressed ion chromatographic separation of inorganic anions [92] and the use of pyromellitate eluent for the simultaneous determination of common anions (Cl^-, NO_3^- and SO_4^{2-}) and divalent cations [93]. Inorganic cations and anions were separated simultaneously using sodium sulfosalicylate–EDTA binary eluent on a strong basic anion-exchange column [94], and inorganic anions, magnesium and calcium have been separated with trimellitic acid–EDTA as eluent [95]. Common inorganic anions can be separated on an anion-exchange column of low capacity using a very

diluted solution of alkanesulfonate as eluent components and conductimetric detector [96]. The determination of mixtures of carboxylic acids and selected inorganic anions proposed by Magyani [97] involves an ion exclusion separation column with sodium octanesulfonate as eluent. The retention of these solutes was controlled by a combination of ion-exclusion through the Donnan potential and hydrophobic interactions. The performance of cyanuric acid as eluent for suppressed anion chromatography has been investigated [98]. Due to the very late elutions of polythionates because of their strong retentions onto a conventional ion-exchanger separation column, Miura et al. [99] proposed an ion-pair chromatography using a silica octadecylsilane (ODS) column with mobile phases of acetonitrile in water containing phthalate and tetrapropylammonium salt as ion pair reagent. The proposed method was successfully applied to the determination of the oxyanions of sulfur added to hot-spring waters. The temperature of the mobile phase can be used as an optimization parameter in ion chromatographic analysis; the character of the temperature dependence of the retention time for each ion is unique and depends on the sorbent used [100].

An electrochemical process called electro-elution ion chromatography was used to generate or moderate the mobile phase composition inside the column [101]. The main advantage of this process is that only water is required as the mobile phase for anion and cation analysis. Small et al. [102] described how electrically polarized ion-exchange beds pumped with water could produce electrolytes of steady and controllable concentration. Such devices make it possible to use water as the pumped phase in IC, thus avoiding off-line eluent preparation. Control of electrical current flowing through the devices allows precise control of the concentration of eluent that they deliver. This provides a new way of performing gradient and isocratic elution. Using water as the carrier and two small beds of resin, one as a generator the other as suppressor, and periodically reversing their roles through automatically switched valves, they developed a form of continuous IC that involves little intervention by the user. Another modality of the latter system consisted in the 'ion reflux', applied to IC. In one embodiment of ion reflux, continuous eluent generation, ion separation,

and continuous suppression are accomplished within a single bed [103].

An electrochemical process was used to regenerate the solid-phase ion suppressor for continuous unattended operation [104]. Electrolysis of the detector effluent generates hydronium or hydroxide ions, which automatically replace the eluent cations or anions on the suppressor. A common micromembrane suppressor, usually used to chemically suppress eluent conductance in IC, was successfully used to effect ion replacement reactions in suppressed eluent stream [105]. A small inexpensive system was described that allows high-performance suppressed anion chromatography on a capillary scale [106]. The system uses a novel electrodialytic NaOH eluent generator that is deployed on the high-pressure side of the pump and thus requires no special measures for electrolytic gas removal. This device permits both isocratic and gradient operation. Huang et al. [107] reported preliminary experiments and theoretical discussion on the feasibility of a novel approach for the determination of very weak acids using a commercial micromembrane suppressor and a low concentration of regenerant. A relatively more concentrated hydroxide ion can be employed as the eluent with low background conductance while the analyte ions were detected as negative peaks.

6. Detection

Suppressed and non-suppressed conductivity are the favored detection techniques in IC of inorganic anions, but the high electrolyte concentration required to elute most analyte ions in a reasonable time is a serious limitation in this detection system. Therefore, other detectors are being made available for ion separation techniques.

Although it is known that only a limited number of common inorganic anions are detectable by direct photometric detection, the wide use of this technique, due to its analytical qualities, stimulated a search for suitable visualization anions and, in this context, various constituents were tested. Inoue et al. [108] developed a sensitive and selective IC determination of bromate with postcolumn conversion into tribromide by hydrobromic acid. A high precision determination of bromate was performed by using

the on-line hydrobromic acid generator employing a cation-exchange hollow fiber. Miura et al. [109] proposed a method for IC determination of sulfide, sulfite, thiosulfate and thiocyanate in their mixtures; sulfur anions, in the effluent from the column, were monitored by photometric measurement of the excess of iodine (triiodide) for a postcolumn iodine–azide reaction catalyzed by sulfide, thiosulfate and thiocyanate and for a postcolumn reaction of iodine with sulfite. Therefore, chromatograms obtained for the sulfur anions gave negative peaks, based on the decrease in the absorbance from background. Iodide can be determined with ion chromatography and direct UV–visible detection after preconcentration of the sample [32] and as IBr_2^-, which is formed after the IC separation step in a bromide-containing eluent. The interhalogen compound is formed through addition of a basic hypobromite solution with subsequent acidification [110]. Iodate can be determined by IC and postcolumn reaction with UV–visible detection as I_3^-, which is formed in a postcolumn reaction with an iodide solution and subsequent acidification [110]. Achilli and Romele [111] described a very sensitive bromate IC determination with spectrophotometric detection after post-column reaction with fuchsin in low pH medium, which overcomes the interferences commonly found in IC with conductivity detection. Sub part-per-billion analysis of bromate, iodate and chloride in drinking water were detected via target-specific, post-column derivatization; other sample anions were invisible to the detector [112]. Some common inorganic and organic anions were separated by high-performance ion chromatography coupled with indirect photometric detection and 1,2-dihydroxybenzene-3,5-disulfonate and sodium sulfosalicylate, respectively, as single-column single-component eluents [113].

A method for the simultaneous determination of cyanide and thiocyanate in blood has been proposed [114]. After extraction cyanide was derivatized with 2,3-naphthalenedialdehyde and taurine to give a fluorescent product of 1-cyanobenz[*f*]isoindole. This compound was detected with high sensitivity by fluorometry, and the underivatized thiocyanate was detected by UV absorption.

A faint chemiluminiscence (CL) from the neutralization reaction of nitric acid and potassium hydroxide was enhanced by addition of iron(III) to the

acid. The enhanced CL emission was suppressed by adding inorganic anions such as chloride, bromide, nitrite, nitrate and sulfate. Based on this, a post-column CL detection method [115] was developed for the determination of the anions. The decrease in the CL intensity, which is proportional to the anion concentration, can be monitored easily and rapidly in a flow injection system. A flow-injection chemiluminiscence method has been proposed for sensitive determination of arsenate, germanate, phosphate and silicate. After separation by IC [116], the post-column detection system involved formation of heteropoly acid in H_2SO_4 medium before the CL reaction with luminol in a NaOH medium.

Various atomic spectroscopy techniques are the predominant choices for analysis of metal. Atomic absorption spectrometry with flame (FAAS), graphite furnace (GFAAS) and electrothermal vaporization (ETVAAS) remain the most popular techniques. Except for some special applications for multielement determination, these instruments are dedicated to analysis of one specific analyte at a time. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is capable of multielement determination. The ICP-MS technique is generally 1 order of magnitude or more sensitive than atomic absorption methods and is capable of simultaneous multielement determination. These techniques have been applied as detectors in anion-chromatographic methods when the analyte anion can be monitored as a cation.

To minimize interferences by non-selenium anions in the IC analysis of inorganic selenium anions and amino acid forms an ICP-AES detector was proposed [117]. With the same proposal an electrothermal atomic absorption spectrometry detection was studied [118] and a speciation of selenium method based on microbore anion-exchange chromatography and a Zeeman-effect electrothermal atomic absorption spectrometry for element specific detection via ultra low volume fraction collection has been described [119]. A new on-line method, consisting of liquid chromatography–UV irradiation–hydride generation–quartz cell atomic absorption spectrometry was proposed [120]. All these techniques can be considered as reliable, straightforward systems for selenium speciation. When a zwitterionic stationary phase was used in the determination of inorganic

anions, the analyte anions were quantified by measuring their countercations with ICP-AES, where the calibration curve of the countercation measured by ICP-AES could be used [83].

The popularity of ICP-MS is rapidly rising as seen by the increasing number of publications. The determination of bromate in drinking waters proposed by Creed et al. [121] presents the drawback of the co-elution of chloride and bromate, but ICP-MS provided the selectivity to circumvent the co-elution, a shortcoming of direct conductivity detection. The online-coupling of IC–ICP-MS combined with a high-capacity and high-performance anion exchanger and NH_4NO_3-based elution system allowed the determination of bromate in almost every water without any sample pretreatment [122]. Nowak and Seubert [55] developed a method for ultra-trace determination of bromate in drinking waters using on-line coupling of IC and ICP-MS. ICP-MS was used as element-specific detector for sulfide, sulfite, sulfate and thiosulfate after their chromatographic separation [123]. Bromate, iodate and other halogen anions were determined by IC with ICP-MS. The advantages of ICP-MS as an element-selective detection method were evaluated for bromate and iodate by considering the comparison with the post-column derivatization described in a previous paper [124]. For the determination of iodine species an ion chromatograph was coupled with an ICP-mass spectrometer [125]. Li et al. compared two IC detection methods for the determination of four selenium compounds. Detection was carried out using an on-line ICP-MS or a FAAS as the selenium-specific detector. More powerful selenium detection was achieved with an ICP-MS. To increase the nebulization efficiency, an ultrasonic nebulizer replaced the Meinhard concentric glass nebulizer. The ICP-MS signal intensity was increased with ultrasonic nebulization by a factor of 7–31 times [126]. Goessler et al. also proposed ICP-MS as a selenium-specific detector [71] for the determination of inorganic and organic selenium compounds. In this case, also with the aim of increasing the nebulization efficiency, the Meinhard concentric glass nebulizer was replaced by a hydraulic high-pressure nebulizer. The determination of anionic, neutral and cationic species of arsenic in environmental samples was carried out by IC with ICP-MS detection, the gradient method was

used to determine arsenic species in highly ferrous/ferric-contaminated leachates of lignite spoil [127]. A speciation method using IC coupled with ICP-MS was described for simultaneous analysis of eight halides and oxyhalogens: chloride, chlorite, chlorate, perchlorate, bromide, bromate, iodite and iodate [128]. IC–ICP-MS has been applied to the determination of halogens, with special reference to iodine, in geological and biological samples [47]. A particle beam interface was studied for coupling IC with mass spectrometric detection [129]. Several prerequisites must be fulfilled, including mobile phases containing volatile buffers and high amounts of organic solvents at low flow-rates.

Charles et al. [37] developed an electrospray ion chromatography–tandem mass spectrometry (IC–MS–MS) method for the analysis of bromate at sub-ppb levels in water; the methanolic sulfate eluent permits IC–MS coupling via an electrospray interface. They proposed two methods for analyzing chlorite, chlorate, bromate and iodate by IC coupled with electrospray and ionspray tandem mass spectrometry (IC–MS–MS) [130,131]

The use of evaporative light scattering detection (ELSD) has been proposed as an effective alternative for the determination of ions such as chloride [132]. Indeed, ELSD is commonly referred to as a sensitive universal detector in liquid chromatography for solutes, which are less volatile than the eluting solvents [133]. Different carboxylic anions derived from volatile acids compatible with ELSD volatility requirements have been investigated as electronic competitors in order to manage the retention of inorganic anions [59].

Yang et al. proposed a bulk acoustic wave sensor as an ion chromatographic detector for the simultaneous determination of NO_3^-, Cl^-, NO_2^-, $H_2PO_4^-$ and SO_4^{2-} [134], and for determination of iodide [135].

During recent years, simultaneously with the IC development, there have been great developments in ion selective electrodes (ISEs), which has brought the possibility of having, for the determination of certain species, feasible as low-cost units. Almeida et al. [68] described the evaluation of a laboratory-made iodide-ISE with tubular configuration, based on a homogeneous crystalline membrane, as detector of a chromatographic system for the determination of

iodide in urine and serum. The tubular detector presents the advantages of being easily connected to the system and having virtually no dead volume. Chen and Alexander [136] proposed the use of a metallic silver wire electrode as potentiometric detector of anions separated by ion and ion-pair chromatography.

Amperometric detection of inorganic anions in ion chromatography has been applied by Kolb et al. [137] for the determination of anions (NO_2^-, Cl^-, I^-, SO_3^{2-}, Br^-, S^{2-}) using a carbon paste working electrode. Casella [138] studied the electrooxidation of thiocyanate on a copper-modified gold electrode and proposed its amperometric determination by IC. An amperometric detector with a glassy-carbon working electrode has been used for the simultaneous determination of sulfite, iodite and rhodanide [139]. Liu et al. [140] reported the determination of sulfite in food by exclusion ion chromatography with pulsed amperometric detection. Ion chromatographic detection of nitrite at a dispersed platinum glassy carbon electrode has been described [141]. Platinum and silver/silver chloride electrodes have been evaluated for simultaneous amperometric and potentiometric detection [142].

7. Applications of ion chromatographic techniques

7.1. General applications

Pohl et al. [143] described the factors controlling ion-exchange selectivity in suppressed IC. A new approach to determining each component of a two-component overlapping peak in single-column anion chromatographic analysis has also been described [144].

Takayanagi et al. [145] reported the ion chromatographic determination of sulfate in a high-salinity solution. The retention characteristics of condensed linear phosphates, P2 to P13, on a strongly basic quaternary amine anion exchanger were studied [146]. The determination of F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} by IC with preconcentration has been reported [147]. A study focused on the development of a single-column IC method and the use of

capillary electrophoresis for the determination of Cl anions has been described [148]. Ding et al. [149] proposed the simultaneous separation of organic acids, inorganic anions and alkaline earth metal cations using a single anion-exchange column.

Caliamanis et al. [150] demonstrated that the conductimetric determination of anions of weak acids in chemically suppressed ion chromatography could be enhanced, by conversion of the acid to a conjugate salt, if the anion was present above what they termed the critical point concentration.

The conversion of boric acid in a more acidic complex, using mannitol or sorbitol as ligands, was exploited to obtain a sensitive and accurate method for the determination of boric acid by IC [151].

Chadwick [152] described the use of a laboratory robot as a tool to prepare multilevel calibration standards for several online IC systems.

Two approaches to interfacing a suppressed ion chromatography system with a suppressed conductometric capillary electrophoresis separation system have been described [153].

7.2. Environmental analysis

The analysis of NO_2 and SO_2 by IC with the use of passive samplers for ambient measurements of NO_2 and SO_2. was reported [154]. A rapid ion chromatographic method, with isocratic separation and micromembrane suppression was performed for the analysis of iodide in soils, and floodplain ground waters [155]. The nitrate, phosphate and sulfate ions formed after the use of hydrogen peroxide at low pH in combination with closed-vessel microwave-assisted digestion for the oxidation of various nitrogen-, phosphorus-, and sulfur-containing compounds in Buffalo River sediments, were determined by IC [45] and total nitrogen and phosphorus were simultaneously determined by IC after microwave-assisted persulfate digestion [46]. IC has been used to determine inorganic and organic anions within landfill leachates. Two procedures are operated on split samples, which have multiple dilutions and vary in sample treatment: gradient ion-exchange chromatography for inorganic anions and isocratic ion-exclusion chromatography for organic anions [156]. Phosphorous and phosphoric acids in air have been determined by IC and capillary isotachophoresis

[157]. The determination of small quantities of nitrogen oxides in air was developed by IC using a chromatomembrane cell preconcentration [54]. Water and acid soluble components in atmospheric dust were measured by IC and other techniques [158]. Total carbon in air particulate matters was determined by thermal combustion–IC [43]. Silver iodide was determined by high-pressure ion chromatography in soil and water matrixes after reduction by zinc [159]. Inorganic anions in drainage water and soil solutions were analyzed by single-column IC [160].

Although most water analysis publications involve environmental samples, all water analyses have been included in the following section.

7.3. Water analysis

Seepage water samples from tin ore tailing were analyzed for arsenic species by an IC–ICP-MS gradient method, as part of a toxicological assessment [161]. Arsenic species were also determined in highly polluted water leachates of lignite spoil using the IC–ICP-MS gradient method [127]. The hyphenated technique of catalytic thermal combustion–IC was applied to the determination of total organic carbon at the $\mu g \ l^{-1}$ level in industrial, environmental, and drinking water [42]. Dahllöf et al. [40] reported on an improved ion chromatographic method for nitrate and phosphate determination in seawater, regardless of salinity, developed using experimental design. A simple and highly sensitive ion chromatographic method with UV detection was developed for iodide in seawater [32]. Several organic and inorganic ions were simultaneous determined by UV in snow samples from Shenyang area [162]. Liu et al. [57] presented a method to determine inorganic ions in oil field water by single-column IC. A non-suppressed IC system with conductivity detection was tested for the determination of chloride, nitrate, sulfate, alkali and alkaline-earth metal ions in polar ice core samples by use of large injection volumes [163]. A chemically suppressed IC system was used for the analysis of major organic and inorganic acid in precipitation samples collected in the city of Maracaibo during a one-year period. Two different isocratic method were used, the first

for inorganic acids, and a second for organic acids [164]. Two different chromatographic methods have been reported for the determination of sulfur anions in hot-spring waters samples: the first [99] with a silica octadecylsilane column and the second with an ion-exchange column [109].

The determination of bromate has traditionally been accomplished using IC, but in response to the need to develop bromate methods with lower detection limits, many researchers have proposed new methods and several works have been published recently in order to improve the sensitivity and selectivity of IC methods for the determination of bromate in drinking waters [33,37,55,56,108, 111,121,124,165–167]. Two methods involve the use of IC followed by postcolumn derivatization, which converts bromate into tribromide, which is then detected either by conductivity [108] or by UV spectroscopy [112]. Detection limits were 0.35 μg l^{-1} and 0.2 μg l^{-1}, respectively. Creed et al. [121] demonstrated bromate detection limits of 0.1–0.2 μg l^{-1}, which could be lowered to 50 ng l^{-1} by coupling the preconcentrator column to an ultrasonic nebulizer.

Yamanaka et al. [124] described the specific determination of bromate, iodate and other halogen species in raw and ozonized water, by direct injection using IC–ICP-MS and post-column derivatization. They achieved detection limits of 0.45 μg l^{-1} for bromate and 0.034 μg l^{-1} for iodate. Nowak and Seubert [55] achieved detection limits of 50–65 ng l^{-1} for bromate by using a high-capacity, high-performance, microbore anion exchanger with IC–ICP-MS, no pretreatment was required, and analysis time was only 8–15 min. Elwaer et al. [166] used on-line separation with an activated aluminum microbore column in a flow injection system coupled to ICP-MS to achieve a detection limit of 60 ng l^{-1} for bromate. A new method which uses IC separation with no pretreatment, followed by a post-column reaction to produce tribromide (Br_3^-) from bromate was applied for determining sub-μg l^{-1} levels of bromate in drinking water [168]. Kohler et al. [169] described the use of a high-capacity resin with photometric detection for determining bromate and nitrite in drinking water. Wagner et al. [170] compared three methods for measuring bromate in drinking water: a modified selective anion concen-

tration method, EPA Method 300.1 and a postcolumn reagent method. Bichsel and Gunten [110] proposed the determination of iodide and iodate in water by two methods using anion-exchange chromatography. Heumann et al. [171] developed an on-line coupling of chromatographic systems (IC, LC, size-exclusion chromatography, GC) with ICP-MS for accurately determining various element species. These species included iodate, iodide, organo iodine species, and heavy metal complexes with humic substances

Inorganic anions (Cl^-, Br^-, NO_3^-, and SO_4^{2-}) were determined in waters by ion-exchange chromatography with chemiluminiscence detection [115], and the applications of IC in the determination of inorganic anions and cations in various waters with elevated mineralization has been discussed by Gros and Gorenc [172]. The high content of hydrogen carbonate anions and dissolved CO_2 in some mineral waters interfere with the determination of anions in such samples by IC. Novic et al. [173] proposed a method to avoid peak deformation and overlapping. Inorganic anions, magnesium and calcium have been simultaneously determined in various environmental water samples, such as rain and river water [95]. Low-level perchlorate analysis in drinking water and groundwater by ion chromatography has been reported [174]. Anions (Cl^-, NO_3^-, and SO_4^{2-}) in natural water were determined by low-pressure ion chromatography [175]. Nitrite and F^-, Cl^-, NO_3^-, Br^-, HPO_4^{2-}, SO_4^{2-} were determined in wastewater, groundwater and surface water samples by enhanced ion chromatography with sequential flow injection analysis [176].

A few developments in new regulations and regulatory methods have taken place in the last 2–3 years that impact on water analysis. Several new regulatory methods for drinking water measurements have been published recently by the EPA. EPA Method 321.8 'Determination of Bromate in Drinking Water by Ion Chromatography Inductively Coupled Plasma–Mass Spectrometry' provides a lower detection limit for bromate of 0.3 μg l^{-1} and provides a degree of selectivity that was not available with former methodology [177]. EPA Method 300.1, 'Determination of Inorganic Anions in Drinking Water by Ion Chromatography' is applicable to a broad range of inorganic anions in drinking water [178].

7.4. Food analysis

IC has been used for the determination of the principal anions of milk, phosphate, citrate and chloride [179], for the determination of iodide in milk and baby formula [180], in dairy products and table salt [135]. Ding et al. [181] proposed a simultaneous determination of organic acids and inorganic anions in tea by IC. Liu et al. [182], described the determination of organic acid and inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) by gradient IC in beverages and citric acids fermenting-medium. IC was proposed as a rapid method to distinguish orange juices from second pressure concentrates [183]. Bello and González [184] proposed the determination of phosphate in cola beverages using nonsuppressed IC as an experiment that could be integrated into existing laboratory courses in analytical chemistry. A simultaneous determination of organic acids and inorganic anions (F^-, NO_2^-, Cl^-, Br^-, NO_3^-) and cations by IC with mixed-bed stationary phase has been described in wine, Japanese sake and instant coffee power without any special pre-treatment procedure [87]. The determination of nitrate in beer by IC has been tested by Buckee [185]. Carboxylic acids and inorganic anions (Cl^-, NO_3^- and SO_4^{2-}) have been determined in wines by ion-exchange chromatography [186]. The use of IC in the liqueur–vodka industry, for the determination of inorganic anions ($H_2PO_4^-$, Cl^-, NO_3^-, SO_4^{2-}) has been proposed by Obrezkov et al. [187]. Ding et al. [188] proposed a simultaneous analysis of organic acids and inorganic anions in beverage (dongjiu) by IC. The determination of alkali metals and inorganic anions in baobab fruit by IC has been described [189]. Buldini et al. [48] reported the determination of some inorganic species (Cl^-, PO_4^{3-}, SO_4^{2-}) in edible vegetables oils and fats. Nitrate contents in red beet products was analyzed by IC [190]. Nitrate and other inorganic anions (Cl^-, NO_2^-, $H_2PO_4^-$, and SO_4^{-2}) were measured in vegetables [134]. Nitrate and nitrite have been determined in meat products [191]. A rapid analytical method for nitrite and nitrate in fish by IC has been proposed [192]. The identification and quantification of some organic acids and inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) was carried out in beet sugar using an IC method [193]. The simultaneous

separation of selenite, selenate, selenocystine and selenomethionine in selenium-rich yeast was studied with ion-exchange chromatography with a selenium-specific detector [118]. Matsunaga et al. [194] described the determination of condensed phosphates in foodstuffs by IC. Sulfite in food was determined by ion-exclusion chromatography with pulsed amperometry [140]. Chen et al. [195] studied an analytical method for inorganic anions in food colorants by IC with ion-exchange preseparation.

7.5. Theoretical and statistical studies, and computational applications

Ando et al. [196] described a theoretical study of the elution profile of a high-concentration sample anion in non-suppressed IC.

The statistical comparison of calibration curves from two similar eluents was carried out in the ion chromatographic quantification of fluoride and acetate [197]. Statistical quality control has been applied to ion chromatography calibrations [198]. Detectors for IC were classified using principal components regression and linear discriminant analysis [199]. The use of factorial experimental design was reported for the rapid evaluation of main and interactive factors affecting linearity in calibration curves for sulfate analysis by IC [200].

Madden et al. [201,202] have compared the performance of several retention models for predicting the retention factors of inorganic anions in non-suppressed IC and in suppressed IC and for optimization of the separation of anions in ion chromatography. Janos [203] reported a retention model in ion chromatography considering the role of side equilibria in ion-exchange chromatography of inorganic cations and anions. Correlation and digital signal processing techniques were applied to the reduction of detection limits of bromate and bromide in model water samples by IC with direct UV detection [204]. Papoff et al. [205] proposed a comparison between experimental and deconvolved peak parameters in IC to enhance the quality of information obtained. The pattern-recognition method was applied for modeling expert estimation of chromatogram quality [206]. Computational chemical analysis was used to study the highly sensitive detection of bromate in IC [207]. A classifier system based on genetic algorithm

methodology was developed for the automatic extraction of production rules from a database of ≈6000 IC method examples; this machine learning strategy generated heuristics that can assist in the choice for a detection method for a specified set of IC method and solute properties [208]. An empirical study for the effectiveness of recombination in a genetic-based classifier system has been applied to the field of IC [209]. An expert system for automated troubleshooting and plausibility testing in IC has been introduced [210].

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