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Environmental applications of ion chromatography in China

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ABSTRACT

A survey of environmental applications of ion chromatography (IC) in China is presented, including air, water and soil pollution. The chromatographic conditions for the analysis of environmentally common and critical compounds are discussed.

INTRODUCTION

Environmental chemists are often required to analyse many samples taken throughout regularly spaced areas in the environment. This enables them to perform a rapid survey of the environment for pollutant sources. However, the problems are compounded by the requirement for multi-component determinations on each sample. Several characteristics of ion chromatography make it attractive for environmental sample analysis, including its speed, simple operation and easily obtainable reagents, together with its versatility and high sensitivity. It can generate an ion profile for each sample and the presence or absence of a wide variety of ions can be ascertained in a single injection. Another feature is the clear separation of many chemically similar species. More recent innovations such as chelation IC, multi-phase separation columns, gradient IC and low-pressure IC offer expanded environmental capabilities. So far, IC has been applied successfully to the determination of ions in diverse types of environmental samples. This paper discusses the applications of IC in air, water and soil pollution studies and special attention is given to acid rain and sample pretreatment.

AIR POLLUTION

The first area in which IC found widespread acceptance was in air pollution analysis. The major areas where IC are used are atmospheric particulates, aerosols, acid rain, sulphur dioxide flue gas and automobile exhaust analysis. Coal combustion is a major source of air pollution in China, especially in cities. Particulates and sulphur dioxide are the two most significant pollutants. Energy consumption in China has increased more than 10-fold over about 30 years [1]. In 1987, about 859 million

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TABLE I

CONTENTS OF MAJOR WATER-SOLUBLE CHEMICAL CONSTITUENT OF AIRBORNE PARTICLES IN DIFFERENT SIZE RANGES (0.1 $\mu g/m^3$)

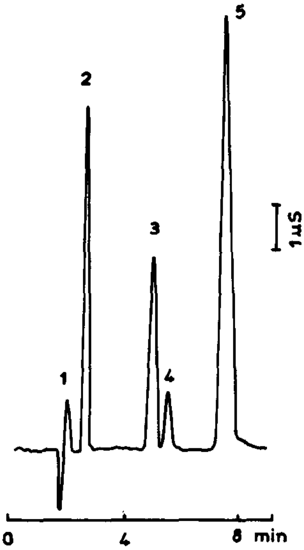
Area	Size range (μm)	Spring 1985				Autumn 1985			
		SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}
Guiyang (urban)	>7	46.9	5.15	11.7	19.0	20.1	2.68	5.53	7.84
	7–3.3	27.8	5.88	8.28	8.83	14.9	1.56	4.83	3.18
	3.3–2	31.6	4.04	9.06	6.40	18.5	1.34	5.73	2.43
	2–1.1	59.5	4.04	15.1	3.36	34.7	1.79	13.8	2.84
	<1.1	184	8.09	27.4	4.05	115	4.46	27.6	3.54
Guiyang (suburban)	>7	48.6	5.88	12.6	18.3	18.8	4.46	4.06	9.64
	7–3.3	20.2	5.88	7.35	5.40	15.2	3.13	4.90	4.98
	3.3–2	21.9	3.86	8.44	3.09	21.2	2.24	7.60	3.45
	2–1.1	37.2	2.75	10.9	3.18	46.3	2.24	15.4	3.00
	<1.1	129	5.14	21.6	22.0	105	3.56	30.3	5.95
Beijing (suburban)	>7	15.1	6.7	5.55	31.6	44.5	24.7	8.83	39.4
	7–3.3	8.88	4.46	4.49	15.7	28.7	22.6	10.6	21.5
	3.3–2	8.24	4.01	6.01	9.48	24.9	19.5	11.0	8.25
	2–1.1	9.15	3.58	7.18	5.03	45.8	44.5	16.2	9.19
	<1.1	47.5	21.5	18.8	18.6	107	106	26.5	7.01

tons of coal equivalent were consumed for energy production in the country, coal accounting for 76% of the total. Table I gives the contents of major water-soluble chemical constituents of airborne particles collected in Guiyang and Beijing. Acid rain and acidification of the environment have emerged as an environmental issue of increasing concern in China. Although the precipitation samples have been collected and analysed for acidity and chemical composition since the late 1970s, in some cities such as Beijing, Shanghai, Chongqing and Guiyang, extensive research and sample monitoring only began after IC had become more popular. The monitoring data gathered so far demonstrate that acid precipitation does occur in some parts of China. Approximately 90% of the sampling sites with mean precipitation pH values lower than 5.6 are situated to the south of the Yangtze River, especially in Sichuan, Guizhou and Jiangxi provinces. Areas with the most serious acid rain problem are in the southwestern region; Chongqing and Guiyang have annual mean pH values of 4.14 and 4.07, respectively. Table II shows the rainwater composition in different areas. Sample preservation is significant in rainwater analysis [2]. The monitoring of sulphite and sulphate is important for the mechanism of the formation of acid rain. Fig. 1 shows the concentrations of SO_3^{2-} and SO_4^{2-} in a typical acid rain sample collected in Guang Zhou; 0.2 ml of formaldehyde and 0.1 ml of 0.2 M Na_2CO_3–0.3 M NaOH were added to 10 ml of sample to prevent sulphite oxidation when the sample was collected. In addition to inorganic ions, some organic acids have been monitored. $AgNO_3$ was added to the rain sample to prevent formic and acetic acids from being decomposed by microorganisms in the water. Figs. 2–4 show ion chromatograms of some typical acid rain samples in Sichuan province which were obtained by low-pressure IC [3,4].

TABLE II

CONCENTRATION OF MAJOR IONS IN RAINWATER SAMPLES (μequiv./l)

Ion	North China			South China			
	Beijing (suburban) 1984	Tianjing (urban) 1981	Beijing (urban) 1981	Guiyang (urban) 1982–84	Guiyang (rural) 1982–84	Chongqing (urban) 1982–84	Chongqing (rural) 1982–84
pH	6.06	6.3	6.8	4.07	4.58	4.14	4.44
SO_4^{2-}	106	317.7	273.1	411	167	307	165
NO_3^-	27.7	29.4	50.2	21	15.9	31.6	18.0
Cl^-	66.2	183.1	157.4	8.2	21.1	15.0	23.9
NH_4^+	127.8	125.6	141.1	78.9	50.6	106	64.1
Ca^{2+}	78	278	184.0	231.2	87.8	110	42
Na^+	13.9	175.2	140.9	10.1	5.9	51.4	45.34
K^+	18.2	59.2	40.2	26.4	7	7.4	23.4
Mg^{2+}	15.6			56.5	29.4	48.3	18.3



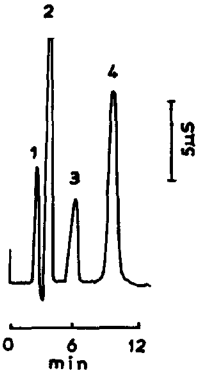


Fig. 1. Chromatogram of anions in acid rain collected in Guang Zhou. Column Dionex HPIC-AS4A; eluent, 2 m*M* Na_2CO_3–3 m*M* NaOH. Peaks (ppm): (1) F^-, 0.23; (2) Cl^-, 1.40; (3) NO_3^-, 6.87; (4) SO_3^{2-}, 1.98; (5) SO_4^{2-}, 14.6.

Fig. 2. Chromatogram of anions in acid rain obtained by low-pressure IC. Column, low-pressure YI; pressure, 43 p.s.i.; eluent, 1.4 m*M* Na_2CO_3; flow-rate, 1.0 ml/min. Peaks (ppm): (1) F^-, 0.30; (2) Cl^-, 1.04; (3) NO_3^-, 2.0; (4) SO_4^{2-}, 3.2.

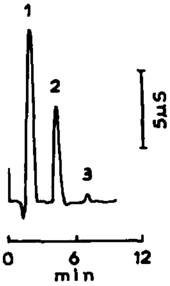


Fig. 3. Chromatogram of organic acids in acid rain obtained by low-pressure IC. Column, low-pressure ICE; pressure, 30 p.s.i.; eluent, 1 mM HNO_3; flow-rate, 0.6 ml/min. Peaks: (1) inorganic acid; (2) formic acid; (3) acetic acd.

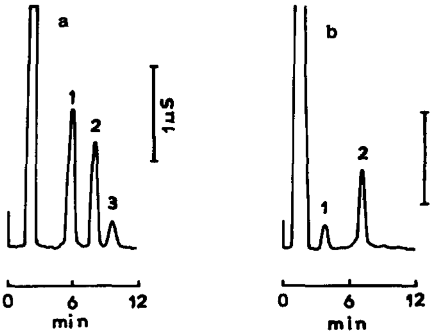


Fig. 4. (a) Chromatogram of alkali metals in acid rain obtained by low-pressure IC. Column, low-pressure CI; pressure, 30 p.s.i.; eluent, 0.75 mM HNO_3; flow-rate, 0.7 ml/min. Peaks (ppm): (1) Na^+, 0.24; (2) NH_4^+, 0.63; (3) K^+, 0.10. (b) Chromatogram of alkaline earth metals in acid rain obtained by low-pressure IC. Column, pressure and flow-rate as in (a); eluent, 1 mM ethylenediamine–2.2 mM HNO_3. Peaks: (1) Mg^{2+}; (2) Ca^{2+}.

WATER POLLUTION

Drinking water

Water quality assessment and water pollution analysis are natural applications of IC. The general use of IC in these areas has been limited to some extent by the lack of equivalence with published methods of the Environmental Protection Agency and other guidelines. It is necessary when working under the guidelines and regulations of these agencies to use equivalent methods; once approval of IC has been achieved, its widespread acceptance for these types of analyses can be expected. IC has been used for routine water analysis for the determination of anions and cations in drinking water in some Chinese cities [5]. Because of the deleterious effects of nitrite on humans, there is great interest in the control of its concentration in drinking water. Drinking water from various cities has been analysed for some harmful agents, such as chromium(VI), cyanide, arsenic and halogenated organic acids. Using a new column from Dionex, chlorite, chlorate and bromate can be measured down to the low ppb level while other common anions are being simultaneously measured.

Industrial waste water

The next area of interest is industrial waste water. Using IC, an industrial waste water laboratory can not only measure the ions of interest more economically, but can also monitor the other ions which are present. Often this added information can help in solving pollution problems by providing a complete ion characterization of the waste stream. In addition to the classical use of IC for commonly occurring anions and cations in industrial waste water, IC can also be used for some of the less common but very toxic chemicals such as chromate and arsenite. Chromium, arsenic and selenium are elements with variable oxidation states, which influence their chemical properties and toxicities. Environmentally, chromate and arsenite are of primary concern because of their greater toxicity than chromium(III) and arsenate, respectively. The determination of different oxidation states is of great interest. With IC, chromium(III) and chromium(VI) can be separated and detected with a single injection. Arsenate, selenate, selenite and seven common anions were separated by anion exchange and detected by conductivity detection with a single injection. Arsenite was separated on an ion-exclusion column and detected with amperometric detector [6]. The selectivity and sensitivity are satisfactory.

The results for the determination of chromium, arsenic and selenium are illustrated in Table III. The relative standard deviations are in the range 0.4%–4.4% and the detection limits are in the range 0.5–40 ppb.

Fig. 5 shows the detection of arsenate in semiconductor waste water. Most analytical procedures such as atomic absorption spectrometric, photometric and electrochemical methods are based on either total measurement or on preliminary chemical separation. IC can separate and determine different oxidation states simultaneously. If the oxidation states of a compound are stable in aqueous solution, it is possible to determine them by IC.

The determination of cyanide in various samples is very important environmentally because of its large-scale industrial uses and its extreme toxicity. In all the analytical methods developed so far for cyanide and sulphide, removal of interferences is a necessary first step when analysing most samples. In the IC method, cyanide and sulphide are separated and thus are determined simultaneously [7]. IC with an electrochemical detector has been used to determine free cyanide in ground water and waste water. When large amounts of chloride are present in the sample, ion-exclusion separation is a good choice.

Soil

Environmental studies usually overlap with agricultural studies in the fields of soil, plant and ground water analysis. The ions of particular interest here are those which strongly influence the plant growth process.

TABLE III

LINEARITY, RELATIVE STANDARD DEVIATIONS (R.S.D) AND DETECTION LIMITS (D.L.) FOR DIFFERENT ELEMENTS

Species	Linearity correlation coefficient	Range (ppm)	R.S.D. (%)	Level (ppm)	D.L. (ppb)
Cr(III)	0.9990	0.04–0.8	0.4	0.1	40
	0.9994	0.80–12.0	1.0	5.0	
Cr(VI)	0.9993	0.0003–0.05	4.4	0.005	0.5
	0.9996	0.05–5.00	1.1	0.2	
As(III)	0.9993	0.002–0.150	3.1	0.1	2
	0.9988	0.15–3.00	2.5	1.5	
As(V)	0.9989	0.008–0.250			8
	0.9995	0.25–10.00	1.5	5.0	
Se(IV)	0.9992	0.008–0.250			8
	0.9993	0.25–10.00	0.65	5.0	
Se(VI)	0.9987	0.008–0.250			8
	0.9995	0.25–10.00	0.97	5.0	

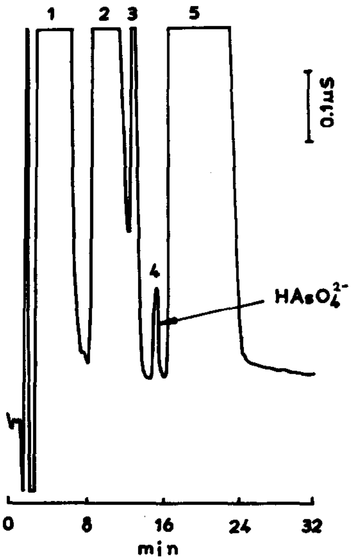


Fig. 5. Chromatogram for detection of HAsO$_4^{2-}$ in semiconductor waste water. Column, Dionex HPIC-AS4A; eluent, 7.5 m*M* NaHCO$_3$–1.2 m*M* Na$_2$CO$_3$. Peaks: (1) Cl$^-$; (2) NO$_3^-$; (3) HPO$_4^{2-}$; (4) HAsO$_4^{2-}$; (5) SO$_4^{2-}$.

Sample pretreatment is an important problem in soil analysis using IC. Extending IC to the analysis of soil has been hindered by the sample preparation problems associated with soil samples. Chromatographic procedures require that a sample to be analysed is in solution, and preferably in aqueous form in the case of IC. Dis-

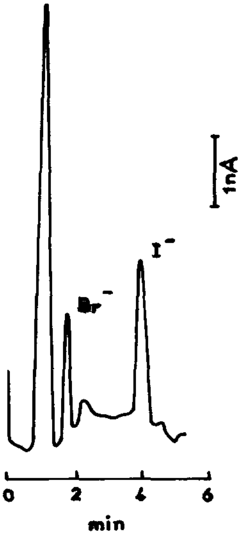


Fig. 6. Chromatogram of Br$^-$ and I$^-$ in soil. Column, Dionex HPIC-AS5; eluent, 0.015 *M* NaNO$_3$; detector, electrochemical with silver electrode, 0.26 V. Peaks: Br$^-$, 34.5 ppb; I$^-$, 15.7 ppb.

TABLE IV

EXTRACTANTS AND MONITORED IONS

Extractant	Ions
H_2O	F^-, Cl^-, NO_3^-
2 m*M* Na_2CO_3–2 m*M* NaOH	
3 m*M* $NaHCO_3$–2.4 m*M* Na_2CO_3	
5 m*M* $NaHCO_3$–5 m*M* K_3PO_4	
10 m*M* LiCl	NO_3^-, SO_4^{2-}
10 m*M* KCl	
3.2 m*M* $Ca(H_2PO_4)_2$	
10 m*M* $Ca(C_2H_3O_2)$	
0.1 m*M* $NaHCO_3$	F^-, Cl^-, NO_3^-, SO_4^{2-}
0.5 m*M* $NaHCO_3$	PO_4^{3-}
30 m*M* NH_4F–17 m*M* HCl	NO_3^-, SO_4^-, PO_4^{3-}
1 *M* $NH_4(C_2H_3O_2)$	Na^+, K^+, Mg^{2+}, CA^{2+}

solution of the sample in acids should be avoided when determining anions, unless a subsequent large dilution with water is possible, because the acid anions that are added could result in overloading of the analytical column.

Two procedures have been used in soil sample pretreatment. One is extraction [8], and Table IV gives a list of the extraction reagents that have been used for monitoring anions and cations. The method used to prepare the extract must give quantitative extraction of these ions in soils. Sometimes, these extraction procedures were repeated several times.

The other procedure is fusion–ion exchange [9]. Soil samples were weighed as air-dried powders into a ceramic crucible and an excess amount of NA_2CO_3 and ZnO was added. The flux and sample were mixed in the crucible and the covered crucible was heated for 30 min at 700°C. An excess amount of deionized water was added to the cooled crucible to dissolve partially the fused material, the solution was transferred to a volumetric flask and an excess amount of a strongly acidic cation-ex-

TABLE V

COMPARISION OF THE RESULTS OBTAINED BY IC AND CERTIFIED VALUES (CV) OF SOIL STANDARD SAMPLES

Samples[a]	Br^- (μg/g)		I^- (μg/g)		F^- (μg/g)		Cl^- (μg/g)	
	CV	IC	CV	IC	CV	IC	CV	IC
GSS1	2.9	2.6	2.0	1.9				
GSS2	4.5	4.5	1.8	1.9	220	213		
GSS3	4.3	4.2	1.4	1.4				
GSS4	4.0	4.0	9.0	10.0				
GSS5	1.8	1.6	3.8	3.9	50.0	48.7		
GSS6			19.4	19.8			98.0	92.0

[a] Certified soils reference materials from the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, Beijing, China.

change resin was added to remove the metal ions and CO_2. Fig. 6 shows the determination of Br^- and I^- in soil. Table V compares the results obtained by IC and the certified values for standard samples. The values obtained by the IC method were in close agreement with the published values for geological standards. The high precision of the procedure for the analysis of soil is also illustrated.

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