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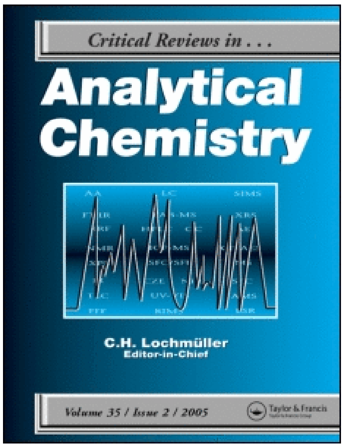

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# Applications of Ion Chromatography for the Determination of Inorganic Cations

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**Ion chromatography is an analytical technique that has revolutionized analysis of inorganic and organic ions, and has changed analytical chemistry in dramatic ways during the past 30 years. Due to a strong environmental impact, metal ion determination and speciation have received significant attention in the last years. Acceptance of ion chromatography for anion analysis was very rapid, primarily because of lack of alternative methods that could quickly and accurately determine anions in a single analysis. However, the situation regarding the analysis of cations was quite different, as there are many fast and sensitive spectroscopic methods, as well as polarography and stripping voltammetry. This paper is a review of application of ion chromatography for the determination of inorganic cations of alkali, alkaline earth, ammonia, heavy and transition metals as well as lanthanides and actinides in environmental samples.**

**Keywords** Ion chromatography, alkali and alkaline earth metals, heavy metals, transition metals, lanthanides, actinides

## INTRODUCTION

A variety of methods have been used for analyses of inorganic cations: traditional spectroscopic techniques such as colorimetry; wet chemical methods such as gravimetric analyses, turbidimetry, and titrimetry; also electrochemical techniques such as using an ion-selective electrode and amperometric titrations. Some of these methods suffer from interferences and limited sensitivity; they can be labor intensive and are often difficult to automate.

The most popular and useful are rapid and sensitive spectroscopic methods like atomic absorption spectroscopy (AAS), inductively coupled plasma – atomic emission spectroscopy (ICP-AES), and inductively coupled plasma – mass spectrometry (ICP-MS), as well as electrochemical methods, such as polarography and stripping voltammetry—all available for cation analyses.

Unfortunately, some of these methods suffer from spectral and chemical interferences, limited sensitivity, labour-intensity and problems with automating, and some are unsuitable for direct trace analyses in complex matrices or for studies on metal speciation (1–3).

The environmental and toxicological effects of metals' presence often depend on its form. The determination of the total metal content using AAS or ICP methods do not provide this information. An alternative to spectroscopic methods are liquid chromatography methods, which can be divided into:

1. Ion chromatography (ion-exchange: cation, anion and ion-exclusion),
2. Reversed-phase ion interaction chromatography,
3. Chelation chromatography, and
4. Multidimensional and multimode chromatography (e.g., ion-exchange coupled with ion-exclusion, or using two or more columns, switching the total flux or a portion of eluate from one to another).

The most popular is ion chromatography, which can be used for the determination of ionic solutes such as: inorganic cations (including alkali metals, alkaline earth metals, heavy metals, transition metals, and rare earth metals, carboxylic, phosphoric and sulfuric acids, detergents, carbohydrates, low-molecular-weight organic bases, ionic metal complexes), and first of all—inorganic anions (4, 5).

Modern ion chromatography was first reported in 1975 in a landmark paper by Small, Stevens, and Baumann (6). Although the term ion chromatography incorporates several separate mechanisms for ion separations, such as ion-exclusion and ion-pairing, the majority of methods use anion- or cation-exchange substrates.

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TABLE 1
Cations determined by ion chromatography methods

| Analyte groups | | Examples of analytes | Separation mechanism | Detection mode |
|---|---|---|---|---|
| Inorganic | Alkali, alkaline earth metals and ammonia | $\mathrm{Li^+}$ , $\mathrm{Na^+}$ , $\mathrm{K^{+,}}$ $\mathrm{NH_4^+}$ , $\mathrm{Rb^+}$ , $\mathrm{Cs^+}$ , $\mathrm{Mg^{2+}}$ , $\mathrm{Ca^{2+}}$ , $\mathrm{Sr^{2+}}$ , $\mathrm{Ba^{2+}}$ | Cation-exchange | Suppressed and non-suppressed conductivity |
| | Heavy and transition metals | $\mathrm{Cu^{2+}}$ , $\mathrm{Ni^{2+}}$ , $\mathrm{Zn^{2+}}$ , $\mathrm{Co^{2+}}$ , $\mathrm{Cd^{2+}}$ , $\mathrm{Pb^{2+}}$ , $\mathrm{Mn^{2+}}$ , $\mathrm{Fe^{2+}}$ , $\mathrm{Fe^{3+}}$ , $\mathrm{Sn^{2+}}$ , $\mathrm{Sn^{4+}}$ , $\mathrm{Cr^{3+}}$ , $\mathrm{V^{4+}}$ , $\mathrm{V^{5+}}$ , $\mathrm{UO_2^{2+}}$ | Anion-exchange ion-exclusion, | UV/Vis, AAS, ICP, ICP-MS, ICP-AES |
| | Lanthanides, actinides | $\mathrm{La^{3+}}$ , $\mathrm{Ce^{3+}}$ , $\mathrm{Pr^{3+}}$ , $\mathrm{Nd^{3+}}$ , $\mathrm{Sm^{3+}}$ , $\mathrm{Eu^{3+}}$ , $\mathrm{Gd^{3+}}$ , $\mathrm{Tb^{3+}}$ , $\mathrm{Dy^{3+}}$ , $\mathrm{Ho^{3+}}$ , $\mathrm{Er^{3+}}$ , $\mathrm{Tm^{3+}}$ , $\mathrm{Yb^{3+}}$ , $\mathrm{Lu^{3+}}$ , $\mathrm{Am^{3+}}$ , $\mathrm{Cm^{3+}}$ , $\mathrm{Pu^{3+}}$ | Anion-exchange, cation-exchange | UV/Vis, AAS, ICP, ICP-MS, ICP-AES |
| Organic | Low molecular weight amines, alkylamines, mono-, di-, tri-, tetramethylamine, alkanolamines, monoethanolamine, diethanolamine | | Cation-exchange, ion-pair | Suppressed and non-suppressed conductivity |
| | High molecular weight amines alkylamines, aromatic amines, cyclohexamines, quaternary ammonium ions, polyamines | | Cation-exchange, ion-pair | Suppressed and non-suppressed conductivity, UV/Vis |

With respect to the use of conductometric detection, two ion-exchange chromatographic modes are defined: suppressed and non-suppressed ion chromatography.

In the suppressed ion chromatography, before detection, the eluate is driven through a suppressor device. Meantime, the background conductivity is greatly reduced so that the sensitivity, with which sample ions can be detected, is increased.

Non-suppressed ion chromatography is performed without the use of the suppressor unit but with ion exchangers of low capacity and very diluted eluents so that the background conductivity is quite low. Ion chromatography with suppressed conductivity detection is used most widely and generally offers the best performance.

Taking into consideration analytical conditions used in the determination of inorganic cations (separation column, eluent, and detection mode), ion chromatography methods can be divided into two groups of analytes:

- Alkali, alkaline earth metals, and ammonium and
- Heavy and transition metals, lanthanides, and actinides.

Cation exchangers are usually made of organic polymers (styrene-divinylbenzene; ethylvinylbenzene-diviniylbenzene, polymethacrylate, polyvinyl); however, a variety of other substrate materials is also available (e.g., latexed cation exchangers and silica-based exchangers).

Detection of alkali, alkaline earth metals, and ammonia is based on a conductivity detector. Next, heavy metals, transition metals, and rare earth elements are usually detected by spectrometric methods.

Division of ion chromatography methods, including separation mechanism and detection mode used, is given in Table 1.

The main goal of ion chromatography as an analytical technique is to provide complete information about the ionic composition of an analyzed sample. It is often necessary to use two different sets of ion chromatography conditions for separation and determination of the cationic and anionic species.

In this connection, data on the ionic composition of a sample can be obtained either by two parallel analyses on two different ion chromatographs, or by two consecutive analytes of the same sample with one instrument but with different columns and under different elution conditions. The ideal case can be the simultaneous determination of cations and anions by ion chromatography from a single injected sample (7). The eluent selection criteria for the simultaneous determination of anions and cations were described by Tarter (8).

The emphasis of ion chromatographic application of inorganic cations determination is mostly on the following areas: environmental analysis, power plant chemistry, semiconductor industry, metal processing, pharmaceutics, biotechnology, mining, agriculture, food and beverages, electroplating, and the pulp and paper industry. In spite of the strong competition from atomic spectrometric techniques, the ion chromatography of metal cations is now well established as a relatively cheap method with ease of automation and on-line capability, it is particularly attractive in a wide variety of routine trace analysis.

Methods for cation analysis tend to be based upon spectroscopic techniques, although ion chromatography offers the advantage of providing information on metal speciation. Unlike the spectroscopic methods, ion chromatography can distinguish different metal oxidation states such as Cr(III)/Cr(VI), Fe(II)/Fe(III), or As(III)/As(V).

Moreover, ion chromatography has also been used to determine stable metal complexes. A further advantage of ion chromatography over AAS is its relatively wide dynamic range, which means that it is possible to determine low analyte concentrations in the presence of high levels of other species, which would tend to cause problems in the nebulizers used in atomic spectrometry (9).

The majority of inorganic cations, listed as primary drinking water contaminants, are transition metals which are usually analyzed using spectroscopic methods, such as AAS, ICP-AES, or ICP-MS. However, the United States Environmental Protection Agency (US EPA) approved ion chromatography for the analyses of the alkali and alkaline earth cations and ammonium in rain water and wet precipitation, and provides a straightforward method for the simultaneous analyses of these cations. The International Standard Organization (ISO) published Method 14911 for the simultaneous determination of dissolved alkali and alkaline earth cations, ammonia, and manganese in water and wastewater using suppressed ion chromatography.

Recently, ion chromatography became well established as a regulatory method for the analysis of inorganic ions in water and wastewater (10). Regulatory ion chromatographic methodss recommended by ISO, US EPA, and American Society for Testing and Materials (ASTM) for environmental samples in the range of inorganic cations are listed in Table 2. The ion chromatography procedures worked out by the world-leader ion chromatography manufacturers Dionex and Metrohm are listed in Tables 3 and 4, respectively.

## ALKALI, ALKALINE EARTH METALS AND AMMONIA

When H. Small and co-workers (6) introduced the concept of ion chromatography with conductometric detection in 1975, the major part of their work was dedicated to the determination of alkali, alkaline earth, and ammonia cations. This system consists of a low-capacity separation column and a high-capacity suppressor column, containing a surface-sulfonated styrene-divinylbenzene copolymer resin and a strongly basic anion-exchange resin in the hydroxide form, respectively.

After a separation of cationic species has been accomplished on the separation column with an appropriate eluent, the latter is neutralized in the suppressor column. It reduces the background conductivity of the eluent. Simultaneously, cationic analytes are converted into their hydroxides which allows for their sensitive, conductometric detection. The main difficulty which had to be overcome was the different selectivity of the ion-exchange resins, normally used to separate monovalent and divalent cations, respectively. These cation exchangers were characterized by a much larger selectivity for divalent cations than for monovalent cations; thus, divalent cations have resolutely longer retention times than monovalent.

Due to large differences in selectivity of alkaline earth towards alkali cations, HCl is needed to elute the monovalent cations, while stronger divalent eluent components (e.g., *m*-phenylenediamine) can be used for the elution of divalent cations.

In non-suppressed ion chromatography mixtures of ethylenediamine and aliphatic carboxylic acids such as tartaric acid or oxalic acid are typically employed. For the simultaneous determination of alkali metals, alkaline earth metals, and ammonia on carboxylate-based acid cation exchangers, methanesulfonic acid or sulfuric acid are usually recommended as eluents.

The breakthrough was the introduction of a new kind of cation-exchange resin (latex-coated, e.g., Dionex IonPac CS3) and replacement of *m*-phenylamine by the zwitterion 2,3-diaminopropionic acid monochloride (DPA). From then it was possible to simultaneously analyze both groups of cations, in the presence of ammonium, in one column and to improve peak efficiencies, although analysis still required a long time and a baseline resolution was not completely achieved.

Next, progress was achieved by introducing a different kind of column containing carboxylate functionalities, instead of traditional sulfonic acid with a low selectivity for hydronium acid (so-called "*Schmoburg column*"). The stationary phase, based on a poly (butadiene-maleic acid) copolymer silica gel coated, coupled with eluents containing slightly acidic complexing agents (e.g., tartaric acid), is used for analysis of alkali, alkaline earth, and ammonia cations in non-suppressed ion chromatography.

The elution order of alkali, alkaline earth metals, and ammonia cations depends on many factors (e.g., column selectivity, eluent type) and usually is as follows: $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, and $Ba^{2+}$ .

Interestingly, the transition metal manganese can also be analyzed together with such metal ions as alkali and alkaline earth metals, although it is generally assumed that the transition metal hydroxides formed in the suppressor system will precipitate and, thus, may not be detected by suppressed conductivity ion chromatography. However, the kinetics of this reaction is not the same for all metals, especially because a weakly acidic milieu ($pH = 6$) prevails in the suppressor after the suppressor reaction, but many transition metals only precipitate at pH values above 7.

Determination of ammonium by any method other than ion chromatography is very difficult, thus one of the most important advantages of ion chromatography is simultaneous separation and detection of alkali, alkaline earth metals, and ammonia, as well as some organic amines (11–13).

Environmental samples, at low levels of ammonium in matrices with high concentration of sodium, are a typical case. Unfortunately, ammonium and sodium ions have similar selectivity for the common stationary phases. This problem can

TABLE 2
Ion chromatography methods for inorganic cations analysis established by ISO, US EPA and ASTM

| Method number | Method name | Analytes | Matrices |
|---|---|---|---|
| | ISO Methods | | |
| 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 | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mn^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $Sr^{2+}$, $Ba^{2+}$ | Drinking water, wastewater, ground water |
| ISO 10304-3 (1997) | Water Quality - Determination of Dissolved Anions by Liquid Chromatography of Ions – Part 3: Determination of Chromate, Iodide, Sulfite, Thiocyanate and Thiosulfate | $CrO_4^{2-}$ | Wastewater |
| ISO 16749 (2005) | Workplace Air - Determination of Hexavalent Chromium in Airborne Particulate Matter - Method by Ion Chromatography and Spectrophotometric Measurement Using Diphenylcarbazide | $CrO_4^{2-}$ | Airborne particulate matter |
| | US EPA Methods | | |
| US EPA Method 200.10 (1997) | Determination of Trace Elements in Marine Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma - Mass Spectrometry | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $VO^{2+}$, $VO_2^{2+}$, $UO_2^{2+}$ | Brines, seawater, marine water, estuarial water |
| US EPA Method 200.13 (1997) | Determination of Trace Elements in Marine Waters by Off-Line Chelation Preconcentration with Graphite Furnace Atomic Absorption | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$ | Brines, seawater, marine water, estuarial water |
| US EPA Method 218.6 (1994) | Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography | $CrO_4^{2-}$ | Drinking water, ground water, wastewater |
| US EPA Method 300.7 (1995) | Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Wet deposition, rain water, snow, dew, sleet, hail |
| US EPA Method 1636 (1996) | Determination of Hexavalent Chromium by Ion Chromatography | $CrO_4^{2-}$ | Drinking water, ground water, wastewater |
| | ASTM Methods | | |
| D 5257-93 | Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography | $CrO_4^{2-}$ | Drinking water, ground water, wastewater |

(*Continued on next page*)

TABLE 2
Ion chromatography methods for inorganic cations analysis established by ISO, US EPA and ASTM (*Continued*)

| Method number | Method name | Analytes | Matrices |
|---|---|---|---|
| D 6504-00 | Standard Practice for On-Line Determination of Cation Conductivity in High Purity Water | Total cation conductivity of $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | High purity water |
| D 6832-02 | Standard Test Method for the Determination of Hexavalent Chromium in Workplace Air by Ion Chromatography and Spectrophotometric Measurement Using 1,5-Diphenylcarbazide | $CrO_4^{2-}$ | Workplace air |
| D 6919-03 | Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Reagent water, surface water, ground water, wastewater |
| D 6994-04 | Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection | $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$, $Cu(CN)_6^{4-}$, $Ni(CN)_6^{4-}$, $Ag(CN)_6^{5-}$ | Drinking water, ground water, wastewater |
| UOP 959-98 | Ammonium Determination in Aqueous Solutions by Ion Chromatography | $NH_4^+$ | Drinking water, waste water |
| WK653 | New Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Reagent water, surface water, ground water, wastewater |

be solved by a column-switching technique or by applying the appropriate columns and eluents. The separation can be improved by using step gradient eluents utilizing organic solvents; however, gradient elution techniques in cation exchange chromatography are less common than in anion exchange chromatography.

Determination of alkali, alkaline earth metals, and ammonia is the most often used application of ion chromatography in the range of cation analyses. After the publication of ISO 14911 Method the number of laboratories applying cation ion chromatography has significantly increased. The examples of applications of ion chromatography (literature data encompassing years 1980–2008) for the determination of alkali, alkaline earth metals, and ammonia in different types of samples include: analyzed ions, separation column, eluent, detection mode, and sample matrix (Table 5).

## HEAVY AND TRANSITION METALS, LANTHANIDES, AND ACTINIDES

Because of a strong environmental impact, determination and speciation of heavy and transition metals, as well as rare elements have received particular attention within the last few years (52, 53). Due to the lack of simple and sensitive colorimetric methods, the trace analysis of heavy and transition metal ions represents a considerable challenge. For many years the choice of analytical techniques for metal analysis in samples of wide ranging composition has been mainly AAS, ICP, ICP-MS, and ICP-AES (54). Using these methods, removing sample matrix interferences and/or preconcentration is necessary.

Nowadays the most promising analytical techniques used for metal speciation analysis are hyphenated techniques. They rely on chromatographic separation (e.g., ion chromatography)

TABLE 3
Selected ion chromatography methods for cation analysis recommended by Dionex

| Method number | Method name | Analytes | Sample matrix |
|---|---|---|---|
| AN 4 | Analysis of Engine Coolants by Ion Chromatography | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Coolants |
| AN 25 | Determination of Inorganic Ions and Organic Acids in Non-Alcoholic Carbonated Beverages | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Non-alcoholic drinks |
| AN 69 | Determination of Aluminum in Complex Matrices Using Chelation Ion Chromatography | $Al^{3+}$ | Waters |
| AN 72 | Determination of Trace Metals in Water Miscible Organic Solvents by Ion Chromatography/Inductively Coupled Argon Plasma Spectroscopy (IC/ICAP) | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3}$, $Pb^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $VO^{2+}$, $VO_2^{2+}$ | Waters, alcohols, acetonitrile |
| AN 73 | Determination of Trace Transition Metals in Reagent-Grade Acids, Bases, and alts Using Ion Chromatography/Inductively Coupled Argon Plasma Spectroscopy (IC/ICAP) | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $Al^{3+}$ | Water solutions of: acid, base and their salts |
| AN 77 | Elimination of Iron and Aluminum as Matrix Interferences for Determination of Transition Metals Using Chelation Ion Chromatography | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $Al^{3+}$ | Water solutions with high Al and Fe contents |
| AN 79 | Determination of Uranium and Thorium in Complex Matrices Using Chelation Ion Chromatography | $Th^{3+}$, $UO_2^{2+}$ | Complex matrix water samples |
| AN 80 | Determination of Dissolved Hexavalent Chromium in Drinking Water, Ground Water, and Industrial Wastewater Effluents by Ion Chromatography | $CrO_4^{2-}$ | Drinking water, wastewater, ground water |
| AN 86 | Determination of Trace Cations in Power Plant Waters Containing Morpholine | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Reagent water |
| AN 94 | Determination of Trace Cations in Concentrated Acids Using AutoNeutralization Pretreatment/Ion Chromatography | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Concentrated acids |
| AN 106 | Ion Chromatography in the Pharmaceutical Industry | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Pharmaceuticals |
| AN 108 | Determination of Transition Metals in Serum and Whole Blood by Ion Chromatography | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $Al^{3+}$, $Fe^{3+}$, | Serum, blood |
| AN 120 | Determination of Calcium and Magnesium in Brine | $Mg^{2+}$, $Ca^{2+}$ | Brines |
| AN 131 | Determination of Transition Metals at ppt Levels in High Purity Water | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $Fe^{3+}$, | High-purity water |
| AU 137 | Determination of Trace Lithium in Industrial Process Waters | $Li^+$ | Industrial process water |
| AN 141 | Determination of Inorganic Cations and Ammonium in Environmental Waters by Ion Chromatography Using the IonPac CS16 Column | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | River water, lake water, ground water, sea water |

(*Continued on next page*)

TABLE 3
Selected ion chromatography methods for cation analysis recommended by Dionex (*Continued*)

| Method number | Method name | Analytes | Sample matrix |
|---|---|---|---|
| AN 144 | Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography | $CrO_4^{2-}$ | Drinking water |
| AN 152 | Determination of Sodium at the Parts-Per-Trillion Level in the Presence of High Concentrations of Ethanolamine in Power Plant Waters | $Na^+$ | Power plant water |
| AU 155 | Determination of Cations and Amines in Hydrogen Peroxide by Ion Chromatography Using a RFIC$^{TM}$(Reagent-Free) System | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Hydrogen peroxide |
| AN 158 | Determination of Trace Sodium and Transition Metals in Power Industry Samples by Ion Chromatography with Non-suppressed Conductivity Detection | $Na^+$, $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Mn^+$, $Zn^{2+}$, $Fe^{3+}$, | Wastewater, reagent water |
| TN 10 | Determination of Transition Metals by Ion Chromatography | $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$ | Water |
| TN 23 | Ion Chromatography of Lanthanide Metals | $La^{3+}$, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Tm^{3+}$, $Yb^{3+}$ | Wastewater |
| TN 24 | Determination of Chromium by Ion Chromatography | $Cr^{3+}$, $CrO_4^{2-}$ | Wastewater |
| TN 26 | Determination of Cr(VI) in Water, Wastewater, and Solid Waste Extracts | $CrO_4^{2-}$ | Wastewater, soild waste extracts |
| TN 27 | Determination of Lanthanides Metals in Digested Rock Samples by Chelation Ion Chromatography | $La^{3+}$, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Tm^{3+}$, $Yb^{3+}$ | Rocks |

combined with highly selective and accurate detection modes (e.g., ICP-MS and ICP-AES) (55, 56).

Moreover, these new high-cost technologies are often beyond the reach of most laboratories in many developing countries. Hence, a great need still persists for investigating a cheaper, faster, more accurate, and highly sensitive analytical method for the determination of heavy and transition metals at trace levels, especially in the range of speciation analysis.

Until recently, analytical methods (e.g., spectrometric) allowed analysts to determine the total content of metals only, but it was soon realized that this analytical information was insufficient.

Biochemical and toxicological investigation has shown that for living organisms the chemical form of a specific element or the oxidation state in which that element is introduced into the environment is as important as its quantities.

Recently, speciation analysis plays a unique role in the studies of biogeochemical cycles of chemical compounds, determination of toxicity and ecotoxicity of selected elements, quality control of food products, control of medicines and pharmaceutical products, technological process control, research on the impact of technological installation on the environment, examination of occupational exposure and clinical analysis (57).

Ion chromatography makes it possible to perform a fast and sensitive determination of heavy and transition metals on the detection levels in the lower $\mu$g/L range and separation times of about 15 minutes.

There is a significant number of ion chromatography methods developed for the determination of metal pollutants in a wide variety of environmental samples (58). The review of current state and progress of ion chromatography as an analytical tool for trace metal analysis in environmental samples is described by Shaw and Haddad (59).

Because heavy and transition metal ions are forming in the suppressor insoluble hydroxides, they can not be analyzed using suppressed conductivity method. The separation of heavy and transition metals with ion exchangers requires a complexation of the metal ions in the mobile phase to reduce their effective charge density. Because the selectivity coefficient for heavy and

TABLE 4
Selected ion chromatography methods for cation analysis recommended by Metrohm

| Method number | Method name | Analytes | Sample matrix |
|---|---|---|---|
| C-1 | Sodium, Potassium, Calcium and Magnesium in Drinking Water | $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Drinking water |
| C-2 | Sodium, Potassium, Calcium and Magnesium in Cooling Water | $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Coolants |
| C-14 | Sodium, Ammonium, Potassium, Calcium and Magnesium in Wastewater | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Wastewater |
| C-18 | Determination of Lithium, Sodium, Ammonium, Potassium, Manganese, Calcium, Magnesium and Strontium in Sewage Sludge After Digestion with $HNO_3$ | $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Mn^{2+}$, $Sr^{2+}$ | Sewage sludge |
| C-19 | Determination of Sodium, Ammonium, Potassium, Calcium and Magnesium in Rain Water | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Rain water |
| C-23 | Determination of Sodium, Ammonium, Diethanolamine, Diglycolamine and Potassium in Wastewater | $Na^+$, $NH_4^+$ | Wastewater |
| C-44 | Determination of Cations in Tap Water | $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Drinking water |
| C-55 | Determination of Lead, Zinc, Indium, Cadmium, Cobalt, Ammonium, Potassium, Manganese, Magnesium and Calcium | $Zn^{2+}$, $In^{2+}$, $Co^{2+}$, $Cd^{2+}$, $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Wastewater |
| C-69 | Zinc, Sodium, Calcium and Magnesium in an Industrial Bath | $Zn^{2+}$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ | Wastewater |
| C-79 | Nickel, Zinc, Cobalt, Iron(II) and Manganese in LiBr Using Post-Column Reaction | $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Li^+$ | LiBr |
| C-97 | Cations in Ethanol Used as Biofuel | $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Ethanol |
| C-98 | Lanthanides by Ion Chromatography Applying Non-Suppressed Conductivity Detection | $La^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Tm^{3+}$, $Yb^{3+}$ | Wastewater, solid samples |
| C-99 | Lanthanides in a Rock Sample by Ion Chromatography Applying Non-Suppressed Conductivity Detection | $La^{3+}$, $Nd^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Yb^{3+}$ | Rock samples |
| C-103 | Standard Cations in Lake Water on the Metrosep C 3 – 250 Column | $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Lake water |
| C-106 | Lanthanides by Ion Chromatography with Post-Column Reaction and UV/VIS Detection | Lanthanides | Solid samples |
| U-24 | Vanadium Speciation Applying Ion Chromatography with UV/VIS Detection | $V^{3+}$, $V^{5+}$ | Solid samples |

transition metals of the same valency are so similar, a selectivity change is obtained only by introduction of a secondary equilibrium, such as a complexation equilibrium established by adding appropriate complexing agents to the mobile phase.

When selecting a ligand for the separation and elution of heavy and transition metal ions from cation exchangers, the following guidelines should be taken into account:

- Metal ions and ligands must form neutral or anionic complexes,
- Different complex formation constants for the various metals increase the selectivity, and
- The transition metal complexes being formed should be thermodynamically stable and kinetically labile.

Ion chromatographic separation by anion exchange of metal ions involves their presence as negatively charged complexes which can be obtained off-line and on-line. In the case of the off-line method metal complexes are formed before the chromatographic separation, because complexes must be stable enough to

## TABLE 5
The examples of applications of ion chromatography for the determination of alkali, alkaline earth metals and ammonia

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ | Dionex Fast Cation I, Fast Cation II | 17 mM HCl + 0.26 mM DPA | Suppressed conductivity | Drinking water, waste water, surface water | (14) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^+$ | $TSK_{gel}$ IC cation SW | 3.5 mM EDTA + 10 mM citric acid | Non-suppressed conductivity | Waste water, drinking water | (15) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex CS1 | 0.028 mM $Ce(NO_3)_3$ | Indirect fluorescence | Rain water, fog, clouds, aerosols | (16) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | $TSK_{gel}$ Super-IC-Cation | 2.4 mM 5-sulfosalicylic acid | Non-suppressed conductivity | River water | (17) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac Fast Cation I, Fast Cation II | 19 mM HCl + 0.3 mM DPA | Suppressed conductivity | Snow, ice cores | (18) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS10 | 40 mM HCl + 12 mM DPA | Suppressed conductivity | Organic rich natural water from peatlands | (19) |
| $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Rb^+$, $Cs^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ | Dionex IonPac CS 10 | 40 mM HCl + 20 mM DPA | Suppressed conductivity | Rain water | (20) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Waters IC Pak C M/D | 3.0 mM $HNO_3$ + 0.1 mM EDTA | Non-suppressed conductivity | Rain water | (21) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Sykam LCA K01 | 4.5 mM $HNO_3$, 1 mM histidine + 1 mM DPA + 12 mM HCl | Suppressed conductivity | Fog | (22) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12 | 20 mM MSA | Suppressed conductivity | Rain water, snow | (23) |
| $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ | Dionex IonPac CS 12 | 20 mM MSA | Suppressed conductivity | Mineral water | (24) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Sr^{2+}$, $Ca^{2+}$ | Dionex IonPac CS 12 | 20 mM DPA | Suppressed conductivity | Mineral water | (25) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12 | 21 mM MSA | Suppressed conductivity | Snow | (26) |
| $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{-2+}$ | Waters IC-PAK CM/D | 7.5 mM citric acid + 1.0 mM PDCA | Suppressed conductivity | Drinking water | (27) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Sr^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12A | MSA | Suppressed conductivity | Fertilizer industry wastewater | (28) |
| $K^+$, $Na^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac Cation Fast I, IonPac CS10 | 50 mM HCl + 5.1 mM DPA | Suppressed conductivity | Ice cores | (29) |
| $Li^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS15, IonPac CS12A | $H_2SO_4$+ 18-crown-6 | Suppressed conductivity | Biological samples | (30) |
| $Li^+$, $K^+$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12A | MSA | Suppressed conductivity | High purity water | (31) |
| $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | $TSK_{gel}$ Super IC-cation | $H_2SO_4$+ amino acids | Suppressed conductivity | River water, tap water, pond water | (32) |

(*Cintinued on next page*)

## TABLE 5
The examples of applications of ion chromatography for the determination of alkali, alkaline earth metals and ammonia (*Continued*)

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| Analytes | Column | Eluent | Detection mode | Sample matrix | References |
| $Li^+$, $Na^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12A | 11 mM $H_2SO_4$ | Suppressed conductivity | High purity water, drinking water | (33) |
| $K^+$, $Na^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12 | 20 mM MSA | Suppressed conductivity | Fog | (34) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Waters IC-PAK CM/D | 5 mM $HNO_3$+ 0.1 mM EDTA | Suppressed conductivity | Mineral waters | (35) |
| $Na^+$, $NH_4^+$, $K^+$ | Metrosep C2 | 4 mM tartaric acid + 0.75 mM DPA | Non-suppressed conductivity | atmospheric particulate matter | (36) |
| $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, $Sr^{2+}$ | Laboratory-made iminodiacetic acid bonded silica column | $KNO_3$ | UV-Vis | Brines | (37) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | TSKgel Super-IC-Cation | 1.75 mM 5-sulfosalicylic acid | Non-suppressed conductivity | Tap water, river water | (38) |
| $Na^+$, $K^+$ | Dionex IonPac CS12 | 20 M MSA | Suppressed conductivity | Fog water | (39) |
| $Mg^{2+}$, $Ca^{-2+}$, $Sr^{2+}$, $Ba^{-2+}$ | Laboratory-made silica-based chimica bonded | 1.5 mM $HNO_3$ | Suppressed conductivity | Oil field water | (40) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{-2+}$ | Laboratory-made aluminium-adsorbing silica | 1.2 mM tyramine + 0.2 mM oxalic acid + 5 mM 15-crown-5, 5 mM 18-crown-6 | UV ($\lambda = 265$ nm) | Waste water | (41) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12 | 20 mM MSA | Suppressed conductivity | Rain water | (42) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS16 | 26 mM MSA | Suppressed conductivity | Surface water, drinking water, waste water | (43) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Metrohm Cation 1-2 | 4 mM tartaric amid + 0.75 mM DPA | Suppressed conductivity | Rain water | (44) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Metrohm Cation 1-2 | 10 mM tartaric acid | Non-suppressed conductivity | Rain water | (45) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Dionex IonPac CS12 | 20 mM MSA | Suppressed conductivity | Rain water | (46) |
| $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ | Metrohm Cation 1-2 | 4 mM tartaric acid + 0.75 mM DPA | Suppressed conductivity | Rain water | (47) |
| $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, | Dionex IonPac CS12A | MSA | Suppressed conductivity | Rain water | (48) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Rb^+$, $Cs^+$ | Laboratory-made silica-based chimica bonded, Nucleosil 50-5 IDA | $HNO_3$ | Non-suppressed conductivity | Drinking water, river water | (49) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$ | Laboratory-made ultra-short silica-based chimica bonded, Nucleosil 50-5 IDA | $Na_2CO_3$, citric acid, ethylene diamine | Non-suppressed conductivity | Water | (50) |
| $Li^+$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{-2+}$ | Dionex IonPac CS12A | MSA, Amido-sulfonic acid | Suppressed conductivity | Water, wastewater | (51) |

avoid decomposition during separation or ligand must be added to the eluent.

In the on-line method, complexation is performed in the chromatographic column by adding the proper ligand to the eluent. Among many ligands (mainly organic acids) used for the simultaneous ion chromatography of metals, the most common eluents used are oxalic acid, tartaric acid, citric acid, pyridine-2,6-dicarboxylic acid (PDCA), $\alpha$ -hydroxyisobutyric acid (HIBA), 1,2-diaminocyclohexanetetraacetic cid (DCTA), dietyloenetriaminopentaacetic acid (DTPA), tetraacetic acid (EGTA), and ethylenediaminetetraacetic acid (EDTA).

The separation of various heavy and transition metals may be optimized by varying the pH value. If weak organic acids are used as complexing agents, lowering pH leads to a decrease in the effective ligand concentration.

The ability of metals to form anionic complexes is used for the separation of transition metals on anion exchangers. Such separations are based on the significant differences in the stability of these complexes with anionic complexing agents and the different affinity of anionic complexes towards the stationary phase of anion exchangers.

The most important parameter determining retention is the valency of complex, which, in turn, depends on the charge numbers of the central metal ion and the ligand, as well as on the coordination number of the complex.

Since EDTA forms, at the proper pH values, negatively charged complexes with divalent and trivalent metal ions, the possibility of simultaneous separation of anions from metal ions is also feasible just as the speciation of metal ions. In these procedures complexes can be obtained in two ways. The first way is through its formation before the chromatographic separation. It is pre-column complexation; complexes must be stable enough to avoid decomposition during separation or ligand must be added to the eluent. The second way is based on the complexation in the chromatographic column itself.

Ion chromatography of metal-EDTA complexes can be performed with anion-exchange columns and anions and metals can be separated as anionic complexes in the same run. Analysis of cations such as $Fe^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Cd^{2+}$, and $Fe^{3+}$ are often carried out with an eluent mixture of oxalic and citric acid, and detection via post-column reaction (PCR) of the column effluent with 4-(2-pirydylazo)resorcinol (PAR) and subsequent photometric detection of the resulting chelate complexes at 520 nm.

For a long time, post-column derivatisation with PAR was limited to the analysis of iron, copper, nickel, manganese, cadmium, lead, zinc, uranium, and lanthanides. It was connected with kinetics of complex formation with PAR, which is hindered by the complexing agents present in the mobile phase (60).

In the past, the main problem was related to the lack of resolution between $Fe^{3+}$, $Cu^{2+}$, and $Ni^{2+}$ ions. These difficulties were finally remedied in the mid-1980s, when Dionex introduced new IonPac CS5 separation column. That column is a latexed anion exchanger with mixed anion and cation exchange capacity. In contrast to IonPac CS5 separation column, the IonPac CS5A column commercialized in 1996 is a bifunctional latexed cation exchanger. This column is the most effective analytical column for heavy and transition metal separation.

Some of ion chromatography methodologies use a rather complex instrumentation (detectors, gradient pumps, and several arrays of separation columns) for achieving a better separation and detection of these elements as well as for optimizing the analysis time. Gradient pumps, for example, enable ion chromatography analyses to be carried out with gradient concentration programs of eluent. Such an instrumental feature constitutes a strong limitation, especially for laboratories which are still using a former or standard ion chromatography instrumentation based on the use of an isocratic high-pressure pump.

The analysis of natural-water brines, which include seawater, subsurface brines, geothermal brines, and very high salinity groundwater, is being complicated by high ionic strength and excess of chloride in the sample (61).

For these kinds of samples the selectivity of the chromatographic separation can be enhanced by the use of chemically bonded phases, where complexation reactions in the stationary phases, ion-exchange due to free or protonated chelating groups which act as ion-exchange sites, and, in some cases, complexation in the eluent are responsible for the separation (62). A recent review of chelating ion chromatography has been given by Paull and Haddad (63) and Ding and Mou (64).

Ion chromatography is a powerful tool for speciation analysis of different metal ions. Depending on oxidation state, metal ions can have radically different properties [e.g., Se(IV)/Se(VI) and As(III)/As(V)]. Arsenic can exist as As(V) and the inorganic arsenate ion ($AsO_4^{3-}$), $HAsO_4^{2-}$ in aquatic systems, or As(III) and the arsenite anion ($AsO_3^{3-}$). Selenium is another oxyanion that is toxic dependent upon its chemical form and subsequent bioavability.

It is an essential element for life, but becomes toxic at a concentration <4 mg/L; therefore, it is important to monitor the concentrations of this element in soils and water and its subsequent entry into food chain. The World Health Organization (WHO) guideline for drinking water quality defines a limit of 0.01 mg/L for selenium as well as for arsenic. Papers published since 1980 on As and Se speciation in environmental waters have been recently reviewed by Guerin et al. (65).

Another well known example of a heavy metal which toxicity depends on its oxidation state is chromium. Cr(III) and Cr(VI) ions differ with regards to their biological, chemical, and toxicological properties. Cr(III) compounds are essential in the human body, playing a vital role in the metabolism of glucose, while Cr(VI) is toxic and carcinogenic (66).

The WHO guidelines set a limit of 0.05 mg/L for this metal in drinking water, while the California Department of Health Services recently issued a public health goal of 0.0025 mg/L total chromium and 0.0002 mg/L for Cr(VI).

The chemistry of chromium is complex, because depending on sample pH and its matrix, chromium can occur in many

TABLE 6
The examples of applications of ion chromatography for the determination of heavy metals and transition metals

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cu^{2+}$ | Dionex AS9-HC | $Na_2$ $CO_3$ | Suppressed conductivity | Water | (80) |
| $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Mn^{2+}$ m, $Zn^{2+}$ | IonPac SCS1 (250 mm × 4 mm I.D.) | 2.5 mM MSA + 0.8 mM oxalic acid | Non-suppressed conductivity | Mineral water, beer | (81) |
| $Pd^{2+}$, $Pt^{2+}$ | Dionex IonPac AG4-SC, IonPac AG10, IonPac AG11, IonPac AG15, IonPac AG16 | Oxalic acid, HCl, $HNO_3$, $HClO_4$ | ICP-MS | Urban road dust, atmospheric particulates | (82) |
| $Fe^{3+}$, $Fe^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Mn^{2+}$ | Dionex IonPac CS5A | 7.0 mM PDCA + 66 mM KOH + 74 mM formic acid | UV ($\lambda = 530$ nm) | Industrial waste water | (83) |
| $Cu^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$ | Merck Chromolith Si | 80% MeCN + 10.3 mM $CH_3COONH_4$ | UV ($\lambda = 510$ nm) | Drinking water | (84) |
| $Fe^{3+}$, $Fe^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$ | Dionex IonPac CS2 | 10 mM oxalic acid + 7.5 mM citric acid or 40 mM tartaric acid + 12 mM citric acid | UV ($\lambda = 520$ nm) | Ground water | (85) |
|  | Dionex IonPac CS5 | 6 mM PDCA, 50 mM oxalic acid + 95 mM LiOH |  |  |  |
| $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Fe^{2+}$ | Dionex IonPac CS5A | PDCA | UV ($\lambda = 530$ nm) | Biological samples | (86) |
| $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Fe^{3+}$ | Ion Pac CS5A | 160 mM $NaNO_3$ + 36 mM oxalic acid |  | Airborne particulates | (87) |
| $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$ | Mini-column packed with Chelex-100 resin | Tartaric acid + oxalic acid | Non-suppressed conductivity | Drinking water, wastewater | (88) |
| $Zn^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zr^{4+}$, $Pb^{2+}$, $Fe^{3+}$<br>$Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Fe^{3+}$ | Wescan cation | Tartaric acid, oxalic acid, perchloric acid, LiOH, $HNO_3$ | UV/Vis ($\lambda = 520$ nm) | Water | (89) |

(*Continued on next page*)

TABLE 6
The examples of applications of ion chromatography for the determination of heavy metals and transition metals (*Continued*)

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Mo^{2+}$, $Pb^{2+}$, $Fe^{3+}$ | Dionex IonPac AS11 | $HNO_3$ | ICP-MS | Ground water, surface water | (90) |
| $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Cd^{2+}$, $Al^{3+}$, $Pb^{2+}$, $Fe^{3+}$ | Dionex IonPac CS5A | Oxalic acid + $NaNO_3$ | UV/Vis ($\lambda = 560$ nm) | Drinking water | (91) |
| $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$ | Dionex IonPac CS5A | Oxalic acid + citric acids | UV/Vis ($\lambda = 520$ nm) | Airborne particulates | (92) |
| $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Mo^{2+}$, $Pb^{2+}$, $Fe^{3+}$ | IonPac CG5A+CS5A | 28 mM oxalic acid + 45 mM NaCl + 116 mM $NaNO_3$ + 40 mM HCl | UV/Vis ($\lambda = 530$ nm) | Honey | (93) |
| $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Cd^{2+}$, $Fe^{3+}$, $Pb^{2+}$ | Dionex IonPac CS5A | 28 mM oxalic acid + 250 mM $NaNO_3$ | UV/Vis ($\lambda = 530$ nm) | Atmospheric particulates | (94) |
| $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Mn^{2+}$, $Pb^{2+}$ | Dionex IonPac CS5A | Oxalic acid + NaCl | UV/Vis ($\lambda = 560$ nm) | Biological samples | (95) |
| $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Fe^{2+}$ | Dionex IonPac CS2 | 20 mM Oxalic acid + 20 mM citric acid | UV/Vis ($\lambda = 520$ nm) | Airborne particulates | (96) |
| $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Fe^{3+}$, $Al^{3+}$ | Hamilton PRP-1 | 0.25 mM DPA + 100 mM $KNO_3$ | UV/Vis ($\lambda = 520$ nm) | Water, rice | (97) |
| $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Fe^{2+}$, $Fe^{3+}$ | Dionex HPIC-CSS | Oxalic acid | UV/Vis ($\lambda = 520$ nm) | Ground water, surface water | (98) |
| $Pb^{2+}$, $Fe^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Mn^{2+}$, $Co^{2+}$ | Dionex IonPac CS5A | PDCA | UV/Vis ($\lambda = 520$ nm) | Cosmetic products | (99) |

TABLE 7
The examples of applications of ion chromatography for the speciation analysis of selected heavy and transition metals

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| $Cr^{3+}$, $CrO_4^{2-}$ | Home-made iminodiacetate resin | 0.70 M $HNO_3$ | ICP-MS | Sea water | (100) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Dionex IonPac CS5 | 2 mM PDCA + 2 mM $NaHPO_4$+ 1 mM NaI + 5 mM $CH_3COONH_4$ | On-line thermal lens spectrometric | Drinking water | (101) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Excelpak ICS-A23 | 1 mM EDTA-$2NH_4$ + 10 mM oxalic acid | ICP-MS | Drinking water, waste water | (102) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Dionex IonPac CS5 | PDCA + $(NH_4)_2HPO_4$ + $CH_3COONH4$ + $NH_4OH$ + $NH_4I$ | Laser-enhanced ionization spectrometry | Water | (103) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Dionex IonPac CG2 + IonPac AG4A | $K_2SO_4$+ $HNO_3$ | Chemiluminescence | Water | (104) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Dionex IonPac CS5A | 40 mM $MgSO_4$ + 30 mM $HClO_4$ | UV ($\lambda = 365$ nm) | Drinking water, Drain water, waste water | (105) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Dionex IonPac CG5 + AS7 | 55 mM $K_2SO_4$ + 95 mM $KNO_3$ | Chemiluminescence | Waste water | (106) |
| $Cr^{3+}$, $CrO_4^{2-}$, $AsO_4^{3-}$, $AsO_3^{3-}$ | Waters IC-Pak A HC | NaOH + $KNO_3$ | ICP-MS | Drinking water, waste water | (107) |
| $Sb^{3+}$, $Sb^{5+}$ | Hamilton PRP-X100 | Phthalic acid, tartaric acid, 4-hydroxybenzoic acid, benzoic acid, citric acid | ICP-MS ICP-AES | Surface water, solid extracts | (108) |
| $AsO_4^{3-}$, $AsO_3^{3-}$ | Hamilton IC PRP X-100 | $Na_2CO_3$ | ICP-MS | Surface water | (109) |
| $AsO_4^{3-}$, $AsO_3^{3-}$ | IC Hamilton PRP X-100 | $KH_2PO4$ | ICP-MS | Plant | (110) |
| $AsO_4^{3-}$, $AsO_3^{3-}$ | Dionex IonPac AS-9 | NaOH, $Na_2CO_3$+ $NaHCO_3$ | ICP-MS | Soil | (111) |
| $AsO_4^{3-}$, $AsO_3^{3-}$ | IC Wescan Anion-S $C_{18}$ | EDTA | ICP-AES | River water, wastewater | (112) |
| $AsO_4^{3-}$, $AsO_3^{3-}$, $SeO_4^{2-}$, $SeO_3^{2-}$ | IC Biosil 125 SEC | $CH_3COONH_4$ | ICP-MS | Fish tissue | (113) |
| $AsO_4^{3-}$, $AsO_3^{3-}$, $SeO_4^{2-}$, $SeO_3^{2-}$ | Metrohm Metrosepp Anion Dual 3 | $NH_4NO_3$ | ICP-MS | Fish tissue | (114) |
| $Cr^{3+}$, $CrO_4^{2-}$ | Chromabond-$NH_2$ | $HNO_3$ | DRC-ICP-MS | Milk powder | (115) |

## TABLE 8

The examples of applications of ion chromatography for the lanthanides and actinides determination

| Analytes | Analytical column | Eluent | Detection mode | Sample matrix | References |
|---|---|---|---|---|---|
| $Sc^{3+}$, $Lu^{3+}$, $Yb^{3+}$, $Tm^{3+}$, $Er^{3+}$, $Ho^{3+}$, $Tb^{3+}$, $Eu^{3+}$, $Sm^{3+}$, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $La^{3+}$, $Gd^{3+}$, $Dy^{3+}$ | Supelcosil $C_{18}$, Dionex IonPac CS5A | $\alpha$-HIBA | UV/Vis ($\lambda = 658$ nm) | Geochemical reference materials | (116) |
| $Sc^{3+}$, $Lu^{3+}$, $Yb^{3+}$, $Tm^{3+}$, $Er^{3+}$, $Ho^{3+}$, $Tb^{3+}$, $Eu^{3+}$, $Sm^{3+}$, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $La^{3+}$, | Dionex Ion Pac CS3 | $\alpha$-HIBA | UV/Vis ($\lambda = 658$ nm) | Rocks | (117) |
| $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$, $U^{3+}$, $Np^{3+}$, $Pu^{3+}$, $Am^{3+}$, $Cm^{3+}$ | Dionex Ion Pac CS5A | Oxalic acid + $NaNO_3$ | ICP-MS, ICP-ID/MS | Irradiated nuclear fuel sample | (118) |
| $Lu^{3+}$, $Er^{3+}$, $Gd^{3+}$, $Eu^{3+}$, $Nd^{3+}$, $Ce^{3+}$, $Yb^{3+}$, $Tm^{3+}$, $Ho^{3+}$, $Sm^{3+}$ | Silica-based $C_{18}$ column | $\alpha-$ HIBA | UV/Vis ($\lambda = 580$–$670$ nm) | Water, wastewater | (119) |
| $La^{3+}$, $Ce^{3+}$, $Nd^{3+}$, $Eu^{3+}$, $Sm^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Yb^{3+}$ | Dionex IonPac CS5 | Oxalic acid, diglycolic acid, LiOH | UV/Vis ($\lambda = 520$ nm) | Synthesized samples | (120) |
| $La^{3+}$, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Tb^{3+}$, $Dy^{3+}$, $Ho^{3+}$, $Er^{3+}$, $Tm^{3+}$, $Yb^{3+}$ | Supelco LC-SCX, Supelco LC-18, Dionex IonPac CS5 | $\alpha$-HIBA | UV/Vis ($\lambda = 520$ nad 658 nm) | Magnesium alloys | (121) |
| $Np^{3+}$, $Pu^{3+}$, $Am^{3+}$, $Cm^{3+}$ | Dionex Ion Pac CS5A | Oxalic acid + $NaNO_3$ | ICP-MS | Urine | (122) |
| $Pu^{3+}$, $U^{3+}$ | Dionex Ion Pac CS5A | $HNO_3$ | ICP-MS | Nuclear fuel | (123) |
| $Np^{3+}$, $Pu^{3+}$, $Am^{3+}$, $Cm^{3+}$, $Th^{3+}$, $U^{3+}$ | Dionex IonPac CS5 | Oxalic and diglycolic acid, $HNO_3$ | On-line scintillation detection | Nuclear waste | (124) |
| $La^{3+}$, $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, $Eu^{3+}$, $Gd^{3+}$, $U^{3+}$, $Np^{3+}$, $Pu^{3+}$, $Am^{3+}$, $Cm^{3+}$ | Dionex IonPac CS5 | Oxalic acid, $HNO_3$ | ICP-MS | Nuclear fuel | (125) |
| $Pu^{3+}$, $Am^{3+}$, $U^{3+}$ | Dionex IonPac CS10 | $HNO_3$+DPA | ICP-MS | Fuel leaching solutions | (126) |
| $Th^{3+}$, $U^{3+}$, $Am^{3+}$, $Np^{3+}$, $Pt^{3+}$ | Hamilton PRP-1 | $HNO_3$+DPA | UV/Vis, ICP-MS | Water, biological samples | (127) |
| $Pu^{3+}$, $U^{3+}$, $Np^{3+}$ | Dionex CS10 | 0.6 M $HNO_3$ + 40 mM 2.3-DPA | ICP-MS | Nuclear fuel | (128) |
| $U^{3+}$, $Pu^{+}$ | Dionex IonPac CS10 | $HNO_3$+ DPA | ICP-MS | Nuclear waste | (129) |
| $Am^{3+}$, $Cm^{3+}$ | Nucleosil SA 100 | 2-hydroxy-2-methylbutyric acid | ICP-MS/DTI | Nuclear fuels | (130) |
| $Np^{3+}$, $Pu^{3+}$, $Am^{3+}$, $Cm^{3+}$ | Dionex IonPac CS10 | $HNO_3$+ DPA | ICP-SFMS | Nuclear wastes | (131) |
| Pu-isotopes | TEVA resin, Amberline XAD-7 | $HNO_3$, HCl | Accelerated MS | Water, wastewaters, ashes | (132) |

different forms. This is the reason why there are various detection methods being employed for species analysis of chromium, such as laser-enhanced ionization (67), on-line thermal lens spectrometric detection (68), thermal ionization isotope mass spectrometry (69), chemiluminescence detection (69), or the most popular atomic absorption spectroscopy (70–74) and inductively coupled plasma mass spectrometry detection (75, 76).

These methods are very sensitive; however, in view of complex procedures, as well as price of instruments, their applications in routine laboratories are limited. There is still a need to work out a simpler and more reliable simultaneous method of Cr(III) and Cr(IV) determination on trace level concentration.

Present research describes the simultaneous separation and determination of Cr(III)/Cr(VI) by means of ion-exchange column with mixed bed, oxidation of Cr(III) to Cr(VI), and next their detection at 365 nm in UV detector. This method was applied by Heberling et al. (77) to species analysis of chromium(III) and chromium(VI), on the mg/L level in plating solutions and wastewater using anion-exchange column. Considering the progress in the introduction of new generations of ion exchange resins in separation columns and the necessity of analysis of chromium species on trace levels, this method was developed for the simultaneous determination of Cr(III)/Cr(VI) in environmental samples on the $\mu$g/L level (78).

Transition metal ions may also be separated via ion-pair chromatography on macroporous PS/DVB resins or chemically bonded silica. With oxalic acid as a complexing agent and tetrabutylammonium hydroxide as an ion-pair reagent, the eluent order is opposite to that obtained in cation exchange analysis.

Elution of cations is achieved by their complexation with the eluent ligand and ion-pairing of a negatively charged complex formed with ion-pair chromatography or their cation exchange with counter-ion. The research in this field is devoted to evaluating the nature of concentration of proper ligands and ion-pair chromatography as well as the organic modifier and eluent pH.

Ion chromatography is increasingly used for the separation of lanthanides and actinides. The separation of rare earth elements can be performed either with a cation- or anion-exchange mechanism, according to the eluent composition and to the properties of the stationary phase.

Cation-exchange of lanthanides has been performed in peculiar, latex-agglomerated columns in the presence of appropriate chelating agents. Usually it is $\alpha$ -hydroxyisobutyric acid (HIBA) which formed with lanthanide complexes eluted according to their stability. First eluted Lu (the most stable complex with HIBA) and the last La the (the weaker complex with HIBA).

In the case of anion-exchange separation mechanism, lanthanides have been predominantly separated using a mixed bed column containing both anion and cation-exchanges sites. The determination of lanthanides and actinides is of great importance for many industries, such as the nuclear power and mining industries. In the past, these elements were almost exclusively analyzed with AAS and ICP methods. In many cases, pre-concentrations were necessary, because the detection limits obtained were only in the lower mg/L.

Analysis of environmental samples is difficult, because of coelution problems occurring with some transition metals which are present in much higher concentrations. Luckily, while transition metals form stable monovalent and divalent complexes with PDCA, the lanthanides complexes with PDCA are trivalent.

Based on this charge difference, transition metals can be eluted with PDCA while lanthanides are retained at the beginning of the column. The second step, after complete elution of transition metals, is elution of rare-elements with oxalic and diglycolic acid.

The large review concerning the determination of lanthanides in metallurgical, environmental, and geological samples is written by Rao and Biju (79).

The examples of applications of ion chromatography (literature data encompassing years 1980–2008) for the determination of metal ions in different types of sample matrixes including analyzed ions, separation column, eluent, detection mode, and sample matrix are given in Table 6 (heavy and transition metals), Table 7 (speciation analysis of Cr, As, Sb), and Table 8 (lanthanides and actinides).

## SUMMARY

The present review shows a great potential of ion chromatography in inorganic cation analysis. Ion chromatography methods provide high speed separations in many cases and they are simple enough to be used on a routine basis.

Currently, there is a significant number of ion chromatography methods developed for the determination of cation pollutants in a wide variety of sample matrices.

Ion chromatography has become one of the main powerful analytical tools for the analysis of complex matrices and speciation studies in the field of metal analysis.

When choosing appropriate separation and detection conditions for metal analysis, several factors should be taken into account. They are type and concentration of the species to be analyzed, required resolution and method precision, speed and cost of analysis, and availability and possibility for automation.

Recently developed methods tend to reflect general advances in the field of ion chromatography, such as use of higher capacity columns, larger loop injections, and more complex sample preparation and detection schemes. This, in turn, allows the simultaneous determination of inorganic cations at lower detection limits and expands the range of analytes which can be measured in different matrix samples.

## ABBREVIATIONS

| | |
|---|---|
| **AAS** | atomic absorption spectroscopy |
| **ASTM** | american society for testing and materials |
| **DPA** | 2,3-diaminopropionic acid monochloride |
| **DCTA** | 1,2-diaminocyclohexanetetraacetic acid |
| **DTPA** | dietyloenetriaminopentaacetic acid |
| **EGTA** | tetraacetic acid |
| **EDTA** | ethylenediaminetetraacetic acid |

| | |
|---|---|
| **HIBA** | $\alpha$ -hydroxyisobutyric acid |
| **ICP-AES** | inductively coupled plasma atomic emission spectroscopy |
| **ICP-MS** | inductively coupled plasma mass spectrometry |
| **ISO** | international standard organization |
| **MSA** | methanesulfonic acid |
| **PAR** | 4-(2-pyridylazo)-resorcinol |
| **PCR** | post column reaction |
| **PDCA** | pyridine-2,6-dicarboxylic acid |
| **US EPA** | United States of Environmental Protection Agency |
| **WHO** | World Health Organization |

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