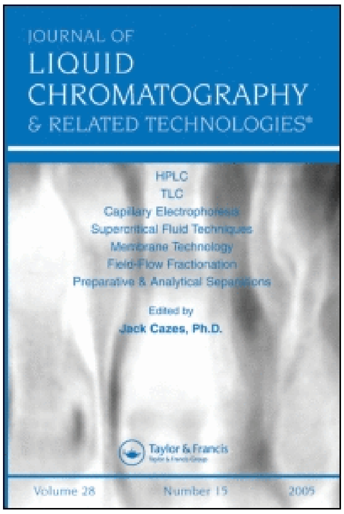

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Determination of Cations and Anions in Environmental Samples by HPLC: Review

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Abstract: Inorganic ionic pollutants are of great environmental concern due to their health related impact. Around 16 inorganic contaminants are to be monitored regarding the primary drinking water regulation set by US, EPA. The permissible limits or guideline values are generally in the range of submicro gram or even less. Moreover, the analytes of concern are present at tracer concentration in the bulk matrices. Of particular concern are non-metallic ions that are difficult to monitor accurately and precisely in the presence of bulk unwanted ions. HPLC has played an important role in analyzing ionic pollutants, in particular, speciation of elements. In this review, some fundamentals of high performance liquid chromatography and, in particular, ion chromatography and ion pair chromatography have been described in some detail. The use of ion chromatography in combination with different types of mass spectrometric techniques has also been outlined. The LC-MS detection limits range from submicrogram to picogram and most of these techniques met the primary drinking water regulation requirement.

Keywords: Anions, Cations, Chromatography, Environmental pollution, LC detectors

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INTRODUCTION

Research on the distribution and transformation of toxic ionic species in the environment has led to an increasing concern for reliable analytical methods that can quantify most of the pollutants. Environmentalists have to analyze diverse nature of samples for assessing the changing trends of pollutants. This enables the regulatory bodies to identify the sources and to enforce regulations. The history and summary of primary drinking water regulations have excellently been documented by Pontius.[1] Currently, there are 16 inorganic contaminants among the 92 regulated for primary drinking water. The detail can be accessed at the web (http.www.gpoaccess.gov/fr/index.html). The areas of concern are terrestrial, marine, and air pollution, mainly due to burning of fossil fuel that is one of the sources of ionic pollutants. In addition to this, industrial, agricultural, and anthropogenic activities are also contributors of inorganic pollution. Soil pollution is due to disposal of electroplating waste and wastewater treatment sludge, which are buried during the landfill. The leachates from such hazardous waste landfills are also polluting underground water. The acid rain is harmful to vegetations, fresh water systems, natural, and urban environments. A great deal of scientific attention has to be given to the determination of these acidic species and their sources, distribution, transportation, and fate in the environment. Nitrate and nitrite are the runoff of nitrogenous fertilizer, leaching from septic tanks and sewage. Nitrate can induce metahemoglobinemia.[2] Nitrite may react with secondary and tertiary amines forming highly carcinogenic nitrosamines.[3] Excess consumption of fluoride released from the aluminum industry may cause fluoride toxicity called fluorosis.[4] The source of bromide as a pollutant is methyl bromide that has been used as a fumigant on plants. The USA, EPA, Method 300, includes determination of the disinfection byproducts (DBP) bromate, chlorite, and chlorate in drinking water. Bromate is produced from the ozonation of source water that contains naturally occurring and polluted bromide from anthropogenic activity, such as from burning coal.[5] The USA EPA has estimated a potential cancer risk equivalent to 1 in 10^4 for a lifetime exposure to drinking water containing bromate at $5\,\mu g\,L^{-1}$.[6] The World Health Organization (WHO) has also recommended bromate provisional guideline value of $25\,\mu g\,L^{-1}$.[7] Chlorite and chlorate are produced as a result of using chlorine dioxide as a disinfectant.[8] The toxic heavy metals enter into the environment through improper disposal of used lead accumulators, corrosion of household plumbing systems, corrosion of galvanized pipes, runoff from waste batteries, and paint effluents. In particular, Hg and Pb interfere with the central nervous system.[9] Cr speciation in tannery wastewater is an important analytical task. Other inorganic pollutants of concern are arsenic, perchlorate, and organotin.

In this review, the fundamentals of HPLC and its role in solving emerging analytical problems has been discussed regarding analysis of inorganic pollutants.

ANALYTICAL TECHNIQUES FOR MONITORING ENVIRONMENTAL IONIC POLLUTANTS

A variety of methods have been employed for the analysis of inorganic ions of environmental concern. Classical techniques are colorimetry, gravimetry, potentiometry, and amperometry. These techniques are mostly single element detection, have limited sensitivity, suffer from interferences, and are time consuming.[10] The majority of cations listed as primary drinking water contaminants are transition metals that are present at tracer levels. These are analyzed using highly sensitive, selective techniques like atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), XRF and anodic stripping voltammetry. However, ASS is a single element detection and multielements emissions techniques are expensive and their operational cost is high, whereas electrochemical techniques require a great control of experimental parameters to avoid electrode fouling.[11] The majority of the anions of environmental concern are nonmetallic and limited methods are available compared to metallic pollutants. In this review, the main focus will be on the application of HPLC for the analysis of inorganic pollutants.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Liquid chromatography is indispensable in modern inorganic analysis. Its various forms like ion chromatography (IC) and ion-pair chromatography (IPC) are suitable for determining perhaps the greatest variety of inorganic ions among the currently available techniques. This includes simple anions, cations, organometallic, and coordination compounds.[12–15] It is intended to evaluate the potential of the HPLC for the determination of ions related to environmental issues. Its chief advantages are as follows:

1. Simultaneous preconcentration and separation of ions on the same column.
2. Minimized matrix interference for improved resolution and detection.
3. Simultaneous determination of cations and anions in a single run.[16]
4. The premier technique for speciation studies regarding the environmental behavior of metal toxicity.
5. It is simple, less expensive, easy to maintain, and more productive.

Based on the above mentioned advantages of HPLC, USA EPA, American Society for Testing and Materials (ASTM) and International Standard Organization (ISO), has approved chromatographic methods for effective monitoring of inorganic pollutants in drinking and waste water.[17]

Separation Methods in HPLC

The ion analysis by HPLC can broadly be classified as depicted in Figure 1. It gives a good range of techniques to be incorporated for ions analysis. However, IC and IPC are extensively used in addressing inorganic environmental related issues. A brief introduction about these is outlined.

Principle of Ion Chromatography

Instrumentation

IC, developed by H. Small et al.[18] is routinely used for the determination of ions of environmental concern. It is a liquid chromatographic method,

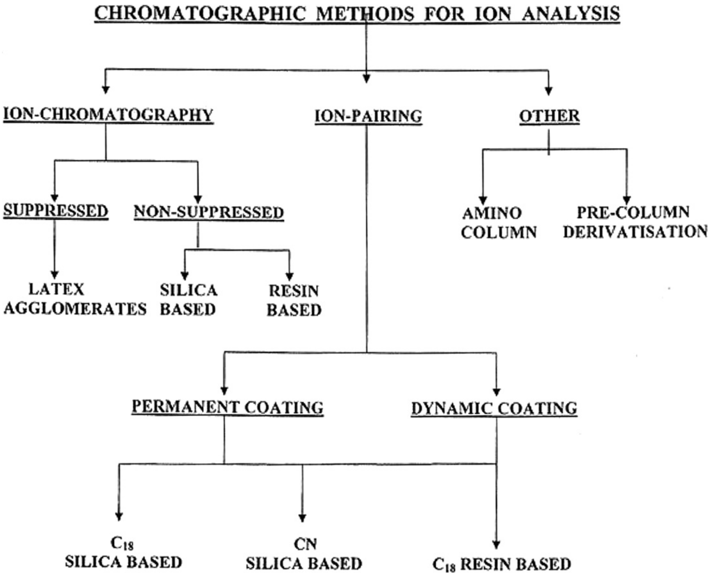

Figure 1. Schematic representation of separation modes of ions using liquid chromatography.

in which a mobile phase permeates through a porous solid stationary phase called the column and elutes the separated ions into a flow-through conductivity detector. The stationary phase is in the form of small diameter, 5–10 μm uniform particles. Generally, the IC separations are performed using silica or polymeric based weak cationic or anionic ion exchangers. A high pressure pump is required to force the mobile phase through the column at typical flow rates of 1–2 $\mathrm{mL\,min^{-1}}$. The sample to be analyzed is introduced into the mobile phase via an injection device prior to the column. The flow through detector cell has μL volume through which the mobile phase passes carrying the separated ions. The frequently, simultaneously determined ions at trace levels in potable and waste water are F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{-3}, SO_4^{-2}, BrO_3^-, I^-, NH_4^+, alkali and alkaline earth. The transition metals can be analyzed by incorporating an appropriate complexing agent in the mobile phase. IC can further be classified as suppressed and non-suppressed.

Suppressed Ion Chromatography

The suppressor idea was inducted to employ conductivity as a detection mode. Conductance suppression is needed when the mobile phase is made of a strong electrolyte that saturates the detector's background response. The simplest means to accomplish conductivity suppression during anionic analysis is to pass post separation column mobile phase through a cation exchange column in the hydrogen ion form called suppressor. The role of the suppressor column in the case of anion separation with mobile phase $NaHCO_3$ is described by Equations 1–2.

$$\text{Resin–H}^+ + (\text{Na}^+ + \text{HCO}_3^-) \longrightarrow \text{Resin–Na}^+ + \text{H}_2\text{CO}_3 \tag{1}$$

$$\text{Resin–H}^+ + (\text{Na}^+ + \text{A}^-)\text{separated anion} \longrightarrow \text{Resin–Na}^+ + \text{HA (analyte)} \tag{2}$$

The combined result of these two processes is that the mobile phase conductance is reduced due to H_2CO_3 formation, whilst the conductance of the analyte ion is distinguished and enhanced by the replacement of sodium ions with hydronium ions. A similar process is applied to suppressed cation exchange chromatography using HCl as eluent. The suppressor is an anion exchange column in the OH^- form as described in Equations 3–4.

$$\text{Resin–OH}^- + (\text{H}^+ + \text{Cl}^-) \longrightarrow \text{Resin–Cl}^- + \text{H}_2\text{O} \tag{3}$$

$$\text{Resin–OH}^- + (\text{M}^+ + \text{Cl}^-) \longrightarrow \text{Resin–Cl}^- + \text{MOH (analyte)} \tag{4}$$

In modern IC systems, the suppressor column has been replaced by a more efficient and robust device called micro membrane suppressor. It has greatly reduced the tedious job of suppressor saturation and its regeneration. The USA, EPA 300.1 and 314.1 methods i.e., determination of inorganic anions in drinking water are based on the ion chromatography micro membrane suppressor. It can tolerate high ionic strength and provide the best minimum detection limits as per agency requirements.[19,20] In another IC suppressed method, perchlorate, nine haloacetic acids, F^-, Cl^-, NO_2^-, and NO_3^- have been monitored in a single run within 34 minutes.[21]

Non-Suppressed Ion Chromatography

In order to avoid the suppressor column and to make IC system simple and easier to operate, Gjerd and co-workers[22] synthesized a range of low capacity macroporous ion exchange resins of 0.007–0.07 meqg^{-1}. Instead of the use of a strong conducting eluent they proposed low conductance aromatic acids for the mobile phase. Later on, instruments were designed that can partly suppress back ground conductance electronically. The efficiency of these low capacity columns was encouraging for monitoring the quality of potable water regarding inorganic pollutants, but the detection limits were some what inferior as compared to suppressed IC. The simplicity, cost effectiveness, relatively high efficiencies (~16000 theoretical plates per meter), and good output for the routine job of these columns had led to the development of a large number of applications for ion analysis.[23] In the analyses of anions by non-suppressed IC, potassium phthalate or p-hydroxy benzoic acid are commonly employed as mobile phase.[24] A dilute solution of nitric acid is used for the separation of alkali metal and NH_4^+ cations. The mobile phase with equimolar concentration of ethylenediamine and tartrate as complexing agent is frequently used for the analysis of polyvalent metal cations and nearly symmetrical peaks were achieved.[25] EDTA can also be used for anions as well as a strong complexing agent for polyvalent metal cations.[26] Water miscible organic solvents, such as methanol, acetonitrile are frequently used as organic modifiers to the mobile phase for the improved separations and to overcome peak tailing and skewing.

pH of Mobile Phase

pH can influence the separation efficiency of the mobile phase. The eluting power of weak aromatic acids in non-suppressed IC is increased with the increase in pH due to its increased dissociation. However, it may early elute the analytes and merge some of the peaks. Similarly, the degree of ionization of solute ions that are derived from weak acids will be pH dependent. So variations of solute charge will influence its affinity towards the functional groups on the stationary phase, hence affect their retention and separation. In the monitoring of NO_3^- and NO_2^- in coastal areas boring water, vegetable spinach and lettuce, it is observed that pH is an important parameter regarding their separation.[27]

ION-PAIR LIQUID CHROMATOGRAPHY

Analysis of metal oxoanions of multiple charges of vanadium, tungsten, molybdenum, and chromium, and non-metals like bromate, iodate, and perchlorate, has been comparatively difficult using conventional ion exchange methods. It is mainly due to their various ionic forms in neutral or slightly alkaline medium and because of insufficient selectivity of the commercially available stationary phase for these ions. Therefore, analysis of such anions using IPC is thought to be advantageous because of the better resolution.[28] In IPC an ion pairing reagent (IPR) that is generally ammonium based is frequently added to the mobile phase to optimize the retention of an oppositely charged ionic solute.[29] However, the incorporation of additional IPRs such as perflourocarboxylic acids,[30] cetylpyridinium,[31] and sulfonium, and phosphonium compounds[32] with unique selectivity has also been reported. Other parameters that can be manipulated for improved separation are the organic modifier contents, the concentration and type of ion pairing reagent, and the concentration of ligand. The greatest edge of IPC in the field of inorganic analysis is the flexibility it offers for adjustment of the ion exchange capacity of the column. The different IPRs containing C4–C18 carbon numbers on silica based reversed phases[33] and silica based normal phase columns[27] have been reported. A recent review by Cecchi, T. is a must read regarding usage of IPC for ions analyses.[34]

Separation Mechanism in IPC

The IPC involves interaction of analytes ions with IPR coated on the stationary phase. The first equilibrium for anionic separation describes the retention of cationic tetraalkyl ammonium R_4N^+ on the column surface, which leads to the formation of a double layer. The R_4N^+ occupies the primary layer with positive charge at the stationary surface, while the co-ion (A^-) of the salt occupies a diffuse secondary layer. The second equilibrium describes the selectivity of any one anion over another in the secondary layer.[35] The efficiency of a separator column is optimized by the nature and concentration of the mobile phase, its pH, and by the presence of a suitable complexing agent that can also greatly influence the separation ability. The mobile phase characteristics, which influence solute retention, are the relative affinities of the analyte and the competing ions of mobile phase. The affinity of the mobile phase ions to the stationary phase is governed by the same factors that affect the affinity of the solute ions, i.e., charge density, degree of hydration, and polarizability. Mobile phase ions of higher affinity to the stationary phase will result in lower interactions of the analyte with the stationary phase that lowers its retention times, and hence, deteriorates column separation. The theory that illustrates the retention mechanism of charged and neutral analytes in IPC has been described elsewhere.[36]

Stationary Phases in IC and IPC

Varieties of phases are being utilized for IC. However, here two major types of stationary phases, which are frequently employed, will be discussed. The functionalized silica based ion exchangers are produced by chemically bonding quaternary amines to form strong anion exchangers (SAX) and alkylsulfonates to form strong cation exchangers (SCX). Their capacity is usually moderate ranging from 0.007–0.04 meqg^{-1} requiring conductivity with or without suppression or UV-Vis detection mode. The advantage of the silica based stationary phase is the better chromatographic efficiency, stability, and durability at high pressure; however their working pH range is 2–8. However, for separation of analytes in complex matrices, ultra fast HPLC regarding improved throughput, sensitivity, and analyte resolution with column packing of sub 2 µm particles has been incorporated.[37] Most ion exchange resins are synthesized by cross linking polystyrene with divinylbenzene (PS-DVB). The SCX and SAX functional groups are chemically bonded and these can be utilized at extreme pH. Their working is affected by pressure variations due to soft and gel nature hence; as a result, the column dimension and flow rates are carefully selected.

Detection in IC

The conductivity detector is known as a universal detector that is relatively simple to operate, highly sensitive, and extremely useful for the analysis of ions. Conductance exhibits a simple dependence on concentration. Thus its measurement is an obvious choice for the continuous monitoring of ionic species in a column eluent. A typical detector cell consists of a microliter volume of insulating material where the electrodes of noble metals or graphite are incorporated. The cell resistance is measured with Wheatstone bridge and it is related to concentration by Ohm's law. The measuring signal conductance of an analyte is determined by several factors, including the ionic strength and type of species in the solution. The detector response varies with the temperature and may take time to attain a stable baseline.[38] That may also affect accuracy and precision of analysis when working at sub microgram level.

Detection in IPC

UV Absorbance Detection

The anions of environmental concern that show absorbance in the range of 195–220 nm are nitrate, nitrite, bromide, bromate, iodide, iodate, periodate, thiocyanate, and thiosulfate.[39] Chloride, fluoride, sulphate, phosphate, and cyanide are transparent in the UV region. This can often be used to advantage in the determination of UV absorbing anions in the bulk presence of UV-transparent ions such as in food samples,[27] samples of oil fields, subsurface brines, and high salinity groundwater.[40] It has added advantages of an early attainment of a stable baseline with minimum drift, improved recoveries, and reproducibility. Therefore, IPC-UV is partly an alternative technique to conductivity detection and a useful tool with added selectivity for routine analysis as shown in Figure 2. The use of conductivity detection has been proposed using the IPRs of moderate hrdrophobicity such as tetrabutylammonium hydroxide for monitoring several anions,[41] as shown in Figure 3. Anions at ppb level in petroleum refinery streams (sour water) using a cyanometallic complex in combination with membrane suppressed conductivity has also been reported.[42]

APPLICATION OF IC AND IPC IN ENVIRONMENTAL STUDIES

Many international organizations such as ASTM, Association of Official Analytical Chemists (AOAS), and USA EPA, have regulatory methods based on IC. Monitoring of ionic pollutants is the largest application area dominated by IC due to the scarcity of alternative methods. Determinations of anions in environmental waters[43] and anions in potable waters by IC have been reported.[44] The determination of anions by suppressed IC is depicted in Figure 4. The separation of ammonium and alkali/alkaline earth cations using suppressed IC with cation self regenerating suppressors is shown in Figure 5. The simultaneous analysis of inorganic monovalent cations in drinking waters using non-suppressed IC has been reported by Fritz et al. and others.[45,46] Burning of fossil fuel, in particular coal, introduces toxic metals in the environment. It is reported that a good particulate suppressing 1000 MW coal fired thermal power generation unit emits annually around 46 kg thorium and 23 kg uranium,

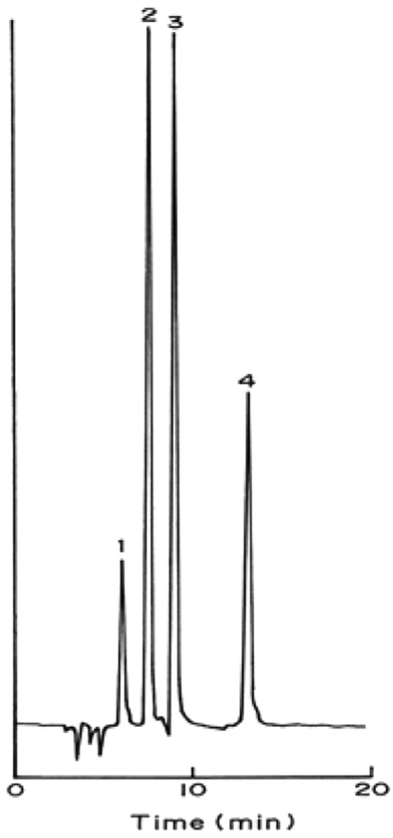

Figure 2. Ion pair liquid chromatography of UV active anions. Eluent: TBA-ClO_4 5 mM, acetonitrile 6%, $NaH_2PO_4 = 15$ mM, pH 2; UV: 240 nm; flow rate: 0.8 mL min^{-1}; column: Eurosphere C_{18}, (250×4.6 mm). Solutes: 1 = nitrite, 2 = bromide, 3 = nitrate, 4 = iodide, each 8 mgL^{-1} (authors' unpublished work).

besides other metals and non-metals.[47] The IPC based method for uranium has been developed[48] and uranium in coal ash has been reported.[49] The advances in the modification of column packing material in particular reduction in particle size has greatly enhanced its resolution efficiency and also significantly reduced the analysis time. An excellent separation of eight anions of environmental concern was optimized by incorporating 3 µm ODS particles.[50] An impressive fast separation of seven anions in less than two minutes has been achieved on a 2 cm C_{18} column.[51] Simultaneous IPC determination of Cr(V1) and Cr(111) with detection limits 0.04 mg L^{-1} and 0.02 mg L^{-1}, respectively, has been achieved and these ions in ground water and fly ash have been monitored.[52] In another IPC method, simultaneous Cr(VI) and

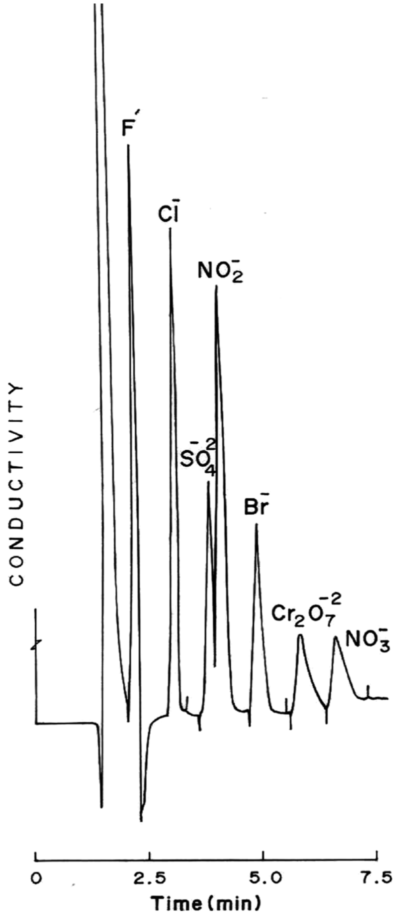

Figure 3. Separation of anions and metal oxyanions using reversed phase ion pair chromatography. Column: Lichrosorb RP-18; Mobile phase: 0.002 mol L^{-1} tetrabutyl ammonium hydroxide and 0.05 mol L^{-1} phosphate buffer; pH 6.7; flow rate: 2 mL min^{-1}; detector: conductivity; injection volume 20 μL, concentration: 1 mg mL^{-1} each in mobile phase. (Reprinted from ref. 41 with permission from Elsevier).

Cr(III) with low detection limits and good reproducibility have been analyzed regarding waste chromium treatment and, subsequently, its removal using algae.[53]

Analysis of Toxic Metals using Post Column Derivatization

The growth in industrial activity is contributing to the diverse nature of pollutants including toxic metals. LC has achieved the separation of

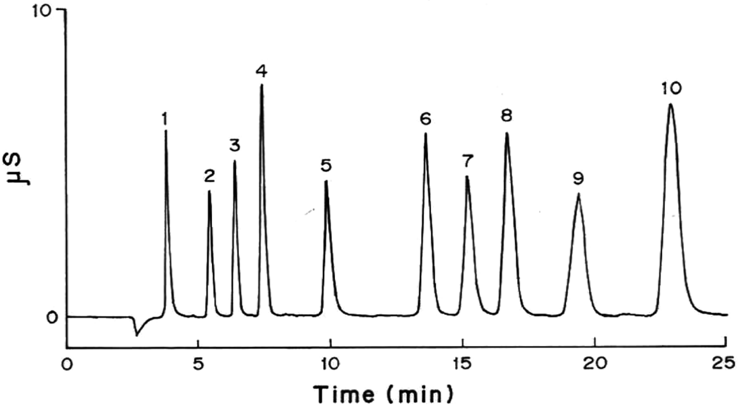

Figure 4. Separation of oxyhalid plus common inorganic anions (ppm) using EPA Method 300.1. Conditions: column Dionex Ion Pac AS9-HC (4 mm ID); eluent: 9 mM sodium carbonate; flow rate: 1.0 mL min^{-1}; detection: suppressed conductivity with an ASRS operated at 100 mA in external water mode; injection 25 μL; solute: 1 = fluoride (3), 2 = chlorite (10), 3 = bromate (20), 4 = chloride (6), 5 = nitrite (15), 6 = bromide (25), 7 = Chlorate, 8 = nitrate (25), 9 = phosphate (40), 10 = sulphate (30) (Reprinted from ref. 17 with permission from John Wiley & Sons).

heavy metal ions however, their sensitivity with conductivity detector is usually low. The usage of a post column reactor, using a color forming chromogenic reagent has been useful for metals of environmental concern, Hg, Pb, Cr, Cu, Fe, Al, Zn.[54] An impressive separation of environmentally related metal ions, Fe(III), Fe(II), Cu, Pb, Zn, Ni, Co, Cd, Ca, Mg, and Mn has been reported on a silica based ion exchange resin with 0.16 mM tartrate buffer, pH 3.2 at 520 nm using PAR.[55] Also, more toxic hexavalent Cr can be determined using a high capacity Dionex AS7 anion exchange column as specified in US, EPA method 218.6. The selective and sensitive detection of Cr(VI) is achieved using a VIS detector after the post column reaction with diphenylcarbohydrazide.[56] Metals, such as Cr(III), Al(III), and Fe(II) have been analyzed in tannery sludges as 8-hydroxyquinolates and the neutral complexes separated on C_{18} reversed phase column and detected using PAR.[57] The determination of transition metals in river water using preconcentration techniques in combination with post column derivitization is shown in Figure 6.

Monitoring of Inorganic Pollutants with Mass Spectrometric Detectors

An increasing trend has been observed in incorporating mass spectrometric detectors in monitoring inorganic pollutants for achieving

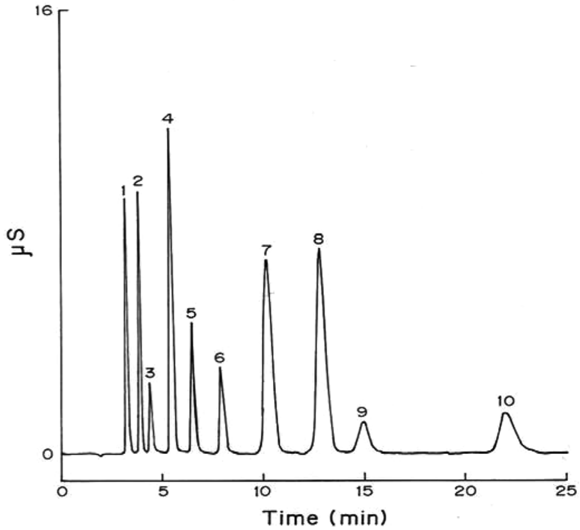

Figure 5. Separation of ammonia and alkali/alkaline earth cations (ppm). Column: Dionex Ion Pac CS 12 A; eluent: 18 mM methanesulphonic acid, flow rate: 1.0 mL min^{-1}, detection: suppressed conductivity with a cation self regenerating suppressor (CSRS) operated at 100 mA in recycle mode, injection volume 25 µL, solute: 1 = lithium (1), 2 = sodium (4), 3 = ammonium (5), 4 = potassium (10), 5 = rubidium (10), 6 = cesium (10), 7 = magnesium (5), 8 = calcium (10), 9 = strontium (10), 10 = barium (10). (Reprinted from ref. 17 with permission from John Wiley & Sons).

detection limits in subnanogram per liter and, in certain cases, even reaching picogram per liter level. The techniques used are LC-electrospry ionization (ESI-MS), LC-inductively coupled plasma-Mass spectrometry (ICP-MS), and ion chromatography-ICP-MS.[59,60] A selected application of these detectors in the analyses of different inorganic environmental pollutants is provided here.

Arsenic in Water

The main source of arsenic contamination is through erosion of rocks, minerals, and soil. It is of great concern regarding public health and its MCL was lowered from 50 to 10 µgL^{-1} by USA, EPA in 2002 and it is being implemented since January 23, 2006. The WHO has the same permissible limit of 10 µgL^{-1}. The recent report has indicated excessive risk of spontaneous absorption, stillbirth, and neonatal death by the long term exposure of arsenic even at lower non-toxic levels. So far, the high level arsenic has been found in wells of Bangladesh and West Bengal,

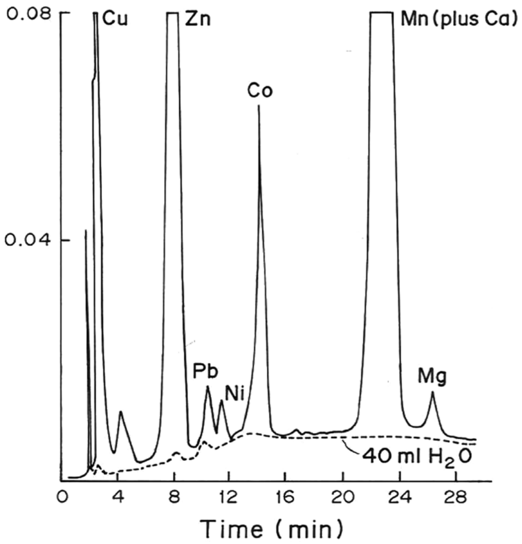

Figure 6. Determination of metal cations (μg L^{-1}) in river water after sample preconcentration. Conditions: column Nucleosil C_{18}, eluent: 2 mM octanesulfonate, 0.35–0.5 M tartarte gradient; detection: VIS at 510 nm after post column reaction with PAR; sample 40 mL river water preconcentrated. (Reprinted from ref. 58 with permission from American Chemical Society).

India, and a large number of people have suffered from arsenic related diseases in this area. Different arsenic species has different toxicities. In water, arsenite III and arsenate IV are normally found. Karthikeyan has reported these in environmental samples.[61] A LC-ICP-MS method has been reported for the determination of diphenyl arsenic in environmental samples including ground water.[62] Ronkart et al. developed LC-ICP-MS to monitor different species of arsenic with minimum detection limit 0.4 pg in water.[63]

Perchlorate

Perchlorate anion is of environmental concern due to its ability to disrupt the thyroid gland's use of iodine in metabolic hormones, which may interrupt normal metabolism, development, and growth, particularly in the fetus. Due to these suspected concerns, U.S EPA has placed perchlorate on the Contaminants Candidate List for further investigations. The possible sources of perchlorate are buried ammunition, the usage of ammonium perchlorate as an oxygenate in solid propellants used in rockets, missiles, and fireworks. Perchlorate is highly water soluble and environmentally stable and it can not be easily removed during the water treatment process. US, EPA has created three suppressed ion chromatography mass spectrometry methods for perchlorate. A sensitive LC-MS/MS and LC-ESI MS method having detection limit 0.05 μg/L has been reported for perchlorate in high salt levels.[64,65] Alternative techniques to IC-MS are surface enhanced Raman Spectroscopy,[66] attenuated total reflectance FT-IR,[67] and chemical sensor.[68] All these mentioned techniques can not reach the sub ppb detection limit. However, these are useful for high contaminated ground water. The two new US EPA methods for perchlorate in hazardous waste LC-ESI-MS detection methods are 6850 and 6860.

Organotins

Organotins are used as antifouling paints and as heat stabilizers in PVC pipes, which are mainly used for water supply. The dialkyl form is most neurotoxic. It is discovered that dibutyltin leaches from PVC drinking water pipes at 1 μg/L levels, therefore, creating a concern regarding its monitoring in environmental samples. Organotins are included on the U.S. EPA Contaminants Candidate list. In this reference, EPA has adopted an official LC-ESI-ion trap MS method 8323 for monitoring of organotin. This method can determine subnanograms per liter of organotins in freshwater.[69]

FUTURE TRENDS

New technologies, in suppressing eluent conductance, particularly online electrolytic self generating membranes and solid based suppressors, enables determination of anions down to ppb levels using $NaCO_3$/$NaHCO_3$ and NaOH systems.[70] In the column development, monoliths both in modified.[71] and unmodified forms have facilitated development of a number of new approaches to chromatographic separation of ions, such as ultra fast IC.[72,73]

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