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Review

Environmental applications of ion chromatography

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1. INTRODUCTION

Ion chromatography (IC) is a versatile, selective and sensitive method for the determination of a variety of anions and cations at trace and ultra-trace levels. It has been applied to hundreds of problems in various fields involving ionic analysis in clinical, food, pharmaceutical, industrial, plating solution and environmental samples. Perhaps the major reason for the rapid growth in popularity of IC is its usefulness in the environmental field. Due to the general complexity of environmental samples, IC has become an integral part in environmental analysis. Detection of specific trace elements at the sub-part-per-billion (10^9) level is a major challenge for the analytical chemist. The enhanced separating powers of the method also permits speciation of environmental contaminants. Different species of elements have different orders of toxicities.

Early publications (1970s) of IC work described environmental applications. Ion chromatography was introduced in 1975[1], but soon after two books were published in 1978 and 1979[2,3]. There is a need to update and assemble new application papers in applied environmental sciences.

Several books[4–8] and general review articles[9–40] have been published on IC in recent years. The most recent book by Smith[5] discusses IC applications up to 1986.

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However, much of the work reviewed focuses on company information and lacks many of the published references. Several review articles on environmental applications have also been published[41–56].

Ion chromatography is a rapidly changing field. This review includes the most recent papers published in the literature as well as information available from the major IC instrument and column manufacturers on environmental pollution applications. The literature is reported according to applications in water, soil, sediment, sludge, plants, air (aerosols) and fossil fuels. A survey of the literature indicates that replication of the analysis can be a problem. Often good or unique work on specific elements can get "buried" with the description on separation of multiple ions. The speciation of different oxidation states of related ions and separation of less common ions have been emphasized in this review.

2. WATER ANALYSIS

IC has shown great promise for the sequential determination of ionic species in a wide variety of water samples. In many cases, little sample pretreatment is required. The technique has an intrinsic ability to cope with complex water samples with large quantities of matrix ions in the detection of the target solutes at trace or ultra-trace concentrations within the sample.

There are numerous reports on the use of IC in the determination of common anions such as Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} in a wide range of water samples such as wastewater, rain water, drinking water, snow and Antarctic ice (Table 1). The use of high-performance liquid chromatography (HPLC) for the determination of organic anions and inorganic ions in such samples has been comprehensively reviewed by Bombaugh[57]. The determination of organic and inorganic pollutants in different water samples using amperometric and colorimetric detection methods was recently reviewed[58]. Amperometric detection tends to be selective and is very sensitive. The sensitivity and effectiveness of IC has also been compared to classical spectrometric methods[59]. Many IC procedures have been standardized against colorimetric, titrimetric, steam distillation, autoanalyzer, atomic absorption spectrometry (AAS) and inductively coupled argon plasma emission spectrometry (ICAP).

In addition to separation and detection of various common anions, IC has been used for the determination of various uncommon species in water. Bromide has been selectively determined in water samples using amperometric detection[60]. In a recent paper by Urasa and Nam[61], chromium(III) and chromium(VI) in water samples were analyzed directly using cation- and anion-exchange columns employing a direct current plasma-AAS as an element-selective detector. Detectable concentrations of chromium species were in the low ppb range using preconcentration procedures. Cyanide, an extremely toxic ion which is used in electroplating and gold industries, has been determined in wastewater by IC using electrochemical detection[41,107,110,114]. The simultaneous determination of CN^-, Cl^-, Br^- and I^- was recently reported with amperometric detection[115].

Different oxidation states of some elements have different levels of toxicities and hence the separation and determination of these species is very important. While ICAP and AAS only detect the total elemental content, IC can determine different species simultaneously. IC has been useful for the speciation of toxic ions such as chromium[61,124], arsenic[91,158] and selenium[135,136].

TABLE 1

APPLICATIONS OF IC IN THE ANALYSIS OF WATER SAMPLES

R.S.D. = Relative standard deviation; Cond. = conductivity; GFAAS = graphite-furnace atomic absorption spectrometry; LOD = limit of detection; DAP = diaminopropionic acid; PDCA = pyridine dicarboxylic acid.

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Rain water, groundwater	Br^-	Dionex AS3	3.0 m*M* $NaHCO_3$– 2.0 m*M* Na_2CO_3	Amperometric	LOD, 10 $\mu g\ l^{-1}$; recovery, 97–110%; Cl^- interferes if Cl^-/Br^- ratio > 1000:1	60
Rain, drinking water, lake and interstitial waters	NO_3^-, SO_4^{2-}, HCO_3^- NO_2^-, $S_2O_3^{2-}$, Cl^- Br^-, $H_2PO_4^-$, $HCOO^-$	Vydac 302IC	4.0 m*M* Sodium hydrogen phthalate	Cond.	Use of several different eluents	62
River water	Cl^-, NO_3^-, SO_4^{2-}	TSKgel IC-anion PW	0.4 m*M* Trimellitate	UV–VIS	LOD, 0.1, 0.2 and 0.1 mg l^{-1} for Cl^-, SO_4^{2-} and NO_3^-, respectively	63
Rain water	CH_3COO^-, $HCOO^-$, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}	Dionex AS3	2.0 m*M* $NaHCO_3$– 1.67 m*M* Na_2CO_3	Cond.	Detection of volatile organic acids and inorganic anions, simultaneously	64
Rain, well water, snow	NO_2^-	Shodex IC I-613	1.0 m*M* Phthalic acid– 0.35 m*M* $(C_4H_9)_4$ NOH– 0.5% tetrahydrofuran	Amperometric	LOD, 3 $\mu g\ ml^{-1}$	65
Rain, wastewater, soil pore water	Cl^-, NO_3^-, SO_4^{2-}, total S	Vydac 302 IC	4.0 m*M* Phthalic acid (pH 5)	Cond.	LOD, 0.6, 0.2 and 0.2 $\mu g\ ml^{-1}$ for Cl^-, NO_3^- and SO_4^{2-}, respectively	66
Rain water, seawater	Dimethylsulfoxide	Bio-Rad HPX-87H	5.0 m*M* H_3PO_4	UV (195 nm)	Ion exclusion; LOD, 10 $\mu g\ l^{-1}$	67
Rain water, Antarctic ice	S(IV)	Dionex AS3	0.9 m*M* Bicarbonate– 0.2% formaldehyde	Cond.	LOD, 0.1 $\mu g\ l^{-1}$; formaldehyde protects against oxidation	68

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TABLE 1 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Rain water	F^-, Cl^-, NO_2^-, SO_4^{2-}, Br^-, NO_3^-, PO_4^{3-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	Semi-automatic (analysis of 60 samples per day)	69
River water	Arsenic anions	TSKgel IC-anion PW	$NaNO_2$	Cond.	Recovery, 88–102%; LOD, 0.3–5 $\mu g\ ml^{-1}$	70
Rain water	Na^+, NH_4^+, K^+	Dionex cation exchange	6.0 m*M* HNO_3	Cond.	Significant variation between IC and AAS at lower ion concentrations	71
Simulated rain water	(i) F^-, Cl^-, NO_3^-, SO_4^{2-}, (ii) Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}	(i) Dionex anion exchange (ii) Dionex cation exchange	(i) 3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3 (ii) 5.0 m*M* HCl	(i) Cond. (ii) Cond.	Required 1–4 ml sample within 0.05–20 mg l^{-1} range	72
Rain water	Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}	Dionex	$NaHCO_3$–Na_2CO_3	Cond.	Step-gradient elution; lacks sensitivity for Mg^{2+}	73
River water	HCO_3^-, CO_3^{2-}	TSKgel IC-Anion PW	0.4 m*M* Trimellitate (pH 7.5)	UV (270 nm)	Compared well with Floco injection analysis	74
Rain, lake	(i) SO_4^{2-}, Cl^-, NO_3^-, F^-, PO_4^{3-}, (ii) Li^+, Na^+, K^+, NH_4^+ Ca^{2+}, Mg^{2+}	Dionex AS4 HPIC-CS3	(i) 1.8 m*M* Na_2CO_3–2.2 m*M* $NaHCO_3$ (ii) 4.8 m*M* HCl–4.0 m*M* DAP · HCl–4.0 m*M* histidine	(i) Cond. (ii) Cond.	Cost-effective compared to spectroscopy methods; LOD, 0.005–0.05 mg l^{-1}	75
Rain water	Alkali and alkaline earth cations	Dionex	35 m*M* HCl	Cond.	LOD, 0.05–0.15 $\mu mol\ l^{-1}$ for alkali ions and 0.2–0.6 $\mu mol\ l^{-1}$ for alkaline earth ions	76
Rain water	Na^+, Cl^-	Bio-Rad S-X2 and Dionex AS4	Lithium hydrogen phthalate–phthalic acid	Cond.	Simultaneous determination of anions and cations; LOD, ng level; R.S.D. <0.5%	77
Natural and wastewater	NO_3^-	C_{18} reversed phase	60 m*M* KH_2PO_4–15 m*M* H_3PO_4	UV (210 nm)	NO_2^- and organic chromophores do not interfere; LOD, 7 $\mu g\ l^{-1}$	78

River and drinking water	Cl^-, NO_3^-	Spherisorb ODS-2 (Phase separations, Queensferry, U.K.)	Sodium hydrogen phthalate	UV	High pH and high ionic strength of eluent not recommended; LOD, 3–4 nmol	79
River water	NO_3^-, NO_2^-	Dionex AS4	4.0 mM Na_2CO_3– 4.0 mM $NaHCO_3$	UV (220 nm)	Time of analysis for NO_3^-, 5 min	80
Lake, sea, well and tap waters	F^-	Shodex IC I-524A	2.5 mM phthalic acid (pH 4.0)	Cond.	Microdiffusion of F^- from sample matrix; LOD, 4 $\mu g\ l^{-1}$	81
River, drinking water	Li^+	HPIC-CS2	8.0 mM HCl	Cond.	LOD, 1 $\mu g\ l^{-1}$	82
River water	Na^+, K^+	Zorbax SIL	0.01 M Lithium acetate	Cond.	Time of analysis, 10 min	83
Pond water	Ca^{2+}, Mg^{2+}, (Sr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{3+})	Dionex cation exchange	1.0 mM $Ba(NO_3)_2$	Cond.	Al^{3+} or Cr^{3+} did not elute under the conditions described	84
River water	Ca^{2+}, Mg^{2+}	Synthesized polystyrene–divinylbenzene	0.12 M $HClO_4$	VIS (590 nm)	Post-column reactor	85
Pond water	Ca^{2+}, Mg^{2+}	Bio-Rad AG1-X8	1.0 mM $Pb(NO_3)_2$	Cond.	Good agreement with AAS	86
River water	Al^{3+}	Dionex CS2	0.2 M $(NH_4)_2SO_4$ (pH 2.8)	UV (310 nm)	Post-column derivatization; LOD, 7 $\mu g\ l^{-1}$	87
Tap water	Al^{3+}	Dionex CS2	0.1 M K_2SO_4 (pH 3.0)	Fluorescence	Post-column reaction; LOD, 1 $\mu g\ l^{-1}$	88
River and sewage waters	NH_4^+	Hitachi 2632 (anion-exchange resin)	Water	Coulometric	Results agree with phenate method; LOD, ng levels	89
River water	Quaternary ammonium compounds	Whatman Partisil PAC 10 (cyano–amino bonded phase)	$CHCl_3$–CH_3OH	Cond.	LOD, 0.02 $\mu g\ l^{-1}$ (50 μl sample size)	90
River water	AsO_3^{3-}, AsO_4^{3-}, SeO_3^{2-}, SeO_4^{2-}	C_{18} reversed phase	1.0 mM Hexadecyltrimethylammonium bromide	GFAAS	LOD, 15–25 ng	91

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TABLE 1 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Seawater	F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}	Dionex anion exchange	2.5 m*M* Na_2CO_3–3.0 m*M* $NaHCO_3$	Cond.	R.S.D. 0.4–4.2%	92
Seawater	Ni^{2+}, Co^{2+}, Cu^{2+}	Waters Nova-Pak C_{18}	10 m*M* CH_3COONa–CH_3OH–H_2O (76:24%) (pH 8.4)	UV (340 nm)	Time of analysis, 20 min	93
Seawater	I^-	TSKgel IC-anion PW (polymethacrylate, anion-exchange capacity, 0.03 meq)	0.1 *M* NaCl + 5 m*M* Sodium phosphate buffer (pH 6.7)	Amperometric	LOD, 5 $\mu g\ l^{-1}$; R.S.D. 3%	94
Seawater	Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}	Waters IC-Pak-C	10 m*M* Phenylethylamine (pH 5.5)	Cond. and UV/VIS	LOD, 0.2–21.0 ng ml^{-1}; aromatic base eluents were assessed	95
Surface water	Cl^-, NO_3^-, SO_4^{2-}	Waters IC-Pak-A	Borate–gluconate	Cond.	System peaks were avoided by treating sample with cation exchanger	96
Surface water	NO_3^-, NO_2^-	Merck LiChrosphere-RP_{18}	*n*-Octylamine (pH 6)	UV	Good agreement with photometric determination	97
Groundwater	Se(IV) and Se(VI)	Dionex AS3	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	Preservation of sample techniques discussed	98
Pore water	Cl^-, F^-, NO_3^-, Br^-, SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–2.0 m*M* Na_2CO_3	Cond.	Results compared with colorimetric methods; LOD, 0.005–0.1 mg l^{-1}; recovery, 97–103%	99
Natural water	F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-}	Waters IC-Pak-A	Borate–gluconate, KOH and lithium benzoate	UV/VIS or Cond.	Time of analysis, 16 min	100

Antarctic snow and ice	NO_3^-, SO_4^{2-}, Cl^-, Na^+, NH_4^+, K^+	Dionex anion exchange; Dionex cation exchange	2.0 m*M* Na_2CO_3– 2.5 m*M* $NaHCO_3$ (anions) 5.0 m*M* HCl (cations)	Cond.	Efforts were made to reduce contamination problems	101
Antarctic ice	(i) Cl^-, $HCOO^-$, methane sulfonate, NO_2^-, NO_3^-, SO_4^{2-}	(i) Dionex 030-985 anion exchange	(i) 0.7 m*M* $NaHCO_3$– 2.0 m*M* Na_2CO_3	(i) Cond.	Sample preservation info. Time of analysis, 30 min	102
	(ii) CH_3COO^-, F^-, Na^+, NH_4^+	(ii) Wescan 269-004 cation exchange	(ii) 4.0 m*M* HNO_3	(ii) Cond.	Sample preservation info.	102
Wastewater	Cl^-, NO_3^-	HIKS-1	1.0 m*M* Tyrosine (pH 10.8)	Cond.	LOD, 10 ng ml^{-1}; R.S.D. <2%	103
River water	NO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}	Dionex AS1	36 m*M* $NaHCO_3$– 24 m*M* Na_2CO_3	Cond.	Complex Fe with cyanide to avoid hydroxide interference	104
Wastewater	Cl^-, NO_3^- PO_4^{3-}, SO_4^{2-}	Dionex 30827	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Compared with various other methods	105
Wastewater	Cl^-, SO_4^{2-}, PO_4^{3-}, $S_2O_3^{2-}$, SCN^-, NO_2^-, NO_3^-	Dionex AS3 or AS5	2.55 m*M* $NaHCO_3$– 2.05 m*M* Na_2CO_3	Cond.	Time of analysis, 15 min	106
Wastewater	CN^-	Dionex AS4	2.2 m*M* Na_2CO_3	Cond.	Oxidation of CN^- to CNO^- by hypochlorite	107
Wastewater	SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	Bio-Rad Bio-gel TSK IC-anion PW	Gluconate–borate (pH 7.6)	UV (254 nm)	Compares with conventional conductivity and electrochemical detection	108
Wastewater	F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}	Dionex 30170	2.1 m*M* $NaHCO_3$– 1.7 m*M* Na_2CO_3	Cond.	Na_2CO_3 fusion used to decompose sample; LOD, 8–10 μg	109
Wastewater	CN^-	Dionex AS3	14.7 m*M* Ethylene-diamine–10.0 m*M* Na_2HBO_3–1.0 m*M* Na_2CO_3	Amperometric	LOD, 0.02 mg l^{-1}; compares well with colorimetric determination	110
Saline water	NO_3^-, PO_4^{3-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 1.9 m*M* Na_2CO_3	Cond.	LOD, 0.1 mg l^{-1}	111
Natural water	S^{2-}	Dionex-AS3	H_3BO_3–NaOH–ethylene-diamine	Amperometric	LOD, 1.9 ng ml^{-1}; R.S.D. 0.64%	112

(Continued on p. 218)

TABLE 1 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Natural water	F^-, Cl^-, NO_3^-, SO_4^{2-}	Anion-exchange resin	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	R.S.D., 1.3%; LOD, 30, 40, 240, 400 pg for F^-, Cl^-, NO_3^- and SO_4^{2-}, respectively	113
Wastewater	CN^-(Cl^-, ClO_3^-, SO_4^{2-})	Dionex anion exchange	2.2 m*M* Na_2CO_3	Cond.	Free CN^- and metal CN^- complexes determined	114
Lake water	CN^-, Cl^-, Br^-, I^-	Vydac 302 IC	Potassium hydrogen phthalate (5.0 m*M*, pH 4.3)	Amperometric	Simultaneous determination; LOD, 0.2–12 $\mu g\ l^{-1}$; recovery 95–105%; time of analysis, 10 min	115
Wastewater	PO_4^{3-}	Dionex anion exchange	3.0 m*M* Na_2CO_3– 1.0 m*M* NaOH	Cond.	LOD, 1.5 mg l^{-1}; R.S.D. 0.49%	116
Refinery wastewater	NH_4^+, ethanolamines	Dionex MPIC NS-1	5.0 m*M* hexane–sulfonic acid	Cond.	Time of analysis, <11 min; R.S.D. 2%; LOD, 0.05–5 mg l^{-1}	41
Wastewater	(i) SCN^-, $S_2O_3^{2-}$, (ii) $S_4O_6^{2-}$, SO_3^{2-}, SO_4^{2-}	Dionex anion exchange	(i) 2.4 m*M* Na_2CO_3– 3.0 m*M* $NaHCO_3$ (ii) 7.2 m*M* Na_2CO_3– 9.0 m*M* $NaHCO_3$	Cond.	Long elution time; badly tailing peaks for $S_2O_3^{2-}$; recovery, 97–101%; R.S.D. 3.8%	117
Wastewater	Borate	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	R.S.D. 0.05–2.6%; recovery, 96.4–99.3%; LOD, 0.05 mg l^{-1}	118
Wastewater	F^-, Cl^-, PO_4^{3-}, NO_3^-, SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Time of analysis, 24 min	51
Wastewater	F^-, Cl^-, NO_3^-, HPO_4^{2-} SO_4^{2-}, I^-, SCN^-, ClO_4^-	Biotronik IC-1000	1.0 m*M* Tyrosine	Cond.	R.S.D. <0.02%; LOD, 0.01 $\mu g\ ml^{-1}$	119
Natural and wastewater	F^-, Cl^-, NO_2^-, PO_4^{3-}, Mg^{2+}, Ca^{2+}, HCO_3^-, CO_3^{2-}	Dionex IC16	Na_2CO_3 or HNO_3	Cond.	Linear response	120

Wastewater	NH_4^+	Dionex CS1	H_3BO_3	Fluorescence	Post-column reaction with *o*-phthaldialdehyde	121
Wastewater	SO_4^{2-} (F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{2-}, and Br^-)	Dionex anion exchange	$NaHCO_3$–Na_2CO_3	Cond.	LOD, 40 $\mu g\ l^{-1}$; R.S.D. <3%	122
Wastewater	Cu^{2+},Pb^{2+},Zn^{2+}, Ni^{2+},Co^{2+},Cd^{2+}, Fe^{2+},Mn^{2+}	Waters μBondapak C_{18}	2.0 m*M* NaOS–30 m*M* tartaric acid– 20 m*M* citric acid (pH 3.4)	VIS (520 nm)	Sensitivity, low ng ml^{-1}; post-column derivatization	123
Wastewater	Cr(VI) + Cr(III)	Dionex CS5	2.0 m*M* PDCA, 2.0 m*M* Na_2HPO_4, 10 m*M* NaI, 50 m*M* $CH_3CO_2NH_4$, 2.8 m*M* LiOH	VIS (520 nm)	Post-column reaction; LOD, 5 $\mu g\ l^{-1}$	124
Acid rain	F^-, Cl^-, NO_3^-, SO_4^{2-}	Dionex AS3	$NaHCO_3$–Na_2CO_3	Cond.	LOD, 0.03–0.25 mg l^{-1}	125
Drinking water	NO_3^-, (F^-, Cl^-, PO_4^{3-}, SO_4^{2-}, Br^-, NO_2^-)	Dionex AS1	4.5 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Compares well with potentiometry; R.S.D. 0.5–2%; LOD, 1 mg l^{-1}	126
Natural water	F^-, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-, SO_4^{2-}	Dionex AS1	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Compares to emission spectroscopy; interferences by humic acid removed by ultrafiltration	59
Natural water	F^-, Cl^-, NO_2^-, NO_3^-, $H_xPO_4^{(3-x)}$, SO_4^{2-}	PRPX-100 polystyrenedivinylbenzene	0.8 m*M* Phthalate (pH 6.8)	UV (265 nm)	LOD, low ng; interference by carbonates; time of analysis, 15 min	129
Drinking water	NO_2^-	High capacity ion-exchange resin	4.0 *M* NaCl	UV (210 nm)	Sample concentration (10–15 ml) through ion exchange; *LOD, 0.1* $\mu g\ l^{-1}$	128
Drinking water, rain, lake water	NO_2^-	Anion exclusion/HS	5.0 m*M* H_2SO_4	Amperometric	Recovery, 96–104%; R.S.D. 2.9–7.3%; time of analysis, 6 min	127
Drinking water	(i) NO_3^-	Waters IC-Pak	5.0 m*M* LiOH	UV (214 nm)	LOD, 0.26 $\mu g\ l^{-1}$	130
	(ii) NO_3^-	Dionex HPIC AS4	28 m*M* $NaHCO_3$– 22 m*M* Na_2CO_3	Cond.	Compared to EPA test method 300.0; LOD, 4 $\mu g\ l^{-1}$	

(Continued on p. 220)

TABLE I *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Natural water	F^-, Cl^-, NO_3^-, SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	R.S.D. <2%	131
Drinking and pond water	NO_3^-	Partisil 10 SAX	1.0 m*M* Potassium hydrogen phthalate	UV (265 nm)	LOD, 0.1 μg ml^{-1}	132
Natural water	NO_3^-, SO_4^{2-}	Dionex anion exchange	0.5 m*M* Potassium hydrogen phthalate	Cond.	Time of analysis, 20 min includes cleanup procedure to remove humic substances	133
Tap water	Cl^-, NO_3^-, SO_4^{2-}	Toyo Soda IC anion PW	2.0 m*M* Tiron	Cond. or UV (290 nm)	R.S.D. 2%; time of analysis, 10 min	134
River and drinking water	Se(IV), Se(VI)	Dionex anion exchange	2.5 m*M* Na_2CO_3–2.0 m*M* KOH	Cond.	Also detects TeO_3^{2-}, TeO_4^{2-}, NO_3^-, SO_4^{2-}, PO_4^{3-}; time of analysis, 30 min; R.S.D. <0.7%	135
River and drinking water	Se(IV), Se(VI)	Nucleosil 55B (Gasukuro Kogyo, Tokyo)	75 m*M* Ammonium phosphate	Fluorescence	Post-column derivatization; time of analysis, 10 min; LOD of Se(IV), 0.17 μg l^{-1}	136
Tap water	F^-	Interaction ORH-801	0.001 *M* H_2SO_4	Cond.	Ion exclusion; time of analysis, <15 min	137
Drinking water	HCO_3^-	Interaction Ion-310	Deionized water	Cond.	Anion-exclusion method; time of analysis, <10 min	137
Drinking water	F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}	Dionex anion exchange	2.0 m*M* Na_2CO_3–0.75 m*M* $NaHCO_3$	Cond.	Recovery, 90–108%; R.S.D. 1–6%	138
Drinking water	Br^-, I^-, NO_2^-, SCN^-	Nucleosil 10-CN	Cetyltrimethylammonium bromide	Amperometric	Ion pair C_{18}; LOD for I^- or SCN^-, 1 μg l^{-1}	139
Natural water	MoO_4^{2-}, WO_4^{2-}	Dionex anion exchange	6.0 m*M* Na_2CO_3	Cond.	LOD, 1 μg l^{-1}; R.S.D. 15%; time of analysis, 17 min	140
Tap water	Al^{3+}	Dionex CG2	0.1 *M* K_2SO_4 (pH 3.0)	Fluorescence	Post-column derivatization; LOD, 1 μg l^{-1}; R.S.D. 3.4%; time of analysis, 2 min	141

Drinking water	(i) NH_4^+, Ca^{2+}, Mg^{2+}	(i) Vydac SC cation exchanger	(i) 1.25 m*M* HNO_3	(i) Cond.	(i) Time of analysis, 10 min	142
	(ii) Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}	(ii) Resin BN-X4 blend	(ii) 1.0 m*M* Ethylene diammonium dinitrate (pH 6.1)	(ii) Cond.	(ii) Time of analysis, 5 min; R.S.D. <2.5%	142
Drinking water	Ca^{2+}, Mg^{2+} (Ni^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Sr^{2+})	Dionex CS-2	2.0 m*M* Ethylenediamine–2.0 m*M* citric acid (pH 4.0)	Cond.	LOD, <20 μg l^{-1}	143
Drinking water	(i) Cl^-, NO_3^-, SO_4^{2-}	(i) Waters IC-pak™ anion	(i) 2.0 m*M* Ethylene-diamine–octane-sulfonic acid (pH 6)	(i) Cond.	Simultaneous analysis of anions and cations; time of analysis, 16 min	144
	(ii) Ca^{2+}, Mg^{2+}	(ii) Cation columns	(ii) 3.0 m*M* Sodium octanesulfonate	(ii) Cond.		144
Drinking water	(i) Na^+, K^+, NH_4^+	(i) Cation exchanger	(i) HNO_3	(i) Cond.	LOD, 1 mg l^{-1}	145
	(ii) Mg^{2+}, Ca^{2+}	(ii) Cation exchanger	(ii) Ethylenediamine	(ii) Cond.	LOD, 1 mg l^{-1}	145
Drinking water	NO_3^-, NO_2^-	Waters μBondapak C_{18}	5.0 m*M* Tetramethyl ammonium phosphate	UV (214 nm)	Time of analysis, 6 min; LOD, 0.1 mg l^{-1}	146
Natural and industrial process stream samples	Cr(III) and Cr(VI)	Dionex-CS2 and Dionex-AS7	7.5 m*M* Trilithium citrate–10 m*M* oxalic acid	Direct current plasma-AAS	LOD, 1 μg l^{-1}; element specific; time of analysis, <6 min	61
Snow	NO_3^-, SO_4^{2-}	Dionex AS1	2.4 m*M* Na_2CO_3–3.0 m*M* $NaHCO_3$	Cond.	Also detected F^-, Cl^-, Br^-, PO_4^{3-}; R.S.D. 3%	147
Fog samples	(i) Cl^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}	(i) Dionex AS4	0.5 m*M* $NaHCO_3$–1.3 m*M* Na_2CO_3	(i) Cond.	LOD, <20 μg l^{-1}; time of analysis, 12 min	148
	(ii) F^-, CH_3COO^-, $HCOO^-$	(ii) Dionex AS4	1.5 m*M* $Na_2B_4O_7$	(ii) Cond.	Time of analysis, 10 min	148
	(iii) Na^+, NH_4^+, K^+	(iii) Sykam LCA K01	4.5 m*M* HNO_3	(iii) Cond.	Time of analysis, 7 min	148
	(iv) Ca^{2+}, Mg^{2+}	(iv) Sykam LCA K01	1.0 m*M* Histidine–1.0 m*M* diaminopropionic acid–12 m*M* HCl	(iv) Cond.	Time of anlysis, 10 min	148

(Continued on p. 222)

TABLE 1 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Antarctic ice	(i) $CH_3SO_3^-$, $HCOO^-$, F^-, Cl^-, NO_3^-, SO_4^{2-}	(i) Dionex AS4	(i) 0.65 m*M* $NaHCO_3$– 2.5 m*M* $NaHCO_3$– 4.0 m*M* Na_2CO_3	(i) Cond.	Time of analysis, 6 min; requires 5 ml sample to reach 10^{-10} g g^{-1}	149
	(ii) Na^+, NH_4^+, K^+	(ii) Dionex CS2	(ii) 25 m*M* HCl	(ii) Cond.		149
Wastewater	Organic acids	Dionex AS2	0.01 *M* HCl	Cond.	Ion exclusion	149
Demineralized water	Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, alkaline earth cations	Silica-based cation exchanger	0.1 *M* Tartrate (pH 3.05)	VIS	Post-column derivatization; LOD, 2 μg l^{-1}	150
Wastewater	CN^-	Dionex AS3	1.0 m*M* Na_2CO_3– 10 m*M* NaH_2BO_3–15 m*M* ethylenediamine	Amperometric	Application to photographic wastes	151
Wastewater	CN^-, S^{2-}, Br^-	Dionex AS3	1.0 m*M* Na_2CO_3– 10 m*M* NaH_2BO_3–15 m*M* ethylenediamine	Amperometric (Ag electrode)	R.S.D. <2%; time of analysis, 8 min	41
Spiked water sampled	Cd^{2+}, Co^{2+}, Mn^{2+}	Dionex CS5	3.0 m*M* Pyridine-2,6-dicarboxylic acid–4.3 m*M* LiOH	UV (520 nm)	LOD, 0.1 μg l^{-1}; recovery, 97–114%; R.S.D. 0.57%	152
Rain water	Organic acids (formic, acetic, propionic, oxalic, malonic, succinic glutaric acid)	Dionex AG3, AS3, AF3	0.1 *M* Octane sulfonic acid	Cond.	R.S.D. 3–4.9%; LOD, 4–10 ng ml^{-1}	153
Rain water	F^-, CH_3COO^-, $HCOO^-$	Dionex AX1	2.0 m*M* $Na_2B_4O_7$	Cond.	Time of analysis, 15 min; R.S.D. 3.7–7.1%; LOD, 0.05–0.91 mg l^{-1}	154
Snow samples (Antarctic)	NO_3^-	Biotronik BT II AN	$2 \cdot 10^{-3}$ *M* Na_2CO_3	UV (215 nm)	R.S.D. 0.1%; LOD, 5 ng g^{-1}	155

Seawater (artificial)	I^-	TSKgel IC anion SW separator	0.5 m*M* Sodium citrate (pH 5.0)	UV/Cond.	R.S.D. 4%; LOD, 3 ng; also detected Cl^-, NO_3^-, ClO_4^-; Cl^-, Br^-, NO_3^- may cause interference if present in large quantities	156
Natural water	I^-	SAX-1	30 m*M* Na_2CO_3	UV (226 nm)/ Cond.	Also separates Cl^-, PO_4^{3-}, Br^-, NO_2^-, NO_3^-, SO_4^{2-}; LOD, 0.005 μg (100 μl); recovery, 95%	157
Natural water	As(III) + As(V)	Bio-Rad organic analysis column (Aminex HPX-87H ion exclusion)	0.01 *M* Orthophosphoric acid	Amperometric/ UV (200 nm)	R.S.D. 1.3%; detection was linear up to 1.0 μM; time of analysis, 20 min	158
River water	Na^+, K^+	Zorbex SIL	0.01 *M* Lithium acetate	Cond.	LOD, 0.005 *M*; time of analysis, 10 min	159
Purified water	F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, SO_4^{2-}	Dionex AS4	2.0 m*M* Na_2CO_3–0.75 m*M* $NaHCO_3$	Cond.	LOD, 3–10 μg l^{-1}; recovery, 90–107%; R.S.D. 0.4–6.3%	160
Lake water	NO_3^-	Dionex AS2	Water	UV (210 nm)	R.S.D. 0.45%; time of analysis, 10 min; LOD, low ppb	161
Natural water	Cl^-, Br^-, NO_3^-, SO_4^{2-}	Wescan anion exchange (269-001)	Sodium hydrogen phthalate	Cond.	LOD, 1 mg l^{-1}; chromatography on a guard cartridge	162
Wastewater effluent	PO_4^{3-}	Dionex AS4	2.25 m*M* $NaHCO_3$–2.0 m*M* Na_2CO_3	Cond.	Other anions separated Cl^-, F^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}	163

Organic acids appear in wastewater as a result of biological decomposition of organic materials. Ion-exclusion chromatography was found to be extremely reliable in the determination of weak organic acids in various water samples[102,153]. McDowell and Stedman[44] reported the interference of carbonic acid in their studies on the determination of formic, acetic, propionic and butyric acids in various water samples. Ethanolamines have also been determined using IC[43].

Another serious pollution problem is acid rain[125]. IC has been applied in the analysis of acid rain to determine the anion and cation composition. There are also several reports on the ionic analysis of Antarctic snow samples[101,102]. Sensitivity is an extremely important parameter since the ion content in these samples can be about 100 times lower than that of comparable samples taken from industrial areas of the northern hemisphere[5].

3. SOIL SEDIMENT, SLUDGE AND PLANT ANALYSIS

IC analysis of the ionic species in complex systems such as soil, sediments, sludges and plants has received little attention in recent years. Soil, sediment and sludge materials are often analyzed with the objective to determine a single constituent. However, the composition of other ions present may be determined by IC. The advantages of IC in the analysis of such complex samples over conventional chemical techniques include the determination of a variety of ions in a single run, speed and speciation and minimal sample preparation. Table 2 shows the environmental applications of IC in soil, sediment, sludge and plant samples.

Dick and Tabatabai[170] were the first to determine NO_3^- and SO_4^{2-} in soil samples using suppressed IC after extraction with LiCl. Inorganic nitrogen and sulfur are of prime importance in soils since they are essential plant nutrients. Frankenberger and co-workers have used IC for the determination of the following ions in soil: Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_3^{2-}, SO_4^{2-}, CN^-, Br^-, I^-, Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} (refs. 115, 167, 168, 185) as well as Sr^{2+} (ref. 185), SeO_3^{2-} (refs. 174,175), SeO_4^{2-} (refs. 173, 175) AsO_4^{3-} (ref. 177), WO_4^{2-}, (ref. 183), MoO_4^{2-} (ref. 182), CrO_4^{2-} ref. 180) $H_2BO_3^-$ (ref. 190) and HCO_3^- (ref. 190). Recently, Mehra and Frankenberger[175] developed an IC method to separate and determine SeO_3^{2-} and SeO_4^{2-}, simultaneously in soils. Speciation of Se is important in understanding its potential toxicity and mobility in groundwater and soils. Simultaneous determination of arsenite and arsenate has also been reported in sediments with no interferences from other anions[196].

IC is becoming an attractive alternative to the conventional spectroscopic methods for determination of metal ions in soil. Meaney *et al.*[205] used IC for the determination of Fe^{3+} and Al^{3+} in soil and clay samples. Bertsch and Anderson[188], using a fully automated IC system, determined Al^{3+} extracts using a UV–visible detector. Alkali and alkaline earth cations in soil have been detected using conductometric detection both by single column and suppressed techniques. Reversed-phase columns have been used for determination of Pb, Zn, Co, Fe and Mn in soils[123]. Determination of total Cu, Ni and Zn in soils has recently been reported by (i) digestion of soil with HF, $HClO_4$ and HNO_3 followed by (ii) extraction of metals as dithiozonate in $CHCl_3$, (iii) destruction of the metal dithiozonate complex with HNO_3 and (iv) final determination by IC using a chromogenic reagent for the detection of the metals by visible photometry[187].

TABLE 2

APPLICATIONS OF IC IN THE ANALYSIS OF SOIL, SEDIMENT, SLUDGE AND PLANT SAMPLES

R_s = Resolution. MS = mass spectrometry; DAN = 2,3-diaminonaphthalene.

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Soil	SO_4^{2-} (total S)	Dionex AS4	18 m*M* $NaHCO_3$–1.2 m*M* Na_2CO_3	Cond.	Time of analysis, 10 min; recovery, 84–98%; sample prep., Na_2O_2 fusion	164
Soil	SO_4^{2-}	(i) Waters IC-Pak A (ii) Vydac 302 IC	(i) Borate–gluconate buffer (ii) 4 m*M* Phthalic acid (pH 4.5)	(i) Cond. (ii) Cond.	Compared extractants: R.S.D. 1.9–8.4%; compared to ICAP; recovery, 97–108%	165
Soil	NO_3^-	Dionex AS4	0.75 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3	Cond.	LOD, 0.1 ng N dm^{-3}; Cl^- interference eliminated with Ag^+ cation-exchange resin; compared well with steam distillation	166
Soil	PO_4^{3-}	Vydac 302 IC	1.5 m*M* Phthalic acid (pH 2.7)	Cond.	LOD, 0.3 $\mu g\ l^{-1}$; time of analysis, 20 min; R.S.D. 1.1% (500 μl); compared well with autoanalyzer	167
Soil	Cl^-, NO_3^{2-}, SO_4^{2-} (NO_2^-, SO_3^{2-})	Vydac 301 IC	4.0 m*M* Phthalic acid	Cond.	Time of analysis, 11 min; LOD, 0.025–1.0 ng l^{-1}; R.S.D. 3.6–8.4%; compared well to conventional methods	168
Soil	Cl^-, NO_3^-, SO_4^{2-}	Wescan Ion-guard anion cartridge (269-003)	15 m*M* Phthalic acid	UV (300 nm)	Time of analysis, 3 min	169
Soil	NO_3^-, SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–1.8 m*M* Na_2CO_3	Cond.	Time of analysis, 12 min; R.S.D. 0.4–4.3%; compared well with methylene blue	170

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TABLE 2 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
					(SO_4^{2-}) and steam distillation (NO_3^-); recovery, 98–102%; LOD, 0.2 μg ml^{-1}	
Soil, plants	Cl^-, NO_3^-, PO_4^{3-} SO_4^{2-}	Apex ODS	0.5 m*M* Tetrabutyl ammonium hydroxide, 50% methanol, potassium hydrogen phthalate	UV (255 nm)	Recovery, 84–108%; time analysis, 20 min; interference by aspartic acid	171
Soil, plants	NO_3^- (NO_2^-)	Dionex AS4	16 m*M* Na_2CO_3– 16 m*M* $NaHCO_3$	UV (220 nm)	Time of analysis, 5 min	130
Soil	Se (total)	Cosmosil 5SL	Cyclohexane–ethyl acetate (95:5)	Fluorescence	Post-column derivatization (DAN); time of analysis, 6 min., R.S.D. 3.9%; recovery, 93–97%	172
Soil	SeO_4^{2-} (NO_2^-, NO_3^-, SO_4^{2-})	Vydac 302 IC	4.0 m*M* Phthalic acid (pH 4.6)	Cond.	Applicable with high SO_4^{2-} levels; R.S.D. 1.46 (500 μl); LOD, 18 μg l^{-1}; compared well with AAS and ICAP	173
Soil	SeO_3^{2-} (Cl^-, NO_2^-, NO_3^-, PO_4^{3-})	Vydac 302 IC	1.5 m*M* Phthalic acid (pH 2.7)	Cond.	Applicable with high Cl^- levels; R.S.D. 2% (500 μl); LOD, 3 μg l^{-1}; time of analysis, 8 min; comparable to AAS and ICAP	174
Soil	SeO_3^{2-} and SeO_4^{2-} (Cl^-, NO_3^-, SO_4^{2-})	Wescan resin-based (269-029)	4.0 m*M* *p*-Hydroxybenzoic acid	Cond.	Humic materials removed through soil phase extraction; LOD, 60–110 μg l^{-1}; R.S.D. 0.9–1.86% (500 μl); time of analysis, 15 min	175
Soil	F^-, Cl^- (NO_2^-, PO_4^{3-}, NO_3^-, SO_4^{2-})	Dionex AS3	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Various extractants used, 0.01 *M* NaOH produces maximum F^- signal; time of analysis, 15 min	176

Soil	AsO_4^{3-} (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-})	Wescan resin-based (269-029)	6.0 m*M* *p*-Hydroxybenzoic acid	Cond.	AsO_3^{3-} was not detected; R_s between AsO_4^{2-} and PO_4^{2-} 1.93; LOD, 92 $\mu g\ l^{-1}$; time of analysis, 20 min; compared well with AAS and ICAP	177
Soil	Br^-, SCN^-, I^-	Whatman Partisil 10 SAX	5.0 m*M* KH_2PO_4–10% CH_3CN organic modifier	UV (205 nm)	Interference with NO_2^-; time of analysis, 23 min; LOD, 1–3 ng	178
Soil	CN^-	Waters IC-Pak anion	5.0 m*M* KOH	Amperometric	LOD, 100 ng ml^{-1}	179
Soil	CN^-, Cl^-, Br^-, I^-	Vydac 302 IC	Potassium hydrogen phthalate (5.0 m*M*, pH 4.3)	Amperometric	Simultaneous determination; LOD, 0.2–12 $\mu g\ l^{-1}$; recovery 95–105%; time of analysis, 10 min	115
Soils, sludges	CrO_4^{2-} (NO_3^-, SO_4^{2-})	Wescan resin-based (269-029)	5.0 m*M* *p*-Hydroxybenzoic acid (pH 8.5)	Cond.	Organic impurities removed through solid phase extraction; R.S.D. 1.98% (500 μl); LOD, 92 $\mu g\ l^{-1}$; compared well with ICAP; time of analysis, 16 min	180
Soil	Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}	Vydac anion exchange	3.0 m*M* Potassium hydrogen phthalate	Cond.	Samples included soil, and drinking water	181
Soil	MoO_4^{2-} (Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-})	Waters TSKgel IC-Pak Anion 1 (26770)	5.0 m*M* *p*-Hydroxybenzoic acid (pH 8.25)	Cond.	LOD, 45 $\mu g\ l^{-1}$; time of analysis, 15 min; R.S.D. 2.7% (500 μl)	182
Soil, sludge	WO_4^{2-} (Cl^-, NO_3^-, SO_4^{2-})	Wescan resin-based (269-029)	5.0 m*M* *p*-Hydroxybenzoic acid (pH 8.5)	Cond.	LOD, 170 $\mu g\ l^{-1}$; time of analysis, 13 min; R.S.D. 1.9% (500 μl); R_s, WO_4^{2-} and SO_4^{2-}, 2.84	183
Soil	Li^+, Na^+, NH_4^+, K^+	DuPont ZIPAX SCX	3.0 m*M* HNO_3	Cond.	Li^+/Na^+ separation poor; time of analysis, 7 min; LOD, 0.1–5.0 mg l^{-1}	184
Soil	Li^+, Na^+, NH_4^+, K^+	Vydac 401 TP cation exchange	1.0 m*M* HNO_3 (pH 2.1)	Cond.	LOD, 0.05–1 mg l^{-1}; time of analysis, 5 min; compared well with conventional methods	185

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TABLE 2 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Soil	Mg^{2+}, Ca^{2+} (Sr^{2+}, Ba^{2+})	Vydac 401 TP cation exchange	5.0 m*M* Ethylenediammonium dinitrate (pH 6.1)	Cond.	LOD, 0.1–1 mg l^{-1}; time of analysis, 4 min; compared well with conventional methods	186
Soil	Ca^{2+}, Mg^{2+} (Sr^{2+}, Mn^{2+} and Zn^{2+})	Dionex CS2	2.0 m*M* Ethylenediamine–2.0 m*M* citric acid	Cond.	LOD for Ca^{2+} and Mg^{2+} were 20 and 10 $\mu g\ l^{-1}$, respectively	143
Soil	Ca^{2+}, Mg^{2+} (Sr^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+})	Dionex cation exchange	0.3 m*M* $Ba(NO_3)_2$	Cond.	Time of analysis, 10 min; compared well with AAS; LOD, 10^{-6} *M*	84
Soil	Li^+, Na^+, K^+, Rb^+, Cs^+	Dionex cation exchange	5.0 m*M* HCl	Cond.	Time of analysis, 12 min; compared well with AAS and flame photometry; R.S.D. 2.3–6.9%	186
Soil	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	Dionex cation exchange	2.5 m*M* HCl–2.5 m*M* *m*-phenylenediamine dihydrochloride	Cond.	Time of analysis, 16 min; compared well with AAS; R.S.D. 2.3–6.9%	186
Soil	Cu^{2+}, Ni^{2+}, Zn^{2+}	Dionex CS5	4.0 m*M* Pyridine 2,6-dicarboxylic acid–50 m*M* CH_3COOH-CH_3COONa (pH 4.8)	UV (520 nm)	Detection as dithiozone complexes; compared well with AAS	187
Soil	Al^{3+}	Dionex CG3	0.4 *M* NH_4Cl (pH 3.1)	UV–VIS	Post-column reaction; LOD, 20 $\mu g\ l^{-1}$ (100 μl); time of analysis,3 min; compared well with AAS	188
Soil	Pb, Zn, Co, Fe, Mn	Waters μBondapack C_{18}	2.0 m*M* NaOS–10 m*M* tartaric acid (pH 3.4)	UV (520 nm)	Post-column reaction; time of analysis, 20 min	123
Soil	Alkyl methylphosphonic acid	Dionex MPIC-NS1	2.0 m*M* Tetrabutylammonium hydroxide–1.0 m*M* Na_2CO_3–10–24% CH_3CN	Cond.	Time of analysis, 15 min; LOD, 0.2 mg kg^{-1}	189

Soil and sediment	Borate, bicarbonate	Wescan ion exclusion column	D-Sorbitol	Cond.	Time of analysis, 6 min; R.S.D. 0.68–1.42%; LOD for borate, 0.1 $\mu g\ l^{-1}$	190
Soil	F^-, Cl^-, NO_2^-, PO_4^{3-}, Ca^{2+}, Mg^{2+}	Dionex anion-exchange resin	Na_2CO_3–$NaHCO_3$	Cond.	Linear response was reported	120
Soils, plants	MoO_4^{2-} (WO_4^{3-})	Cosmosil C_{18}	1.5 m*M* Tiron–30 m*M* tetrabutylammonium bromide	UV (315 nm)	Time of analysis, 11 min; recovery, 97–105%; R.S.D. 2.4–4.5%	191
Plants	NO_3^-	Wescan anion exchange	4.0 m*M* Phthalic acid	Cond.	Used for determination of ^{15}N	192
Plants	NO_3^-, SO_4^{2-} (Cl^-, PO_3^{2-}, Br^-)	Hamilton PRP X-100	0.5 m*M* Pyromellitate buffer (pH 3)	UV (295 nm)	LOD, 2–5 ng; time of analysis, 10 min	193
Plants	Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	Dionex AS4	2.0 m*M* Na_2CO_3–0.7 m*M* $NaHCO_3$ in 2% 2-propanol	Cond.	Time of analysis, 10 min	194
Plants	(i) Li^+, Na^+, NH_4^+, K^+ Rb^+, Cs^+, Ca^{2+}, Mg^{2+}	(i) Dionex CS3	30 m*M* HCl–1.0 m*M* 2,3-diaminopropionic acid–0.5 m*M* $ZnCl_2$	(i) Cond.	Time of analysis, 8 min	194
	(ii) Ca^{2+}, Mg^{2+}	(ii) Dionex CS3	27.5 *M* HCl–2.25 m*M* 2,3-diamino-propionate · HCl–2.25 m*M* L-histidine · HCl	(ii) Cond.	Time of analysis, 12 min	194
Plants	Cl^-, PO_4^{3-}, NO_3^-, SO_4^{2-}, glycolate, malate	Dionex AS3	2.8 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3	Cond.	Time of analysis, 12 min; R.S.D. 0.1–2.1%; compared well to NO_3^- electrode	195
Plants	Cl^-, HPO_4^{2-}, NO_3^-, SO_4^{2-}, malate, oxalate	Dionex AS4	2.8 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3	Cond.	R.S.D. <5%; recovery, 95–104%; compared well with conventional methods; time of analysis, 16 min; sample: tobacco	196
Plants	(i) K^+, Na^+	(i) Dionex cation exchange	(i) 5.0 m*M* HCl	(i) Cond.	Time of analysis, 8 min; compared well with AAS and photometry; R.S.D. 0–7.69%	197

(Continued on p. 230)

TABLE 2 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
	(ii) Ca^{2+}, Mg^{2+}	(ii) Dionex cation exchange	(ii) 2.5 m*M* HCl–2.5 m*M* *m*-phenyldiamine dihydrochloride	Cond.	Time of analysis, 8 min; compared well with AAS; R.S.D. 0–7.14%	197
Plants	HCOOH	Alltech Model OA-1000 organic acid column (58°C)	5 m*M* H_2SO_4	UV (214 nm)	Time of analysis, 12 min; similar results with GC–MS	198
Sediments	Cl^-, NO_3^-, SO_4^{2-}	Dionex AS4	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	High Cl^- concentration interferes with NO_3^- and SO_4^{2-} determination; time of analysis, 25 min	199
Sediments	I^-	Dionex AS3	20 m*M* $NaNO_3$–25 m*M* NaOH	Amperometric (Ag^+ electrode)	R.S.D. 3.5%; recovery 90–111%; time of analysis, 10 min	200
Sediments	AsO_3^{3-}, AsO_4^{3-}	Dionex AS1	3.0 m*M* $NaHCO_3$–1.4 m*M* Na_2CO_3	Cond.	No interference from NO_3^-, PO_4^{3-}, SO_4^{2-}; time of analysis, 30 min	201
Sludges	Cl^-, NO_3^-, SO_4^{2-}	Dionex AS4	2.8 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3	Cond.	Time of analysis,12 min	202
Soil	NO_3^-	Waters C_{18} Radial-Pak	Tetrabutylammonium hydrogen sulfate	UV (220 nm)	Time of analysis, 6 min; compared well with colorimetric method	203
Soil, plants	Total S	Dionex AS3	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	Time of analysis, 8 min; compared well with methylene blue method; R.S.D. 0.3–6.5%	204

The chief advantage of IC in plant nutrition studies is its ability for rapid analysis of many anions including intracellular organic acids. Little sample preparation is required for these analyses. Deproteinised plant extracts (obtained routinely by boiling) avoid column contamination. Other advantages of IC in the anion analysis of plant extracts have been described recently by Grunau and Swiader[195]. However, they emphasized the need for precaution such as the use of membrane filters for the removal of interfering extractables since some of these extractables may cause column poisoning. Various digestion methods have been reported including wet and dry procedures[194,195,197].

4. AIRBORNE MATERIALS

IC is a valuable tool for the determination of ions of various airborne samples such as ambient air, aerosols and dust (Table 3). The sample species may be gases including NO_x, SO_x or mists such as H_2SO_4 that have been emitted from anthropogenic sources. Airborne samples also include non-volatile salts and inorganic ions sorbed on particulates such as fly ash or dust.

An airborne sample must first be dissolved in a solvent before it can be analyzed by IC. But this is not always so straightforward. For example, if SO_2 is collected, it must first be converted to an ionic form such as SO_4^{2-} (refs. 208,209) before the IC sample analysis can be performed. Peroxybenzoylnitrate is determined by hydrolysis of the sample into the benzoate anion which is then determined by IC[206]. Sulfuryl fluoride is hydrolyzed to F^- for the IC analysis[207].

Collection of airborne samples is performed with an impinger or sampling train where the gas is sparged through a collection solvent. Frequently, the impinger solvent contains a reagent to convert the sample into the ionic form, *e.g.*, NO_2 to NO_3^-, SO_2 to SO_4^{2-}.

Impingers containing solvents may not be convenient for field investigations or for monitoring worker exposure. Solvent-free systems are often preferred. Much of the recent work describes solid trapping samplers. Gases are passed through the sampler and then desorbed with a solvent. The sampler may be an activated carbon cartridge or flow-through denuder. Although activated charcoal may be used for direct sampling, frequently the support is coated with a chemical to make it more reactive with the target species, i.e., triethanolamine-coated supports to collect SO_2 and NO_2 (refs. 208–210).

Airborne particulates can be dry-filtered out of the air and extracted with a solvent before analysis. Frequently, water or the IC eluent is used as the extraction solvent.

Once the sample is collected, the chromatography becomes fairly straightforward. Tsitouridou *et al.*[235] reported a comprehensive study on eluent and column selection for determination of more than 15 different ions in aerosol and fog water samples. Anion-exchange chromatography is most commonly used for anion samples, but ion-exclusion chromatography is becoming popular for weak inorganic and organic acid samples[217].

Much of the work on airborne samples involves the determination of Cl^-, NO_3^- and SO_4^{2-}. However, as indicated in Table 3, there are considerable studies conducted on other ions of interest. For example, determination of ammonia[211–213], amines[211]

TABLE 3

APPLICATIONS OF IC IN THE ANALYSIS OF AIRBORNE SAMPLES

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Air	Peroxybenzoylnitrate	Dionex anion exchange	2.6 m*M* $NaHCO_3$– 3.0 m*M* Na_2CO_3	UV (224 nm)	Potential interference by C_6H_5CHO and C_6H_5COOH; LOD, 0.03 $\mu g\ l^{-1}$	206
Air	Sulfurylfluoride	Dionex AS-1	3.5 m*M* Na_2CO_3– 4.0 m*M* NaOH	Cond.	Determination based upon hydrolyis with detection of F^- and SO_4^{2-}: recovery, 95.8%; R.S.D. 11%	207
Air	Sulfur dioxide nitrogen dioxide	Dionex AS-4A	8.0 m*M* Na_2CO_3– 3.0 m*M* $NaHCO_3$	Cond.	Trapped on Sep-Pak C impregnated with triethanolamine–potassium hydroxide; R.S.D. 2.4–5.3%; recovery, 85–105%	208
Air	Sulfur dioxide nitrogen dioxide	Dionex AS-1	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Trapped on triethanolamine impregnated with molecular sieve; recovery, 85%	209
Air	Nitrogen dioxide	Dionex AS-4A	2.0 m*M* Na_2CO_3– 0.7 m*M* $NaHCO_3$	Cond.	Trapped on Sep-Pack C_{18} impregnated with triethanolamine; R.S.D. 2.7% (84 ng ml^{-1}); recovery, 87–94%	210
Air	Ammonia and amines	Dionex cation exchange	HCl–HNO_3	Cond.	Trap ammonia/amines by oxalic acid–glycerol treated filter paper; LOD, 8.4 ng ml^{-1} NH_3, 7.9–12.1 ng ml^{-1} amines	211
Air	Ammonia	Dionex cation exchange	5.0 m*M* HCl	Cond.	LOD, 10 $\mu mol\ l^{-1}$; R.S.D. $<3\%$; compares favorably to colorimetric method	212
Auto exhaust	NH_3, alkylamines	Dionex cation exchange	2.5 m*M* HNO_3	Cond.	Agreed well with spectroscopy at $>10\ \mu g\ ml^{-1}$ NH_3	213

Air	F^-	Dionex anion exchange	0.3 m*M* $NaHCO_3$	Cond.	Al did not interfere; LOD, 0.1 $\mu g\ ml^{-1}$	214
Air	Cl^-, NO_3^-, SO_4^{2-} acetate, formate, oxalate	Dionex AS-3	2.2 m*M* Na_2CO_3– 2.8 m*M* $NaHCO_3$	Cond.	Components of copper patina	215
Air	Formaldehyde	Dionex anion exchange	5.0 m*M* $Na_2B_4O_7$	Cond.	Charcoal adsorption; detected as $HCOO^-$; recovery, 99%; R.S.D. 8%	216
Air	Di- and monomethyl sulfate	Dionex anion exchange	3.0 m*M* Na_2CO_3– 2.6 m*M* NaOH	Cond.	Collected on filter pack adsorbent bed; LOD, 2–10 nmol	218
Air	N_3^-	Dionex AS2	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Air bag inflator effluent; R.S.D. 2.5%; linear range, 0.1–10 $\mu g\ ml^{-1}$	219
Air	N_3^-	Dionex AS1	2.0 m*M* NaOH– 2. 4 m*M* Na_2CO_3	Cond.	Air bag inflator effluent; Br and adipate cause interference; R.S.D. 2.5%; LOD. 0.5 $\mu g\ ml^{-1}$ (100 μl)	220
Air	HCHO, CH_3CHO	Dionex AS1	1.5 m*M* $NaHCO_3$– 5.0 m*M* $Na_2B_4O_7$– 6.0 m*M* Na_2CO_3	Cond.	Conversion to formate; R.S.D. 2.6%; LOD, 0.5 ng ml^{-1}	221
Air	AsO_3^{3-}, AsO_4^{3-}, monomethyl arsonate, dimethyl arsinite	Dionex anion exchange	2.4 m*M* $NaHCO_3$– 1.9 m*M* Na_2CO_3– 1.0 m*M* $Na_2B_4O_7$	AAS	R.S.D. 11%; LOD, <10 ng ml^{-1}; time of analysis, 10 min.	222
Air	SO_2	Dionex anion exchange	3.0 m*M* Na_2CO_3– 3.0 m*M* $NaHCO_3$	Cond.	Conversion to SO_4^{2-}; recovery 83–98%; R.S.D. 2.4–7.5%; LOD, 6.0 $\mu g\ ml^{-1}$	223
Air	SO_2	Dionex AS1	$NaHCO_3$–Na_2CO_3	Cond.	Impinger, H_2O_2 solution with conversion to SO_4^{2-}	224
Air	NO_2, NO_x	Dionex AS4	0.20 m*M* Na_2CO_3– 0.75 m*M* $NaHCO_3$	Cond.	Collected in alkaline $KMnO_4$ and converted into NO_2^-; LOD, 13 mg NO_x/m^3	225
Air	NO_2	Dionex AS3	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	LOD, 0.25 $\mu g\ m^{-3}$; R.S.D. 5.7%	226

(Continued on p. 234)

TABLE 3 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Air	H_2SO_4 mist	Dionex anion exchange	4.0 m*M* Na_2CO_3–4.0 m*M* $NaHCO_3$	Cond.	Collected on PTFE filter; extracted with benzylaldehyde; interference by benzoic acid; LOD, 0.005 $\mu g\ m^{-3}$	227
Air	Cl_2, ClO_2	Dionex AS3	Na_2CO_3–$NaHCO_3$	Cond.	Time of analysis, 25 min; R.S.D. 1.4–7.3%; LOD, 0.02 $\mu g\ ml^{-1}$ ClO_2 and 0.06 $\mu g\ ml^{-1}$ Cl_2	228
Air	$HCOO^-$, CH_3COO^-	Dionex AS1	5.0 m*M* $Na_2B_4O_7$	Cond.	LOD, 0.2 $\mu g\ m^{-3}$ for formic acid and formaldehyde and 0.4 $\mu g\ m^{-3}$ for acetic acid and acetaldehyde	229
Air	$ClCH_2COOH$	Dionex anion exchange	1.5 m*M* $NaHCO_3$	Cond.	R.S.D. 1.7%; no interference by glycolic acid, acetic acid, dichloroacetic acid, F^- and Cl^- compounds or water vapor	230
Air	Ammonium sulfamate	Dionex anion exchange	3.0 m*M* Na_2CO_3–2.0 m*M* $NaHCO_3$	Cond.	R.S.D. 1.3–3.5%; retention time, 3.4 min; recovery 94–100%; LOD, 0.9 mg m^{-3} (90-l sample)	231
Air	SO_4^{2-}, CO_3^{2-}, NO_3^-	(i) Dionex 35311 (ii) Dionex 30890	(i) 1.5 m*M* Na_2CO_3–1.9 m*M* $NaHCO_3$ (ii) 70 m*M* Na_2CO_3	Cond.	Samples collected in alkaline $KMnO_4$; recovery, 99–102%; R.S.D. 0.4–4.6%	232
Air	$HCOO^-$, CH_3COO^-, $CH_3CH_2COO^-$, Cl^-, NO_2^-, NO_3^-, SO_2	Dionex AS2	1.0 m*M* Tridecafluoroheptanoic acid, 1% isopropanol	Cond.	Recovery, 95–98%	64
Air	Chloroacetyl chloride	Dionex AS1	1.5 m*M* $NaHCO_3$	Cond.	Recovery, 99%; R.S.D. 7.2–8.8%, LOD, 0.01 $\mu g\ ml^{-1}$	233

Air	Cl^-, NO_2^-, NO_3^-, SO_4^{2-}	Vydac 302 IC	1.6 m*M* Salicylate	UV and fluorometry	LOD, 2.3–3.2 mg l^{-1}; time of analysis, 25 min	234
Aerosol	(i) Cl^-, NO_2^-, NO_3^- SO_4^{2-} (ii) Na^+, NH_4^+, K^+ (iii) F^-, glycolate, lactate, formate, formic acid	Wescan anion/R Wescan cation Wescan ion exclusion	(i) 4.0 m*M* Potassium hydrogenphthalate (ii) HNO_3 (iii) H_2SO_4	(i) Cond. (ii) Cond. (iii) Cond.	Portable IC, LOD, 0.02–0.15 mg l^{-1}	236
Aerosol	NH_4^+	Dionex cation exchange	6.0 m*M* HNO_3	Cond.	R.S.D. 0.9–2.9%; time of analysis, 10 min; compared well with ion selectivity method	236
Paint aerosol	Cr(VI)	Dionex AS5	0.5 m*M* NaOH– 7.0 m*M* Na_2CO_3	Cond.	LOD, 0.1 μg ml^{-1}; R.S.D. 4.3%; time of analysis, 8 min	237
Aerosol	SO_4^{2-}, NO_3^-	Dionex AS1	3.0 m*M* $NaHCO_3$– 0.9 m*M* Na_2CO_3	Cond.	Br^- and PO_4^{3-} interfered with analysis; time of analysis, 20 min; R.S.D. 1–3%	238
Aerosol	SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	LOD, 0.5 μg m^{-3}	239
Aerosol	Cl^-, NO_3^-, SO_4^{2-}	Vydac 302	5.0 m*M* Potassium hydrogenphthalate	Cond.	Time of analysis, 7 min	240
Aerosol	Cl^-, NO_3^-, SO_4^{2-}	Dionex AS4	2.8 m*M* $NaHCO_3$– 2.2 m*M* Na_2CO_3	Cond.	LOD, 5 ng m^{-3}; time of analysis, 8 min	241
Aerosol	F^-, Cl^- (NO_2^-, NO_3^-, SO_4^{2-})	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Time of analysis, 20 min	242
Flue dust	AsO_4^{3-}, SO_3^{2-}	Dionex anion exchange	3.5 m*M* Na_2CO_3– 2.6 m*M* NaOH	Cond.	No detection of AsO_3^{3-}; LOD, 1.8 μg ml^{-1} AsO_4^{2-}; oxidation of SO_3^{2-} to SO_4^{2-} by addition of $FeCl_3$ or $CuCl_2$	243
Flue dust	AsO_4^{3-}, AsO_3^{3-} (Cl^-, NO_3^-, SO_4^{2-})	Dionex AS1	3.5 m*M* Na_2CO_3– 2.6 m*M* NaOH	Cond.	Time of analysis, 30 min	244
Flue gas	SO_3^{2-}, SO_4^{2-}, H_2SO_4 mists	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	SO_3^{2-} and SO_4^{2-} are detected simultaneously	245

(Continued on p. 236)

TABLE 3 *(continued)*

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Flue gas	NO_x, SO_x	Toya Soda IC-Anion-PW	0.7 m*M* Gluconate– 0.7 m*M* boron– 0.1 m*M* KH_2PO_4–EDTA	UV–VIS–Cond.	Ions were determined from flue gas scrubbing	246
Flue gas	SO_3^{2-}, SO_4^{2-}	Dionex anion exchange	9.0 m*M* $NaHCO_3$– 7.2 m*M* Na_2CO_3	Cond.	IC method was used to determine sulfoxy ions in flue gas desulfurization solutions	247
Flue gas	Hydrogen halides and halogens	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	No SO_2 or NO_x interference; recovery 99.4%; LOD, low $\mu g\ ml^{-1}$	248
Flue gas	Cl^-, SO_3^{2-}, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+	(i) Dionex anion exchange (ii) cation exchange	(i) 3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3 (ii) 5.0 m*M* HNO_3	Cond.	Time of analysis, 30 min	249
Combustion gases	F^-, Cl^-, NO_x, SO_3^{2-}, SO_4^{2-}, Br^-, HPO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$– 4.0 m*M* Na_2CO_3	Cond.	Column temperature critical to obtain good resolution	250

Dusts, fly ash	F^-, Cl^-, NO_2^-, NO_3^-, I^-, SO_4^{2-}, PO_4^{3-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	Time of analysis, 16 min; R.S.D. 0.12–9.99%; compared well with ion selective electrodes, potentiometry, AAS, ICP	251
Coal fly ash	F^-, Cl^-, NO_3^-, SO_4^{2-}	Dionex anion exchange	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	R.S.D. <3%; LOD, 0.05–150 μg ml^{-1}; unable to detect PO_4^{3-}	252
Diesel exhaust	Formic acid	Dionex ICE	5.0 m*M* $Na_2B_4O_7$	Cond.	Time of analysis, 11 min; peak height linear from 0.1–4 μg ml^{-1}; LOD, 0.05 μg ml^{-1} (100 μl sample)	217
Fuel combustion products	F^-, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-, SO_x^-, Mg^{2+}, Ca^{2+}, Na^+, NH_4^+, K^+	Dionex AS1	3.0 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	Cond.	Time of analysis, 20 min; compares to ASTM methods with greater sensitivity	253
Atmospheric pollutants	NO_2^-, NO_3^-, SO_4^{2-}	IC-PAK anion	Potassium hydrogenphthalate *vs.* borate–gluconate	Cond.–UV (284 nm)	IC compared well to colorimetric method for NO_2^-; time of analysis, 16 min; LOD by UV for SO_4^{2-}, 5 ng (50 μl sample)	254

TABLE 4

APPLICATIONS OF IC IN THE ANALYSIS OF FOSSIL FUELS

Sample	*Ion*	*Analytical column*	*Eluent*	*Detector*	*Comments*	*Ref.*
Fuels, coal	F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, NO_3^-, SO_4^{2-}	Dionex anion exchange	Na_2CO_3–$NaHCO_3$	Cond.	Compared well to ASTM methods; LOD, 2–10 $\mu g\ ml^{-1}$	255
Fuels	Total S (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-})	Dionex anion exchange	2.4 m*M* $NaCO_3$– 3.0 m*M* $NaHCO_3$	Cond.	Compared well to ASTM methods; R.S.D. 0.7%; LOD, 2 $\mu g\ ml^{-1}$ SO_4^{2-}	256
Fuel oil	Total S	Dionex AS1	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Compared well with titrimetry	257
Fuel oil	Total S	Dionex AS1	3.0 m*M* $NaHCO_3$– 2.4 m*M* Na_2CO_3	Cond.	Compared well with X-ray fluorescence and titrimetry; LOD, 0.007%; R.S.D. 2.7%; time of analysis, 25 min	258
Crude oil	Total S (Cl^-, NO_3^-, SO_4^{2-})	Waters IC-Pak	Borate–gluconate–acetonitrile–glycerol	Cond.	Recovery, 95.7–102.2%; R.S.D., 1.0–2.9%; LOD, 0.5 $\mu g\ kg^{-1}$; time of analysis, 15 min	259
Coal, ash, geological materials	F^-	Dionex AS3	1.5 m*M* $NaHCO_3$	Cond.	LOD, 1 ng; R.S.D. 4.9%; compared well with ion selective electrode	260
Coal	Total Cl^-	Wescan 260-001	Potassium hydrogenphthalate	Cond.	Extraction with dimethyl sulphoxide; converted to Cl^-	261
Coal	Cl^-, NO_3^-, NO_2^-, SO_4^{2-}	SAX 1	4.0 m*M* Na_2CO_3– 4.0 m*M* $NaHCO_3$	Cond.	Precision not satisfactory for NO_2^-, NO_3^-; time of analysis, 10 min	262
Coal	Ag, Al, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Ti, V, Zn	100Å μStyragel	Pyridine (chloroform, tetrahydrofuran)	ICP-AES	LOD, 3–530 ng ml^{-1}; size-exclusion chromatography; multiple peaks of Fe	263

and alkylamines[213] have been reported. Acetate, formate and oxalate[215], sulfamate[231], monochloroacetic acid[230], chloroacetyl chloride[233], formic acid[64,217,235], dimethyl- and methyl-sulfate[218], azide[219,220], formaldehyde[216] and acetaldehyde[221] have also been monitored.

5. FOSSIL FUELS

The elemental composition of fossil fuels such as coal and various petroleum products is an important environmental consideration in the use of these energy sources. IC can be used to determine the fuel elemental composition for halogens, N, S, P and various metals. The samples may first be combusted in an oxygen bomb or a furnace, the gases are absorbed in water and the ions are determined by IC. In other cases, the sample is simply extracted with a solvent. Dimethyl sulfoxide has been used to leach Cl^- from a number of coal samples[261]. Water extract of coal has been used by Honma *et al.*[262] for the determination of Cl^-, NO_2^-, NO_3^- and SO_4^{2-}. Recently Burns *et al.*[264] found IC to be very attractive for the separation of a number of radionuclides of elements such as plutonium, americium, curium, uranium and thorium in radiochemical wastes. Table 4 lists the applications of IC in the analysis of fossil fuels.

6. CONCLUSIONS

New analytical developments in IC have allowed the simultaneous determination of ions from complex matrices at trace levels. IC can be tailored to be selective for specific target solutes in the presence of other matrix ions, *i.e.*, SeO_4^{2-} *vs.* SO_4^{2-} (ref. 173), SeO_3^{2-} *vs.* Cl^- (ref. 174) and AsO_4^{3-} *vs.* PO_4^{3-} (ref. 177). Much of the IC applications involve suppressed systems marketed by Dionex (Sunnyvale, CA) but recent advances have now become available with non-suppressed systems (single column ion chromatography, SCIC).

Important parameters in optimizing the separation and detection of target solutes include choice of eluent, concentration of the mobile phase, working pH, column selection and choice of detectors. Among the most popular eluents, low ionic strength aromatic organic acids (phthalate, benzoate and citrates) and mineral acids have been used as the mobile phase in SCIC. Stationary phases include macroporous styrenedivinylbenzene resins, quaternized silica and polymethacrylate gels. Conductivity is frequently used as the mode of detection in IC but other detectors include absorbance (UV or visible light), fluorescence, AAS, coulometry and amperometry. Electrochemical detection is popular because of its high selectivity and its ability to detect ultra-trace levels.

New developments in IC do not simply involve "pick and choose" of each component (mobile phase, column and detector), but require extensive knowledge in determining the compatibility of these components in developing a useful analytical system. The pK_a of the target ion of interest must be known as well as the presence of potential interfering substances. Column selection is based on the upper and lower pH limit of the mobile phase to optimize separation.

Among the advantages of IC are: (i) its relatively high sensitivity with detection limits in the low $\mu g\ ml^{-1}$ (conductivity, UV/VIS, AAS), low $ng\ ml^{-1}$ (amperometry) and pg ml^{-1} range (fluorometric detection); (ii) simultaneous determination of several species and other elements, *e.g.*, separation and determination of SO_3^{2-}, SO_4^{2-} and $S_2O_3^{2-}$ (ref. 108); (iii) IC is non-destructive and fractions can be collected for further confirmation; (iv) the cost of IC is relatively low (the system can be modified easily by combining different components to accommodate changes in analytical requirements); (v) sample preparation is often minimal. IC can be used in routine analysis of environmental samples and operated after minimal instruction.

7. SUMMARY

Ion chromatography (IC) is going through rapid growth and popularity because of its usefulness in the applied environmental field. This review includes recent IC applications in rainwater, groundwater, surface water, wastewater, drinking water, fog samples, ice, snow, soil, sediments, sludge, plants, air, exhaust, aerosols, flue dust, fly ash, fuel oil and coal. A major emphasis of this review is on speciation of ions.

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