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## Review

# Applications of anion chromatography in terrestrial environmental research

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### Abstract

Ion chromatography can be applied to characterise single samples for a wide range of ionic species, at elevated or trace concentrations, or with automation may be used to determine many of the common ions on several thousand samples per year. It has been applied to a wide range of sample types of environmental interest. Examples of applications are given for the common sample types, i.e. atmospheric gases and particulates, water, biological materials and soil. The recent literature in the field of anion chromatography, as applied to environmental research, is reviewed (102 references). Suppressed and non-suppressed systems are covered, as are comparisons with other methods of analysis. Development of sample preparation methods, stationary and mobile phases, detection systems and techniques are also discussed. © 1997 Elsevier Science B.V.

*Keywords:* Reviews; Ion chromatography; Water analysis; Environmental analysis; Soil; Air analysis

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## 1. Introduction

The main objective of this article is to review the applications of anion chromatography to research into the terrestrial environment. This covers such areas as atmospheric inputs to ecosystems, the movement of nutrients and pollutants within the ecosystems and ultimately the outputs into streams, rivers and lakes. Some of the most recent developments in techniques that have applications in this area will also be discussed.

Chromatography is a physical technique for the separation of substances by means of their equilibrium distribution between two phases—one of which is stationary and the other mobile [1]. Chromatography of ions is part of a family of liquid chromatographic techniques which are derived from high-performance liquid chromatography [2]. The separation of components is based on the charge and size of the ions. An editorial in *The Analyst* in 1988 [3] predicted that any future developments in chromatography would “probably be led by a practical demonstration on real samples of commercial value”. This has indeed proved to be the case with applications being found in the electronics industry [4–6], the food industry [7,8] and the water industry [9–12].

The work of Small [13] initiated the development of modern, chemically suppressed, ion chromatographic techniques with conductivity detection and this has led to a vast number of papers, books and articles on the application of ion chromatography to environmental research. In the formative years of ion chromatography (IC) Colenutt and Trenchard [14] reviewed the development of the technique in the context of environmental analysis. At about the same time Rowland [15] reported on the installation of an ion chromatograph for the analysis of samples from a range of ecological research projects, especially ones

connected with acid rain research. Sample pre-treatment and column clean-up procedures were discussed.

Non-suppressed techniques were also developed, e.g. by Gjerde et al. [16], where the background conductivity of the eluent was subtracted electronically rather than reduced chemically. An example of this technique being used in environmental research is the work of Cape [17], who used it to study the chemistry of acidic deposition. In the early days of IC there was a clear distinction between chemically suppressed and non-suppressed techniques. Chemically suppressed systems tended to be more expensive, but had the advantages of being more robust and more sensitive. Since that time the number of manufacturers of instruments and columns has increased and a variety of ion-exchange columns is now available for a multitude of applications. The design of conductivity detectors has improved and there is now a variety of detection techniques available. The distinctions between suppressed and non-suppressed methods have become less clear over recent years as some manufacturers now use electronic suppression or some other way of subtracting the background signal.

Earlier commercial development concentrated on the determination of anions. The determination of cations and organic acids followed later, with the development of new resins to perform the separations and new means of detecting the separated components. Procedures have been reported which improve sensitivity through concentration of the sample, either before injection by absorption onto a stationary-phase cartridge, or through using a concentrator or guard column in place of the injection loop [2].

The technique of IC is now accepted as the standard method for many determinations. For example, it is now the Standard Method (No. 4110) in the

USA for the determination of the common anions in surface, ground and waste waters as well as drinking water [18]. Eluent is 1.7 mM  $\text{NaHCO}_3$ –1.8 mM  $\text{Na}_2\text{CO}_3$  with chemical suppression and conductivity detection. It also forms the basis of several of the recommended methods used by the water industry in the UK [1,2]. The technique is also sufficiently reliable and well established for papers on long-term quality control using ion chromatography to have appeared, e.g. Rowland et al. [19].

Ion chromatography is also an attractive technique for laboratories which need to determine many of the ‘common’ anions on several thousand samples, but do not have the throughput to justify the purchase of large automatic analysers, usually based on colorimetric procedures. It eliminates the need to use hazardous reagents which are often integral to colorimetric procedures. However it is relatively slow, typically analysing less than 10 samples per hour. Automatic sampling and injection systems are available which enable analysers to be left unattended to perform longer runs of analyses.

Ion chromatography has the advantage of requiring only relatively small volumes of sample which can be crucial when analysing samples such as soil and sediment pore waters, or precipitation samples, where sample volume may be limiting. The technique also has the ability to provide the sequential measurement of the common anions such as bromide, fluoride, chloride, nitrate, nitrite, phosphate and sulfate. It can be used to effectively distinguish between oxy-ions (sulfite/sulfate and nitrite/nitrate) [18].

Ion chromatography has become a complimentary technique to others such as inductively coupled plasma optical emission spectrometry (ICP-OES), ICP-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and continuous flow colorimetry (CFC)/flow injection analysis (FIA). With its unique ability to quantify multiple ionic species in a single injection, it has found its place into virtually every environmental research laboratory in the world.

## 2. Recent reviews

A review of ion chromatography as a single technique would be an enormous undertaking these

days. Modern reviews tend to cover either a field of application or a particular aspect of chromatography. Hayakawa et al. [20] produced a review entitled ‘Recent Advancement of Ion Chromatography’ in 1994. This covered the fields of environmental samples, foods, biological materials and drugs since 1990. The review is in Japanese but contains a useful reference list. Hayakawa and Yamamoto then went on the next year to review ‘Advances of Indirect Photometric Detection in Liquid Chromatography’ [21]. This covered similar fields of applications, again was in Japanese, and also had a useful reference list (125 articles cited).

Otu et al. [22] reviewed the literature covering Cyanide and Metal Cyanide Complexes, with several of the 85 references being related to environmental samples.

Analytical Chemistry in June 1995 [23] contained the latest in its series of bi-annual Application Review articles, covering the literature between approximately January 1993–December 1994 with sections on air pollution and environmental analysis being of particular interest. This was followed in June 1995 by a Fundamental Review edition [24], with references to developments in techniques rather than applications.

Singh et al. [25] reviewed the literature on the application of suppressed ion chromatography for the analysis of low concentrations of anions in the presence of high levels of matrix ions. This covered such matrices as subsurface waters, well waters and aqueous extracts of sandy soils. A list of 99 references were cited.

Henshall [26] reviewed anion-exchange HPLC methods for the determination of sugars, sugar alcohols and polysaccharides in foods and beverages, with 29 references. There are some similarities between food and beverage samples, and some of the types of sample found in environmental research.

## 3. Atmospheric inputs

Ion chromatography is a robust technique, with the capability of dealing with a variety of different extracts arising from aerosol and particulate collectors. Measurement may be directly on the extract from filters, bulk collectors, particle collectors, solu-

tion bubblers or diffusion tubes, or following concentration on solid cartridges or guard columns. This section covering recent innovations and applications also includes developments in the analysis of precipitation.

### 3.1. Gaseous and particulate measurements

Recent publications using ion chromatography for assessing atmospheric composition have covered a range of alternative methods for trapping and analysing particulates.

Mateu et al. [27] compared the performance of various filters used for trapping inorganic species, including chloride, nitrate and sulfate in airborne particulates. Anions were analysed by IC, metals by ICP-AES or electrothermal AAS (ETAAS), and ammonium by CFC. Liu and Dasgupta [28,29] developed electrostatic aerosol collectors for sampling airborne particles using corona discharge and electrostatic sample collection. When coupled to an ion chromatograph, levels of sulfate in the  $\text{ng/m}^3$  range were measured. Bennett et al. [30] compared sulfur measurements from a fine particle collection network with results from concurrently measured total particulate sulfate and gaseous sulfur dioxide results.

Methods applied to the assessment of  $\text{SO}_2$ ,  $\text{NO}_2$  and combustion gases have recently been reported. Velasquez et al. [31] measured atmospheric  $\text{SO}_2$  concentrations in the city of Cabimas, Venezuela. Samples were collected in dilute hydrogen peroxide and analysed as sulfate, after the method developed by Mulik et al. [32]. A detection limit of 0.044  $\mu\text{g/ml}$  of sulfate was reported. Results were compared with those obtained from a *para*-rosaniline colorimetric method. Downing et al. [33] reported a diffusion tube method for monitoring  $\text{SO}_2$  levels in air. This involved passive collection of  $\text{SO}_2$ , followed by extraction into dilute hydrogen peroxide and analysis as above. De Santis et al. [34] described an annular, alkaline active carbon coated denuder for the sampling of atmospheric  $\text{NO}_2$  and peroxyacetyl nitrate (PAN). The gases collected were extracted into water and analysed as nitrite and nitrate by IC. Dabek-Zlotorzynska et al. [35] compared IC with capillary zone electrophoresis (CZE) and photometric techniques for the determination of nitrate and

sulfate in atmospheric aerosols. Factors compared included detection limit, analysis time, accuracy and precision. No systematic differences between the techniques were reported. Kuroda [36] described a round robin test to determine the levels of precision achieved by ion chromatography in the determination of hydrogen chloride, nitric oxide and sulfur dioxide in combustion gases. High precision but poor accuracy were reported.

Fluoride ions have been difficult to quantify using ion chromatography in the past because the peak appears very close to the water dip and it is co-eluted, or can be difficult to distinguish from low-molecular-mass organic acids. Lamb et al. [37] reported using a macrocycle (cyclic organic compound)-based ion chromatographic system, where a commercial anion-exchange column was loaded with the macrocycle and then used to analyse fluoride in atmospheric samples. Fluoride was separated from both the water dip and organic acid anions. A detection limit of 0.15  $\mu\text{M}$  was reported using hydroxide eluent. Results compared well with known values and ion-selective electrode results. Columns have recently been developed (e.g. Dionex AS14) which enable fluoride to be separated from acetate and quantified.

Tomioka et al. [38] used prepared iron(III) oxide and camellia leaves to capture environmental dry deposition (EDD) (as  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  and HF). The captured EDD was then decomposed and analysed by IC. By using an ion-exchange treatment, recovery of fluoride and sulfur were improved to 93 and 96%, respectively.

### 3.2. Wet deposition

Concentrations of anions in rain water are in the order of mg/l, making IC the method of choice for the determination of chloride, nitrate and sulfate in this type of sample.

Stevens et al. [39] used ion chromatography in their study of the effect of atmospheric N inputs on water quality in a variety of catchment areas in Wales. Positive relationships were shown between forest stand age and  $\text{NO}_3^-$  concentrations in streamwater. Typical concentrations of  $\text{NO}_3^-$ -N in streamwater were on average 0.7 mg N/l, compared to the working detection limit of the IC method of

0.01 mg N/l, based on a chemically suppressed/conductivity detection system with 10  $\mu$ S full scale setting and 50  $\mu$ l injection loop.

Van den Hoop et al. [40] compared three techniques (CZE, IC and ion-selective electrode potentiometry (ISE)) for the measurement of fluoride in Dutch rainwater. Results obtained via CZE and ISE were comparable, but concentrations measured by IC were significantly higher. Udisti and Casella [41] developed a sampler for collection of fractions of a single rainfall event. IC was used to analyse the fractions collected and results were given for a number of rainfall events. Tanaka et al. [42] investigated a method for determining anions and cations in acid rain and related waters. The method involved simultaneous ion-exclusion/cation-exchange chromatography. A weakly acidic polyacrylate cation-exchange resin was used with 5 mM tartaric acid–7.5% methanol–water as eluent. Measurement was by conductivity detector. Detector response was positive for anions and negative for cations; analysis time was about 30 min per sample. Oikawa et al. [43] developed a very useful monitoring system for acid precipitation based on the combination of a pH and conductivity monitor and an ion chromatograph. The system was capable of unattended operation for periods of up to 2 weeks, which is ideal for research in remote areas. Tanner and Chan [44] reported anion concentrations in rainwater in Hong Kong. Replicates of both bulk and ‘wet only’ samples were compared. Factors influencing the composition of the samples were discussed.

Achilli et al. [45] developed a remote-controlled switching system, which switched from anion to cation columns to determine the major ions present in fog samples. Results were compared with those obtained by spectroscopic and FIA methods.

Udisti et al. [46] evaluated two IC methods for the determination of anions and cations in snow samples from Antarctica. A method was proposed for the simultaneous determination of mono- and di-valent cations with detection limits below 1  $\mu$ g/l. Alternative isocratic and gradient elution procedures for the determination of fluoride, acetate, formate and methanesulfonate ions were proposed and discussed.

Ammann and Rüttimann [47] developed a step-gradient method using a weak borate eluent and a Dionex AS11 column to separate low-molecular-

mass organic acids. Analysis time was 25 min. They also used a Dionex AS10 column with 7 mM borate as eluent to separate fluoride and formate. They then used the methods developed to analyse fog, rain after roof run off and also lake sediment pore water. Detection limits below 1  $\mu$ M were achieved. Morales et al. [48] reported on the measurement of organic acids in rain water in Venezuela. Formic, acetic and pyruvic acids were measured. Detection limits were estimated at <0.2  $\mu$ M.

#### 4. Water analysis

The application of ion chromatography is well documented; the technique is now specified in Standard Methods [18]. In environmental research the water matrix presented for analysis is diverse. Precipitation solutions, once filtered, are clean and offer little potential threat of contaminating chromatography columns. Other water samples, such as soil solution or polluted river water may contain contaminants which adhere to the stationary phase and interfere with the chromatography.

##### 4.1. Throughfall and stemflow

In forest ecosystems there is interest in collecting canopy drip, known as throughfall, to assess the movement and transfer of nutrients from plant to soil. Stevens et al. [39] showed that throughfall samples from sitka spruce plantations can contain up to twice the concentration of  $\text{NO}_3^-$  observed in the incident rainfall. Leaching of tree stems as rainwater trickles down the trunk (stemflow) also contributes to element cycling. As a direct result of the way they are produced, throughfall and stemflow may contain significant levels of dissolved organic carbon (DOC) arising from dissolution of resinous residues. Rowland et al. [19] showed that the matrix of stemflow samples (and soil waters from organic horizons) has a gradual detrimental effect on the separation efficiency of columns. Norton et al. [49] used ion chromatography to re-analyse samples where high levels of DOC had caused interference in colorimetric analytical methods used previously for chloride determinations. The interference was shown to be overcome by using ion chromatography.

#### 4.2. Soil solution

Adamson et al. [50] monitored the chemistry of soil solution and throughfall at a variety of sites around Britain and Emmett et al. [51] showed the response of throughfall and soil water chemistry to nitrogen additions at Aber Forest in Wales.

Soil solution is a very unstable sample matrix, especially in anaerobic soils. The act of removing it from the soil can initiate changes within the sample due to oxidation and de-gassing. The interesting work of Steinmann and Shotykh [52–54] has attempted to address this stability problem.

Steinmann [52] described a novel sampling system that he called 'Peepers' for collecting pore waters from lake or sea sediments. Steinmann and Shotykh measured anions and cations [53] and also [54] sulfide and acid-volatile sulfur in organic-rich natural waters from peat bogs in the Franches-Montagne region of the Jura Mountains, Switzerland; the combination of 'Peepers' and ion chromatography was particularly appropriate for measuring reduced species as the sample collection system meant that the samples were neither oxidised nor de-gassed prior to analysis. This in turn meant that volatile and unstable compounds were still present in the samples injected into the chromatograph.

#### 4.3. Drainage and stream waters

Adamson and Hornung [55] used ion chromatography to study the effect of clearfelling a Sitka Spruce plantation at Kershope Forest in Cumbria, UK. Drainage water from each experimental plot was sampled at weekly intervals from 1982 to 1987 inclusive. This covered the period from 1 year prior to felling to 4 years afterwards. Nitrate levels were typically 1–2 mg/l prior to felling, rising to a maximum of about 9–11 mg/l in the year following felling, and then slowly falling over the next few years. Satisfactory comparisons between ion chromatography and colorimetric methods were reported.

Reynolds et al. [56] used ion chromatography to model nitrogen budgets in a headwater catchment in Wales over a 10-year period. Variations in streamwater nitrate concentration were discussed in relation to the processes controlling nitrate supply from the catchment and nitrogen depletion within the stream

channel. In a later paper [57], Reynolds et al. showed the effect of conifer harvesting on streamwater chemistry. IC and CFC methods were reported to have been run concurrently for a while to confirm that the methods gave comparable results. Changes in nitrate concentrations were observed as a result of tree harvesting.

Emmett et al. [58] quantified the impact of a riparian wetland on streamwater quality. Ion chromatography was used for anion determinations, in conjunction with ICP-OES and CFC which were used to measure the other determinands. Reductions in streamwater loadings of nitrogen, phosphate, total dissolved-P, total monomeric aluminium, total filterable aluminium, iron, DOC and silica were observed after the stream had flowed through the wetland.

It is the reproducibility and stability shown by IC systems that has enabled long-term research projects such as these to take place.

#### 4.4. River, swamp and lake water

Recent publications have reported on the determination of anions, oxoanions and the measurement of carbon, nitrogen and sulfur following sample oxidation. Ohta and Tanaka [59] reported a method for the determination of the common anions ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) plus total carbonate in river, pond and forest soil waters. The best eluent was 0.5 mM 1,2,4-benzenetricarboxylate at pH 6 and detection was at 270 nm.  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in solution were shown not to interfere.

Fung and Dao [60] reported a method for the determination of oxoanions of As, Se, V, W, Mo and Cr in the presence of nitrate in river water. Three mM potassium phosphate (at pH 9) was used as eluent with UV detection at 205 nm. Agreement with results obtained by AAS methods were reported. They also reported [61] a cleanup and enrichment procedure for these determinands using Chelex-100 resin. High levels of the common anions were removed leading to detection limits at the sub-ng/ml levels for some of the oxoanions. Results compared favourably with those obtained by AAS.

Fung et al. [62] developed a method which combined thermal combustion with IC for the determination of total organic carbon in a variety of

water sample types. Carbon was converted to carbonate and analysed by nonsuppressed IC using 0.6 mM potassium hydrogen phthalate as eluent. The detection limit was quoted as 2 µg/l of C. This was reported to be three orders of magnitude lower than that obtained by the old ASTM D2579 method.

The preparation of samples for total nitrogen, phosphorus and sulfur determinations has presented problems for many years. Losses due to volatilisation were of particular concern. The development of bomb oxidation procedures has led to great improvements in this area.

Ledo de Medina et al. [63] developed a method to determine total nitrogen in water samples. This was based on the use of high pressure bombs and oxidation by potassium peroxodisulfate in alkaline conditions. The nitrate produced was analysed by chromatography with recoveries for urea and ammonium chloride being higher than 90%. Results obtained for lake water samples were compared with those obtained using the cadmium reduction method to measure the nitrate. Crowther et al. [64] described a method for the determination of organically bound sulfur in swamp water. Organosulfur compounds were oxidised to oxalate, carbon dioxide and sulfate by mixing with a dilute solution of hydrogen peroxide and exposing to UV radiation in a continuous flow system. Sulfate was then determined by IC using carbonate eluent and conductivity detection. Sulfate was measured in non-oxidised samples and organically bound sulfur was calculated by difference.

#### 4.5. Groundwater

Edgell et al. [65] reported on a collaborative study where 21 laboratories analysed a set of test samples (reagent water, drinking water, groundwater, industrial wastewaters) for chromium(VI) as  $\text{CrO}_4^{2-}$ . After separation the Cr(VI) was derivatised with diphenylcarbazide with measurement at 530 nm. The study reported bias at the lowest concentrations when a single linear calibration was used over three orders of magnitude.

Ledo de Medina et al. [66] reported on the determination of trace levels of phosphate and sulfite in the presence of high concentrations of sulfate. Sulfate was removed by precipitation as lead sulfate

prior to determination of phosphate using a standard carbonate–hydrogen carbonate eluent and conductivity detection. Sulfite was determined by analysing {sulfate+sulfite} by IC. Sulfate was reduced to hydrogen sulfide and determined potentiometrically, in order to quantify sulfite by difference.

#### 4.6. Drinking water

Many of the methods that have been developed for the analysis of drinking water can be directly applied to the analysis of environmental water samples. Most recent interest appears to have been in the analysis of bromate, which arises as a by-product of the ozonation of drinking water.

Joyce and Dhillon [9] developed a method for the quantification of bromate at the 1-µg/l level in samples containing high levels of chloride and sulfate. Chloride levels in samples were reduced by pre-treatment with a silver-form cation-exchange resin and a borate eluent was used to improve the separation of the bromate and chloride peaks.

Koudjonou et al. [11] also described a method for low-level bromate analysis. Interference from nitrate and sulfate was investigated. Three eluents were compared for signal/noise ratio. As a result of inter-laboratory trials a detection limit of 2 µg/l was established. Creed et al. [12] evaluated three columns for the determination of bromate in drinking water. Detection limits, analysis time and tolerance of potential interferences were evaluated. Detection limits were in the 1–2 µg/l range for all three. Coupling a Dionex AG10 column with an ultrasonic nebuliser on an ICP-MS system produced a detection limit of 50 ppt. Precision for pre-concentrated samples was decreased due to interference from an adjacent peak.

Ogura et al. [10] reported on comparisons between ion chromatography, air-segmented auto-analyser and standard manual methods for analysis of waters for public use. Results obtained by IC were in fair agreement with those obtained by standard manual methods. The detection limit for nitrite by IC was lower than that obtained by the standard method, but interestingly results obtained by IC were slightly higher.

Zein et al. [67] used octadecylsilica immobilised with bovine serum as a stationary phase to study the

microcolumn chromatography of inorganic anions. Measurement was by conductivity detector. Detection limits were in the low  $\mu\text{M}/1$  region for chloride, nitrate and thiocyanate in tap water and serum samples.

## 5. Soil, plant material and sediments

This section includes information on a wide variety of sample matrices. Recent publications include references to the application of ion chromatography to extracts or digest solutions from soil, plant material or sediments. Sample cleanup may be an important step in the analysis of these solutions in order to prevent column degradation.

### 5.1. Biological materials

Chadha et al. [68] described a method for the estimation of cyanide in flaxseed, which is being used increasingly in some food products. The sample was homogenised with water, left to stand, filtered and then injected onto a Waters IC Pak anion column. An hydrolysis time of 3 h showed maximum release of cyanide into solution. Ten different cultivars of flaxseed were analysed. Caution was advised on the amount of flaxseed added to foods.

Buldini et al. [69] developed a pre-treatment for the determination of chlorine, bromine, phosphorous and sulfur (plus a variety of metals) in leaves, juices and extracts of vegetables, fruits and plants. The method involved hydrogen peroxide and/or nitric acid UV photolysis at 85°C. Carbonate/hydrogen carbonate eluent and conductivity detection were then used for the determination of the anionic species formed.

Fujimura et al. [70] developed a method which was used for the determination of cyanide in apricot and river water samples. A detection limit of 50 ng/ml in solution was achieved using an eluent of 20 mM dimethylethanolamine, 1.43 mM formic acid, 20 nM triethylenetetramine-N,N,N',N'',N''',N''''-hexaacetic acid hexasodium salt and 0.03 mM borax (pH 10.5). Measurement was by conductivity detector and analysis time was 20 min.

There is a vast number of publications relating to

the application of IC to food. We have highlighted a few which have relevance to environmental samples.

Wagner [8] developed a more environmentally friendly method for the determination of sulfite in mast beer. Sulfite in samples was stabilised by the formation of an adduct with formaldehyde in slightly acidic media. It was then liberated as it entered the sample loop by adjusting the pH, thus avoiding early oxidation to sulfate. Excellent precision was claimed.

Dolenc and Gorenc [7] described a method for the determination of chloride, nitrate, phosphate and sulfate at ppm levels in vinegar with a carbonate/hydrogencarbonate eluent. Sample pre-treatment was used to reduce the influence of acetate on the chloride peak.

Lamb et al. [71] described a method for the aqueous extraction and analysis of glucose, fructose and sucrose from vegetable samples. Sample cleanup procedures were described. Analysis was by Dionex A6 columns, using 0.7 mM sodium hydroxide as eluent with pulsed amperometric detection. Detection limits were  $\sim 15 \mu\text{g}/1$  for glucose and fructose and  $100 \mu\text{g}/1$  for sucrose. Wilson et al. [72] used 160 mM sodium hydroxide as eluent, with triple-pulsed amperometric detection to quantify *myo*-inositol, sorbitol, glucose, fructose, sucrose and raffinose in five tree species. Sample preparation and cleanup was minimal.

Prodolliet et al. [73] reported a collaborative study to determine levels of carbohydrates in digested soluble coffee samples. Mannitol, fucose, arabinose, galactose, glucose, sucrose, xylose, mannose, fructose and ribose were all determined with varying degrees of reproducibility. The precision of the procedure was considered sufficiently good to find the method suitable for use in routine analysis.

### 5.2. Soil extracts

Grimshaw [74] reported on the use of 0.016 M potassium dihydrogen phosphate as an extractant to determine extractable sulfate in soils. This was an improvement on the previously recommended procedure of Probert [75] which used calcium phosphate extractant, as the potassium ion caused less problems with chromatography columns than the divalent calcium ion. This is an example of a method where careful control of reagent concentration avoids cross-



sensitivity interferences. High concentrations of phosphate will interfere with the quantification of low concentrations of sulfate in ratios greater than 500:1 (mass/mass). [1] For example the 0.016 M  $\text{KH}_2\text{PO}_4$  gives a concentration of  $\sim 1500$  ppm  $\text{PO}_4^{3-}$  in solution, so the practical detection limit imposed by cross-sensitivity is  $\sim 3$  ppm of  $\text{SO}_4^{2-}$  in solution.

### 5.3. Sediments

Colina de Vargas et al. [76,77] described methods for the determination of total nitrogen and phosphorous in sediments. Both methods used alkaline persulfate in high-pressure bombs to digest the sediment, followed by analysis of the nitrate and phosphate by ion chromatography without apparent interference from sulfate. Results showed good agreement with previous methods. Galceran et al. [78] performed a comparative study of the separation of phosphate from the other common anions. Direct conductimetric determination was compared with indirect photometric detection. The best detection limit (1 ng) was obtained by indirect photometry with hydrogenphthalate or naphthalenedisulfonate as eluent. Procedures for the removal of sulfate with resins in the barium form were also investigated. The method was applied to saline sediments.

## 6. Applicable developments in techniques

The basic technique of ion chromatography is now firmly established. Modifications and development of new mobile and stationary phases and detection systems continue to appear at a steady rate. Developments in sample preparation methods, which have been somewhat neglected, are also starting to appear in greater numbers. Recent applicable innovations and developments are detailed below.

### 6.1. Sample pre-treatment

Ohta et al. [79] investigated the adsorption of sample anions on injector loops. It was found that dissolution of the sample in eluent prior to injection overcame the problem for acidic and neutral environmental water samples.

Fung and Dao [80] used an oxygen bomb combus-

tion technique to analyse organic compounds and hazardous wastes for a variety of elements. Carbon dioxide generated during combustion gave rise to carbonate in the sample solution which in turn caused baseline disturbance. This was overcome by an ion-exchange pre-treatment. They also applied this oxygen bomb technique to the analysis of fluoride, phosphorus, chloride, bromide, iodide and sulfur in fuel and organic wastes [81]. Buldini et al. [82] developed a method for the determination of impurities of chloride, sulfate, bromide and phosphate (plus  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ ) in carboxylic acids. Samples were mixed with 2 ml of 30% hydrogen peroxide and subjected to UV photolysis for 2 h prior to analysis. Detection limits were of the order of 5–25 ng/ml.

Zerbinati [83] reported on a useful comparison of four types of solid-phase extraction cartridges for the removal of organic anions from aqueous samples. An octadecylsilica cartridge loaded with cetyltrimethylammonium *p*-hydroxybenzoate was found to be the best choice.

Kobayashi [84] developed new preconcentration and analytical methods for a variety of determinands. For inorganic and carboxylic anions *p*-toluene sulfonic acid was used as an eluent. Detection limits in the ppt–ppb range were achieved.

### 6.2. Development of eluents

Mehra and Landry [85] described a scheme using aqueous 1 mM pyridine–2,3-carboxylic acid and pyridine–2,4-dicarboxylic acid as mobile phases for the analysis of anions (chloride, nitrate and sulfate) in simple matrices. Hamilton PRP X 100 columns were used with detection at 280–290 nm. Mehra and Kandil [86] examined four aromatic disulfonic acids as eluents for the determination of ionic species by indirect UV photometry. They found that 0.5 mM 2,5-dihydroxy-1,4-benzenedisulfonic acid at pH 6.4, with detection at 335 nm, offered the best separations for 13 anions. The method was also used to determine chromate with detection at 370 nm and, with the addition of EDTA, 10 cations as their EDTA complexes. The method was applied to a variety of sample types including water and soil.

Ayikoe et al. [87] evaluated novel eluents of the hydroxy- and amino-substituted benzoic acid types.

They proposed the use of 3 mM 4-hydroxy-3-amino-benzoic acid as an eluent for the determination of halides, oxyhalides and pseudohalides in environmental samples using a Hamilton PRP X 100 column. Gautier et al. [88] evaluated 1,2-diamino-cyclohexane tetraacetic acid as an eluent for the separation of the common anions (chloride, nitrate and sulfate) and 18 selected metals using single-column chromatography with UV detection. Effects of pH and eluent concentration were studied. Detection limits were generally below 0.5 µg/l. Results for drinking water and synthetic samples were presented.

Ohta et al. [89] reported a method for the determination of common anions plus Mg<sup>2+</sup> and Ca<sup>2+</sup> in environmental water samples. The eluent was a 0.15-mM pyromellitate (1,2,4,5-benzenetetracarboxylate) at pH 5.5, with measurement by UV detection at 262 nm. Analysis time was 20 min. Ohta et al. [90] then extended this work to include the simultaneous determination of hydrogencarbonate. The eluent was modified to include 22.5% methanol, with pH adjusted to 6.25. The new method was then applied to river water.

Munaf et al. [91] evaluated several mobile phases for the determination of inorganic anions using bovine serum albumin immobilised on silica gel as the stationary phase. 2,6-Anthraquinone disulfonate was found to give the best results, with chloride, nitrate, iodide, thiocyanate and sulfate being separated within 8 min. UV detection was used. Detection limits in the range of 0.9–2.9 µM were obtained. The system was used in the analysis of environmental water and saliva samples. Gao et al. [92] studied the effect of eluent pH, concentration and composition on the retention of ions on a silica-based column. Separation time was less than 6 min for Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. Detection limits were between 1.2 and 2 ng.

Takeuchi et al. [93] optimised the mobile phase used by Zein et al. (sodium iodide and tartaric acid in aqueous solution) when using bovine serum albumin as a stationary phase.

Fujimura et al. [94] described the development of a better eluent (0.7 mM potassium hydrogenphthalate, 0.1 mM sodium tetraborate, 0.5 mM boric acid, 0.1 mM Hepps, 0.05 mM sodium hydrogencarbonate, 5% butanol) for the rapid determination of

fluoride, chloride, phosphate, nitrate and sulfate by indirect photometric ion chromatography. Analysis time was 15 min.

### 6.3. Development of stationary phases

Zein et al. used bovine serum albumin as a stationary phase to separate iodate, bromide, nitrate, iodide and thiocyanate in samples of saliva [95], and chloride, nitrate and thiocyanate in tap water and serum samples [67].

Hou et al. [96] studied the separation of cations and anions using a strongly basic anion-exchange column. They used a sodium sulfosalicylic–EDTA binary eluent and studied the effects of eluent pH, concentration and complexing effect of EDTA.

Galceran and Diez [97] studied the use of column switching techniques for the determination of phosphate in samples containing high (5000 mg/l) levels of sulfate. Detection limits of 50 ng were reported.

Corradini et al. [98] developed a new stationary phase for the measurement of oligosaccharides, isomers of gluco-disaccharides, uronic acids and sugar monophosphates. The stationary phase was formed by nitration of 2.8-µm spherical, non-porous, highly crosslinked styrene–divinylbenzene copolymer beads, followed by reduction of superficially introduced nitro groups with nascent hydrogen and quaternisation of the resultant amino groups with iodomethane.

### 6.4. Analysis of 'unusual' determinands

Ge and Lee [99] described the use of Amadori compounds as intermediates in the determination of phenylalanine, tyrosine, tryptophan, glucose and fructosylphenylalanine. Eluent was a gradient system comprising 0.5 M sodium acetate–0.1 M NH<sub>4</sub>OH, columns used were CarboPac PA-1 and CarboPac PA guard column, with amperometric detection at 0.05 and 0.6 V.

### 6.5. Development of detection systems

Zein et al. [100] improved the detection limits for chloride, nitrate and sulfate by using indirect photometric detection with anthraquinone-disulfonate as the visualisation agent. Sakai et al. [101] developed a

post-column chemiluminescence method based on the reaction between potassium hydroxide (the eluent) and nitric acid. Column effluent was mixed with nitric acid containing iron(III) ions. The eluting anions suppressed the chemiluminescence observed. Calibration was linear over the range 100 ng/ml to 100 µg/ml. The method was applied to the determination of inorganic anions in water samples. Fung and Tam [102] investigated the use of Ru(phen)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> as an ion interaction agent for indirect fluorimetric detection of anions in non-suppressed ion chromatography. They established that a wavelength of 447 nm gave most sensitivity and applied the method to trace anion analysis for environmental and industrial applications.

## 7. Conclusions

Ion chromatography has proved itself to be a powerful technique with many applications in the field of environmental research. It is capable of being used for trace-level determinations when used in conjunction with concentration techniques, or is equally capable of performing analyses where the components are present at higher concentrations. There are many reported applications for the measurement of dissolved substances or, following a digestion procedure, the measurement of total element levels in more complex sample matrices.

Many references to its use now exist, covering a wide range of applications. Methods for the determination of the common cations and anions, as well as some oxoanions are now widely reported. Methods for the determination of organic acids, carbohydrates and other interesting groups of organic compounds have now been developed. Equipment is readily available from a variety of suppliers. Configured systems utilising chemically suppressed conductivity technology have proven capabilities of being used for research over long periods of time, where instrument stability and reproducibility are critical.

Ion chromatography has now become a standard technique, earning its place as a routine method in many analytical laboratories around the world. Developments continue to take place, perhaps not at the same pace as in the earlier years, but with the

possibilities of coupling with other procedures, e.g. ICP-MS, perhaps having the most exciting potential.

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