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Review

Determination of Nitrogen Species (Nitrate, Nitrite and Ammonia Ions) in Environmental Samples by Ion Chromatography

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Abstract

The necessity of environmental protection has stimulated development of all kinds of methods allowing determination of different pollutants in different elements of the natural environment, including methods for determining inorganic nitrogen ions. Many of the methods used so far have proven insufficiently sensitive, selective or accurate and recently much attention has been paid to ion chromatography, which seems most promising. This paper reviews applications of ion chromatography for determining nitrate, nitrite and ammonium ions in environmental samples and in food products along with ISO standards and the relevant methods proposed by the US EPA and Dionex.

Literature examples describe the application of ion chromatography for determining NO_3^-, NO_2^- and NH_4^+ ions in water, waste water, air, food products and other complex matrix samples. Critical analysis of the methods based on ion chromatography is presented.

Keywords: ion chromatography, nitrate, nitrite, ammonia ions

Introduction

Nitrogen - one of the most commonly occurring elements in nature - forms many inorganic ionic species, of which the most important are nitrate, nitrite and ammonium ions.

The main anthropogenic sources of nitrates in the environment are municipal and industrial wastes and artificial fertilizers. Nitrogen oxides present in the air and originating from natural and anthropogenic sources (combustion, transportation) after the reactions with water come back to the earth surface in the form of acid rains [1]. Nitrites appear as intermediates in the nitrogen cycle. They are unstable and, depending on conditions, are transformed into nitrates or ammonia. Their presence in water can be a result of water processing or use of nitrite salts as corrosion inhibitors. Nitrites are commonly used in preservatives. To surface waters they get from the same sources as nitrates, i.e. in municipal wastes, industrial wastes, mining wastes and with water flowing in from artificially fertilized fields. The sources of ammonium ions in surface waters are reactions of biochemical decomposition of organic nitrogen compounds, reduction of nitrites and nitrates by hydrogen sulfide, iron (II), humus substances (or other reducing compounds) and, first of all, municipal wastes, industrial wastes and animal farm wastes. Nitrogen compounds enhance eutrophisation of surface waters. Organic nitrogen compounds undergo biochemical decomposition into nitrites later oxidized to nitrates.

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The main source of inorganic nitrogen ions in the human organism is drinking water and food products, in particular beetroots, celery, lettuce, spinach and preserved meat. An estimated daily dose of nitrates consumed by man reaches 75-100 mg, of which 80-90% come from vegetables and 5-10% from water [2]. The admissible concentration of nitrates and nitrites in drinking water in the majority of countries controlling these parameters is 50 mg L^{-1} and 0.5 mg L^{-1}, respectively. The admissible concentration of ammonium ions expressed in ammonia is 0.5 mg L^{-1} [3,4]. Nitrates and nitrites do not have direct carcinogenic effects on humans, but it is supposed that neoplasmic diseases in people are related to the formation of N-nitroso compounds, of which many are carcinogenic to animals. High concentrations of nitrogen ions in drinking water and other food products can lead to serious problems and diseases. Taken in excess, the compounds increase the risk of appearance of methemoglobinemia, especially in infants below 3 months old, which is directly related to transformation of nitrates in nitrites in humans [5].

EU countries in 1991 approved the Nitrate Directive [6] on the protection of water against pollution by nitrates from agricultural origin. The Directive recommends certain measures to protect the natural environment against degradation caused by nitrogen compounds used for agricultural purposes.

General Principles of Nitrogen Species Determination

Nitrite, nitrate and ammonium ions are determined in drinking waters, surface waters and underground waters, as well as in municipal and industrial wastes. Because of ion instability, the samples should be analyzed immediately after collection [7,8]. The methods of collection and storage of water samples for determination of these ions are described by Gardolinski et al. [9]. Because of low concentrations of the ions to be determined, their direct analysis is not always possible. Some preliminary sample preparation may be needed, including precipitation procedures, ion exchange, distillation, microdiffusion, solvent extraction or thin layer chromatography [10]. Preparation of samples with a complex matrix (blood, food products) is usually time consuming, laborious and, performed incorrectly, can be a source of significant errors. Preliminary preparation of samples for analyses by the methods of ion chromatography and capillary electrophoresis has been described by Haddad et al. [11].

Nitrogen Determination by Classical Methods

There are a number of methods for determining NO_2^-, NO_3^- and NH_4^+ ions. Determination of these analytes in the sample often poses analytical problems related to low selectivity of the methods and the presence of many interfering factors. The classical methods used for these purposes can be divided into weight, titration, spectrophotometric (UV/Vis, IR, fluorimetric) and electroanalytical (including potentiometric based on the use of ion-selective electrodes, voltamperometric, amperometric, coulometric) [12].

The most important methods for determination of nitrates are colorimetric ones (e.g. determination of nitrate nitrogen after a reaction with p-fluorophenol), or reduction in a cadmium column. The method most often used for routine analyses is based on the reaction of nitrate nitrogen with sodium salicylate in an acidic environment, giving nitrosalicylate acid transformed on alkalization into the coloured (yellow) ionized form. Nitrate ions can also be determined by the potentiometric method with an ion-selective electrode [12,13].

The basic method for determination of nitrites in water samples (proposed by Griess over 125 years ago), relies on the reaction of nitrites with sulphanilic acid giving diazo compounds, which couples with 1-naphthylamine. The reaction gives an azo dye of intense red colour. There are other methods that are modifications of that proposed by Griess, e.g. that involving the reaction with sulfanilamide and N-(1-naphthyl)-ethylenediamine) [12, 13].

The method for determination of ammonia was proposed by Nessler in 1856. In this method the Nessler reagent (alkaline solution of mercuric potassium iodide - K_2HgI_4) reacts with ammonia to give a colour complex. Unfortunately, elimination of interfering factors is not always possible in this method. Ammonium ions are often determined by a colorimetric indophenol titration method and a potentiometric method with ion-selective electrode [13].

The US Environmental Protection Agency (EPA) recommends the methods of ion chromatography, potentiometric and colorimetric methods for determining nitrate and nitrite ions [14]. The ISO standard methods used for determinations of nitrates, nitrites and ammonium ions (excluding ion chromatography method) are presented in Table 1. These methods have some advantages and disadvantages. The latter are related to low selectivity, low sensitivity and poor repeatability of determinations. Nevertheless, the search for alternative new methods continues.

Determination of Nitrogen Species by Ion Chromatography

One of the most commonly used methods for determining anions (including NO_2^- and NO_3^-) and cations (including NH_4^+) is ion chromatography. It offers the possibility of simultaneous determination of a few ions in a short time, good reproducibility of results, high sensitivity, the possibility of simultaneous determinations of anions and cations (including organic and inorganic ions), small volume samples and the possibility of using different detectors (from the most popular conductometric one, UV, to mass spectrometry) [15, 16]. Ion chromatography is particularly recommended for speciation analysis. Such analyses have been performed for simultaneous separation and determination of nitrate and nitrite ions [17] or

Table 1. ISO standards for determination of nitrate, nitrite and ammonium ions in water samples.

Method number	Method name	Range [mg L^{-1}]	Main interferences
ISO 7890-1 (1986)	Water quality. Determination of nitrate. Part 1: 2,6-Dimethylphenol spectrometric method	0.006 - 25.0	Strong oxidants, chloride, turbidity
ISO 7890-2 (1986)	Water quality. Determination of nitrate. Part 2: 4-Fluorophenol spectrometric method after distillation	0.22 - 45.0	Calcium, magnesium, turbidity
ISO 7890-3 (1988)	Water quality. Determination of nitrate. Part 3: Spectrometric method using sulfosalicylic acid	0.003 - 0.2	Chloride, nitrite, calcium, magnesium
ISO 6777 (1984)	Water quality. Determination of nitrite. Molecular absorption spectrometric method	0.003 - 0.1	Chloramine, chlorine, polyphosphates, tiosulphates
ISO 13395 (1996)	Water quality. Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection	NO_2^-: 0.32 - 20.0 NO_3^-: 0.01 - 1.0	Organic matter, surfactants
ISO 11905-1 (1997)	Water quality. Determination of nitrogen. Part 1:Method using oxidative digestion with peroxosulfate	About 0.1 for each determined ions	Dissolved or suspended organic matter
ISO 5664 (1984)	Water quality. Determination of ammonium. Distillation and titration method	0.1 - 10.0	Calcium, magnesium, aluminium, phosphates
ISO 6778 (1984)	Water quality. Determination of ammonium - Potentiometric method	0.2 - 50.0	Selected cations present in high concentration, unstable temperature
ISO 5664 (1984)	Water quality - Determination of ammonium. Distillation and titration method.	0.2 - 10.0	Urea and chloramines
ISO 7150-1 (1984)	Water quality - Determination of ammonium. Part 1: Manual spectrometric method	0.003 - 1.0	Magnesium, calcium
ISO 7150-2 (1986)	Water quality. Determination of ammonium. Part 2: Automated spectrometric method	0.5 - 50.0	Magnesium, calcium
ISO 11732 (1997)	Water quality. Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection	0.1 - 10.0	Volatile amines, high convcentration of metal ions

sulphate and sulphite ions [18]. Recently, ion chromatography has been used to determine of side products of water disinfection (bromates, chlorates, chlorites) [19] and metal ion species [20].

Separation and determination of nitrate and nitrite ions by ion chromatography is carried out in anion-exchange columns filled with a suitable exchanger and using a proper eluent (e.g. water solution of sodium carbonate and/or sodium hydrocarbonate) and most often conductometric or UV detection. Nitrogen ion determination by ion chromatography is accompanied by determination of other anions present in the sample, such as: fluorides, chlorides, phosphates, bromides and sulphates. The main problems are related to proper separation of NO_2^- from Cl^- ions. Irrespective of the column used, the retention times of the ions (related to their structure, ionic radius, selectivity against the exchanger) are close and in environmental samples with chloride ions concentrations usually a few times higher than those of nitrite ions, the peak assigned to NO_2^- can be masked by a large peak assigned to Cl^- ions. Consequently, the quantitative analysis of nitrite ions can be very difficult or impossible. The retention times of bromide and phosphate ions are close to nitrate ions but, fortunately, on the majority of anion-exchange columns they can be selectively separated. In determination of ammonium ions, the column is filled with cationic exchanger and a conductometric detector is most often employed. As the ammonium ions are usually determined together with alkali metal ions and alkali earth metal ions, the main problem is related to the overlapping of the peaks assigned to sodium ions (often present in much higher concentration) and the peak assigned to NH_4^+.

The problems related to separation of the pairs of Cl^-/NO_2^- and Na^+/NH_4^+ ions can be solved by optimizing the conditions of analysis, i.e. changing the composition of the eluent, type or pH of eluent, intensity of its flow, type of column and detector. Moreover, the excess ions interfering in the determination can be removed by special cartridges. The effect of eluent and detector on the determination of nitrite ions in the presence of chloride ions in high concentrations has been discussed by Pastore et al. [21]. The use of a classical conductometric detector and water solution of $Na_2CO_3/NaHCO_3$ as eluent, the maximum ratio of the concentrations of the ions Cl^-/NO_2^- ensuring good performance is 200:1. With water solution of NaCl as eluent and UV detector, this ratio increases to 200,000:1, and in the system with NaCl as eluent and an amperometric detector it increases up to 1,000,000:1.

Although ion chromatography has been designed for ion analyses in water, the recent progress in development of new fillings, new detection methods and new preliminary procedures of sample preparation has extended the use of this method to samples with a more complex matrix. A review on the applications of ion chromatography in analyses of biological samples has been prepared by Singh et al. [22] in analyses of food products - by Pereira [23] and Buldini et al. [24]. Compar-

Table 2. ISO standards for determination of nitrate, nitrite and ammonium ions in water samples.

Method number	Method name	Ions determined	Detector	Range for nitrogen ions [mg L^{-1}]	Interferences
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	F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, NO_3^-, SO_4^{2-},	Conductivity	NO_2^- : 0,05 – 20 NO_3^- : 0,1 - 50	Selected organic acids such as: malonic, maleic and ions in high concentration
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	Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-},	Conductivity or UV/vis	NO_2^- : 0,05 – 20 NO_3^- : 0,1 - 50	
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	Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}	Conductivity	NH_4^+ : 0,1 - 10	Selected aminoacids, alifatic amines and some metal ions such as: Zn^{2+}, Ni^{2+} , Cd^{2+}.

Table 3. Ion chromatography-based methods for determination of the NO_3^-, NO_2^- and NH_4^+, recommended by selected American organizations.

Method number	Method name	Ions determined	Matrix
United States Environmental Protection Agency			
300.0	The determination of inorganic anions in water by ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_2^-	Drinking water, surface water,
300.1	The determination of inorganic anions in waterby ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_2^-, ClO_3^-, BrO_3^-	Drinking water, ground water, surface water
300.6	Chlorite, orthophosphate, nitrate and sulphate in wet deposition by chemically suppressed ion chromatography	Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Rain water
300.7	Dissolved sodium, ammonium, potassium, magnesium and calcium in wet deposition by chemically suppressed ion chromatography	Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Rain water
9056	Inorganic anions by ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Water, solids
Association of Analytical Communities (AOAC)			
993.30	Determination of inorganic anions in water using ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Water
National Institute for Occupational Safety and Health (NIOSH)			
4110	Anions determination by ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Water
American Society for Testing and Materials (ASTM).			
D 4327-97	Anions in water by chemically suppressed ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Drinking water, wastewater
D 5085-90	Determination of chloride, nitrate and suplhate in atmospheric wet deposited by chemically suppressed ion chromatography	Cl^-, NO_3^-, SO_4^{2-}	Rain water

ison of different methods of nitrates and nitrites determination in plant samples and biological fluids has been made by Cruiz and Mam [25] and Everett et al. [26]. Determination of nitrites and nitrates in preserved meat has been described by Bernini et al. [27] and in blood serum by Monoghan et al. [28].

Ion chromatography has become a standard method for determining anions and cations in water, air and solid samples. In 1984 the American Society for Testing Materials (ASTM) approved it as the standard method for determining anions in water [29]. The EPA also has recommended

Table 4. Methods recommended by Dionex (Dionex Co., Sunnyvale, CA, USA).

Method number	Method name	Ions determined	Matrix
AN 4	Analysis of engine coolants by ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Cooling solutions
AN 25	Determination of inorganic ions and organic aids in non-alcoholic carbonated beverages	Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, selected organic acids, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Non-alcoholic beverages carbonated
AN 31	Determination of anions in acid rain by in chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Rain water
AN 51	Method for determination of anions in sodium hydroxide	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	NaOH solutions
AN 56	Determination of trace anions and key organic acids in high purity ammoniated and borated waters found in steam cycle power plants	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, selected organic acids	Recylculated water from power plants
AN 78	Determination of trace anions in concentrated hydrofluoric acid	Cl^-, Br^-, NO_2^-, SO_4^{2-}	Fluoric Acid
AN 81	Determination of oxyhalides and other anions by ion chromatography using a borate-based eluent	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_2^-, ClO_3^-, BrO_3^-	Drinking water
AN 86	Determination of trace cation in power plant waters containing morpholine	Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	Recylculated water from power plants
AN 93	Determination of trace anions in concentrated bases using autoNeutralization™ pretreatment and ion chromatography	Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_2^-, oxalate	Concentrated bases
AN 94	Determination of trace cations in concentrated acids using autoNeutralization™ pretreatment and ion chromatography	Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, ethylamines	Concentrated acids
AN 113	Determination of trace anions in high purity waters by high volume/direct injection ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, oxalate	Ultrapure water
AN 114	Determination of trace anions in high purity waters using direct injection and two-step isocratic ion chromatography	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, oxalate	Ultrapure water
AN 136	Determination of inorganic oxyhalide disinfection byproducts anions and bromide in drinking water using ion chromatography with the addition of a postcolumn reagent for trace bromate analysis	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_2^-, ClO_3^-, BrO_3^-	Drinking water
AU 101	Transition metals in power plant high purity water	F^-, Cl^-, Br^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, oxalate	Ultrapure water
AU 102	Trace anions in power plant high purity water and borated water	F^-, Cl^-, Br^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, oxalate	Ultrapure water
AU 103	Trace anions in power plant high purity water	F^-, Cl^-, Br^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, oxalate	Recylculated water from power plants
AU 106	Trace calcium and magnesium in brine	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Mg^{2+}, Ca^{2+}	Brines
AU 121	Monovalent cations in explosives	Li^+, Na^+, NH_4^+, K^+	Explosives

a number of methods which use ion chromatography in analyses related to environmental protection [30]. The ISO standards for anion and cation determination by ion chromatography are given in Table 2, while the standards recommended by select American organizations are given in Table 3. Table 4 presents the application notes on determination of ionic nitrogen species recommended by Dionex - one of the most renowned firms specializing in ion chromatography in the world.

Apart from standard methods, literature gives many examples of applications of ion chromatography in determination of nitrites, nitrates and ammonium ions in all kinds of water samples, municipal and industrial wastes, precipitations, in gases absorbed in solutions, in food products, biological samples and other samples with complex matrix. Selected examples of ion chromatography method applications for determination of nitrates and nitrites, with specified samples, column, eluent and detector, are presented in Table 5 (nitrates and nitrites in water samples), Table 6 (nitrites and nitrates in food products), Table 7 (nitrites and nitrates in air), and Table 8 (nitrates and nitrites in complex matrix samples). Examples of the

Table 5. Examples of ion chromatography applications for determining nitrates and/ or nitrites in water samples.

Sample matrix	Column	Eluent	Detector	References
Waters	Waters IC-Pak Anion HC	Na_2CO_3 + $NaHCO_3$	Conductivity	31
Reference material	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	32
Environmental water	TSK guardgel QAE-SW (Tosh)	Trimetallic acid-EDTA	UV/Vis	33
Polar ice core	Laboratory packed with resins synthetized	Potassium hydrogenphtalate	Conductivity	34
Natural water	Dionex IonPac AS4A	$NaHCO_3$	Conductivity	35
Synthetic samples	TSK-gel IC anion PWXL (Tosh)	Sodium tetraborate, boric acid, potassium gluconate	Conductivity, UV	36
Sea water	Column filled with copper-plated cadmium	Sodium tetraborate, boric acid	UV/Vis	37
Rain water	Dionex IonPac AS4	Na_2CO_3 + $NaHCO_3$	Conductivity	38
Mineral water	Biotronik BT I ANS	Na_2CO_3 + $NaHCO_3$	Conductivity	39
Surface water	Metrohm IC anion	Na_2CO_3 + $NaHCO_3$	Conductivity	40
Drinking water	Biotronik BT II AN	Na_2CO_3 + $NaHCO_3$	Conductivity	41
Snow	Biotronik BT II AN	Na_2CO_3 + $NaHCO_3$	Conductivity	42
Drinking water	Dionex AS11	NaOH	Conductivity	43
Water	Dionex IonPac AS9-HC	Na_2CO_3 + $NaHCO_3$	Conductivity/ UV/Vis	44
Water	ODS column	Phthalate	UV/Vis	45
Drinking water	Metrohm IC Anion Column Super Sep	Phtalic acid	Conductivity	46
Water	Laboratory made anion-exchange column	NaOH + $HClO_4$	Conductivity	47
Groundwater	Dionex IonPac AS11	NaOH	Conductivity	48
Water	Dionex IonPac AS9-SC	HCl + tris-(hydroxy-methyl)--aminomethane	UV/Vis	49
Water	Dionex IonPac AS9-SC	p-toluenesulfonic acid + tris--(hydroxy-methyl)-aminomethane	UV/Vis	49
Water	Dionex IonPac AS5A	$HClO_4$ + tris-(hydroxy-methyl)--aminomethane	UV/Vis	50
Dam water, river water	Laboratory packed bed Cu-Cd reductor column	$Na_2B_4O_7$	Conductivity	51
Power plant water	Dionex IonPac AS10	NaOH	Conductivity	52
Rainwater	Dionex IonPac AS11	NaOH	Conductivity	53
Reference materials	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	54
Fog samples	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	55
Rain	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	56
Waters from peatlands	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	57
Atmospheric aerosols	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	58
Rainwater	Waters IC Pak A HC	Gluconic acid + Boric acid	Conductivity	59
Drinking water	Dionex IonPac AS4A or AS10	NaOH	Conductivity	60
Fog samples	Dionex IonPac AS14	NaOH	Conductivity	61
Rain water	Dionex IonPac AS4 or AS7	Na_2CO_3 + $NaHCO_3$	Conductivity	62

Table 5. continues on next page...

River water	Shimadzu IC-A3	Phthalic acid + tris-(hydroxy-methyl)--aminomethane	Conductivity	63
Waters	Metrohm Star-Ion A300	Na_2CO_3 + $NaHCO_3$	Conductivity	64
Drinking water	Waters IC-Pak C anion	PDCA	UV/Vis	65
Roof runoff waters	Dionex IonPac AS14	Na_2CO_3 + $NaHCO_3$	Conductivity	66
Rainwater	Dionex IonPac AS14	Na_2CO_3 + $NaHCO_3$	Conductivity	67
Drinking water	Dionex IonPac AS17	NaOH	Conductivity	68
Atmospheric aerosols	Metrohm Metrosep SUPP3	Na_2CO_3 + $NaHCO_3$	Conductivity	69
Sea water	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	70

Table 6. Examples of ion chromatography applications for determining nitrates and/ or nitrites in food products.

Sample matrix	Column	Eluent	Detector	References
Meat products	Dionex IonPac AS11	NaOH	UV/Vis	71
Coffee	Mixed bed column packed with anion exchange resin) ICS-A23 and cation exchange resin CH1	Oxalic acid	Conductivity	72
Spinach	IC anion PRP-X100	Phthalic acid, acetone	Amperometric	73
Fruits juice	Dionex OmniPac PAX-500	NaOH-ethanol-methanol	Conductivity	74
Wine	Shimadzu Shim-pack IC-A1	Phthalic acid	Conductivity	75
Orange juice	Hamilton PRPx100	2,5-dihydroxy-1,4-benzenedisulfonic acid + EDTA	UV/Vis	76
Food	Dionex IonPac AS4, AS9	Na_2CO_3 + $NaHCO_3$	Conductivity or UV/Vis	77
Frozen food	Yokogawa ICS-A23 and Yokogawa CH1	Na_2CO_3 + $NaHCO_3$	Conductivity	78
Spinach	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	79
Beer	Dionex IonPac AS4	Na_2CO_3 + $NaHCO_3$	Conductivity	80
Food extracts	Alltech Universal Anion	Lithium 4-hydroxbenzoate	Conductivity	81
Meats	Wescan Anion Exclusion/HS	H_2SO_4	Amperometry	82
Beer	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	83
Rice flour	Dionex IonPac AS 12A	Na_2CO_3/$NaHCO_3$	Conductivity	84
Spinach	Dionex IonPac S4A	Na_2CO_3 + $NaHCO_3$	Conductivity	85
Vegetables	Laboratory packed anion-exchange column	Potasium gluconate + borate acid	Conductivity	86
Fruits	Waters IC-PAK Anion	KH_2PO_4 + Na_2HPO_4	UV-Vis	87
Meat extract	Dionex IonPac AS-3	Na_2CO_3 + $NaHCO_3$	Conductivity	88
Vegetables and salads	Wescan 269-001 anion	Phthalate	Conductivity	89
Infant food	Hamilton PRP-1	Tetrapentyloammonium + aceto-nitrile	UV/Vis	90
Cured meat	Vydac 302 IC, Waters CN	KH_2PO_4	UV/Vis	91
Cured meat	Waters IC-Pak A	KH_2PO_4	UV/Vis	92
Cured meat	Biotronik BT II AN	Chloromethanesulphonic acid	UV/Vis	93
Vegetables	Waters IC Pak	sodium gluconate + borax	Conductivity	94
Edible vegetable oils, fats	Dionex IonPac AS9	Na_2CO_3 + $NaHCO_3$	Conductivity	95

Table 7. Examples of ion chromatography applications for determining nitrates and/ or nitrites in gas samples.

Sample matrix	Column	Eluent	Detector	References
Flue gas	Dionex IonPac AS4A or AS7	Na_2CO_3 + $NaHCO_3$ or NaOH + p-cyanophenol	Conductivity	96
Stack gases	Toyo Soda IC-Anion-PW	Potassium gluconate + sodium borate + EDTA	Conductivity or UV/Vis	97
Ambient air	Biotronik BT I ANS	Na_2CO_3 + $NaHCO_3$	Conductivity	98
Ambient air	Dionex IonPac AS14	Na_2CO_3 + $NaHCO_3$	Conductivity	99
Atmospheric aerosols	RP_{18}	Tetrabutyl-ammonium hydroxide, 3-(N-morpholine)-propane-sulfonic acid (zwitterion), Na_2CO_3	Conductivity	100
Ambient air	Shim-pack IC-A1 or Dionex IonPac AS9-SC	Phthalic acid + tris-(hydroxy-methyl)-aminomethane or Na_2CO_3 + $NaHCO_3$	Conductivity	101
Atmospheric air	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	102
Atmospheric air	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	103
Atmospheric air	Hamilton PRP-X 100	Phthalic acid + acetone	Conductivity	104

Table 8. Other examples of ion chromatography applications for determining nitrate and/ or nitrite ions in samples with complex matrix.

Sample matrix	Column	Eluent	Detector	References
Blood	Dionex IonPac AS12A	Na_2CO_3 + $NaHCO_3$	Culometric	105
Pharmaceutical compounds	Carbon B1-01 (Bio-TechResearch)	TBA, Na_2CO_3, acetonitrile	Conductivity	106
Urine	A C_{18} reversed-phase column (TSKgel, ODS-100S, i.d., Tosoh, Tokyo, Japan) modified by saturation with micelles of 3-(N, N-dimethylmyristylammonio)prop anesulfonate (Zwittergent 3–14)	H_3BO_3 + $Na_2B_4O_7$	Conductivity	107
Fertilizers	Shim-pack IC-A1	Citric acid + NaOH	Fluorescence	108
Human plasma	Ion exchanger based on styrene–divinylbenzene with quarternary amine in the Cl^- form of the HEMA-BIO 1000Q type	$NaClO_4$	UV/Vis	109
Tear fluid, blood serum	Dionex IonPac AS4A	Na_2CO_3 + $NaHCO_3$	Conductivity	110
Human saliva	Dionex IonPac AS12A	Na_2CO_3 + $NaHCO_3$	Conductivity	111
Mouse plasma	Dionex IonPac AS9-SC	Na_2CO_3 + $NaHCO_3$	Conductivity	26
Human serum	Dionex IonPac AS4A, AS9A, AS12, or Nucleopac-PA 100, Carbopac PA	Na_2CO_3 + $NaHCO_3$ or NaCl	Conductivity or UV/Vis	28
Human blood	Anion-exchange LC Sykam	Acetonitrile + methanol + H_2O	Electrochemical or UV/Vis	112
Serum	Anion-exchange Hamilton	Methanosulphonic acid	UV/Vis	113

ion chromatography applications for determination of ammonium ions are given in Table 9.

An important recent achievement of ion chromatography is the use of highly selective microcolumns for fast determinations of anions and cations [130]. The application of a monolithic column covered with didodecyldimethylammonium bromide (DDAB) for fast (about 30 seconds) analyses of iodine, chloride, nitrate, nitrite, phosphate and sulphate ions has been described by Hatsis and Lucy [131]. They used 6 mM o-cyanophenol (pH 7.0) at extremely high flow (up to 10 mL/min) as eluent and a conductometric detector. The limits of detection

Table 9. Examples of ion chromatography applications for determination of ammonium ions.

Sample matrix	Column	Eluent	Detector	References
Beverages carbonated	Mixed bed laboratory packed with Yokogawa ICS-A23 and Yokogawa CH1	Oxalic acid	Conductivity	114
Tea	Dionex IonPac CS3	HCl + 2,3-diaminopriopionic acid	Conductivity	115
Spinach	Dionex IonPac CS1	HCl	Conductivity	116
Bread, cheese	Waters IC-PAK Cation M/D	EDTA + HNO_3	Conductivity	117
Food simulants	Dionex IonPac CS3	HCl + 2,3-diaminopriopionic acid	Conductivity	118
Food extracts	Wescan Cation-R	Lithium hydrogenphthalate	Conductivity	119
Grain	Waters IC-PAK Cation	HNO_3	Conductivity	120
Foods	Metrohm Supersep 125 IC-Cation	Citric acid + PDCA	Conductivity	121
Beer	Dionex IonPac CS1	HCl + m-phenylenediamine	Conductivity	83
Mineral water	Waters IC-PAK CM/D	HNO_3 + EDTA	Conductivity	122
Air in cleanrooms	Dionex IonPac CS15	H_2SO_4 + acetonitrile	Conductivity	123
Fog samples	Dionex IonPac CS12	Methanesulphonic acid	Conductivity	55
Snow and firn samples	Dionex IonPac CS12	Methanesulphonic acid	Conductivity	124
Rain	Dionex IonPac CS12	Methanesulphonic acid	Conductivity	56
Waters from peatlands	Dionex IonPac CS10	HCl + 2,3-diaminopropionic acid	Conductivity	125
Atmospheric aerosols	Dionex IonPac CS10	HCl + 2,3-diaminopropionic acid	Conductivity	58
Rainwater	Waters IC Pak CM/D	HNO_3 + EDTA	Conductivity	126
Drinking water	Fast Cation	HCl + 2,3-diaminopropionic acid	Conductivity	127
Fog samples	Dionex IonPac CS12	Methanesulphonic acid	Conductivity	61
Rain water	Dionex IonPac CS2	HCl	Conductivity	62
Drinking water	Dionex IonPac CS16	Methanesulphonic acid	Conductivity	128
Roof runoff waters	Dionex IonPac CS12A	Methanosulphonic acid	Conductivity	66
Rainwater	Dionex IonPac CS12A	H_2SO_4	Conductivity	67
Atmospheric aerosols	Metrohm Metrosep Cation1-2	Tartaric acid	Conductivity	69
Natural waters	Dionex IonPac CG10 + CG10	HCl	Conductivity	129

for all these ions were on a level of a few to a few dozen μg L^{-1}.

Kitamaki et al., have described simultaneous determination of nitrites, nitrates and ammonium ions in river water samples on microcolumns [132] with NO_3^- and NO_2^- detection by a UV detector at λ=206 nm, ammonium ion detection by a fluorescence detector after the post-column derivatization with o-phthaldehyde in the presence of 2-mercaptoethanol.

Ion chromatography as a method applied first of all for ion separation has also been applied in combination with other analytical methods and has been a reference standard as far as sensitivity, repeatability and efficiency are concerned. A thorough comparison of the methods of injection flow analysis and ion chromatography in application to determine nitrogen ionic species has been made by Ferree and Shannon [133].

The quality of analyses performed by ion chromatography has been confirmed by the fact that it has been proved the most versatile and optimal in the analyses of the contents of the main cations and anions (including ionic nitrogen species) in water samples, performed in 155 laboratories in 30 countries within the "Analytical Quality Control and Assessment Studies in the Mediterranean Basin Project" (AQUACON) [134].

Usually the contents of nitrate, nitrite and ammonium ions are determined using ion chromatography with conductometric or UV detection. However, it has been shown that the sensitivity and selectivity of the determinations can be significantly improved by the post-column derivatization methods. An exemplary solution is the use of the reaction of the formation of tri-iodides with nitrites and their spectrophotometric detection [135, 136]. The method permits determination of nitrites on a level of a few μg L^{-1}, and what is particularly important – there is no interference by the presence of chlorine ions not oxidized by iodides. Another direction for improving ionic chromatography is design and development of new fillings of the ion-exchange columns, e.g. zwitterionic stationary phases [137, 138]. These phases permit a greater differentiation of the retention times of the ions determined so a better selectivity of determinations also of chlorine, nitrite, sodium and ammonium ions, which has been a basic limitation of their determination by ion chromatography.

Although this paper is devoted to the applications of ion chromatography for determinations of inorganic nitrogen ions, related methods such as high-performance liquid chromatography (HPLC) with normal and reversed phase columns should also be mentioned. A review of the applications of HPLC with reversed-phase columns in determination of inorganic ions has been presented by Gennaro and Angelino [139], and a review of the HPLC applications with normal phases for simultaneous determinations of nitrates and nitrites has been made by Butt et al. [140].

Although ion chromatography has been known and used for over 30 years, it is still a modern method whose application has been extended over new groups of compounds and types of samples. The progress in the method over the years of its application has been described by Lucy [141, 142].

In conclusion, it should be noted that the majority of classical methods are much more time-consuming and laborious than ion chromatography, and sometimes require the use of expensive and toxic reagents. Definite advantages of these methods are low cost of analyses, relatively simple and cheap apparatus, and hence a possibility of use in most laboratories. The main advantages of ion chromatography includes the short time needed for analyses, possibility of analysis of small volume samples, high sensitivity and selectivity, and most importantly – a possibility of simultaneous separation and determination of a few ions, or ions of the same element at different degrees of oxidation, which provides more comprehensive information for the sample studied.

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