Ion chromatographic determination of major ions in fog samples

M. Achilli[a],* L. Romele[a], W. Martinotti[b], G. Sommariva[c]

[a]CISE SpA, Via Reggio Emilia 39, 20090 Segrate (MI), Italy
[b]ENEL SpA CRAM, Via Rubattino 54, 20154 Milan, Italy
[c]DIONEX Srl, Via Grigna 9, 20155 Milan, Italy

Abstract

An ion chromatographic configuration including column switching and gradient elution was used for the determination of major cations (Na^+, Ca^{2+}, Mg^{2+}, K^+, NH_4^+) and anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) in fog water samples. The results showed that ion-exchange chromatography compares very well with the more generally used spectroscopic techniques for cation determinations. Detection limits range from 6 μg/l (Na^+) to 40 μg/l (K^+). Precise and accurate analysis of natural fog water samples can be performed with cost and time savings in comparison with other techniques.

1. Introduction

Past observations on the chemical composition of fog water samples collected in Europe, Japan and USA have revealed high acidity [1–3] associated with high concentrations of NO_3^- and SO_4^{2-} [4,5]. These results have given rise to concern over potential damage to vegetation, materials, crops and public health, with growing evidence that the pollutant input in areas characterized by high fog occurrence can be relevant to terrestrial ecosystems. Lindberg et al. [6] and Saxena and Lin [7] suggested that the environmental impact of acidic fog can be as great as, if not greater than, that caused by acid rain.

The chemical composition of fog water as collected from different sites has been determined by several workers [1,8–12]. Spectroscopic techniques have widespread use in the

determination of major cations in liquid samples especially, inductively coupled plasma atomic emission spectrometry (IC-AES) (Ca^{2+}, Mg^{2+}, Na^+) and flame atomic emission spectrometry (FAES) (K^+).

For NH_4^+ determination, the indophenol spectrophotometric method [13] is used normally in manual or automatic systems [flow-injection analysis (FIA)]. Ion chromatography (IC) is generally used for major anion determinations analysis (NO_3^-, SO_4^{2-}, Cl^-, NO_2^-, PO_4^{3-}) [14–18].

In this paper, an IC remote-controlled switching technique with two-column operation is described for both cation and anion determinations in fog water samples. A comparison was made between this and other generally used techniques in our laboratory for alkaline and alkaline-earth metals. The replacement of the potentially dangerous and expensive tetrabutylammonium hydroxide regenerant with a recently developed

* Corresponding author.

self-regenerating suppressor reduces environmental problems caused by liquid waste discharge. The IC technique was applied to fog water samples collected in Po valley (Northern Italy) during the winter season 1993–1994.

Experimental

2.1. Reagents

All chemicals were of analytical-reagent grade and all reagents, eluents and standard solutions were prepared using water purified with a Milli-Q system (Millipore).

$NaCl$, $NaNO_3$, Na_2SO_4, KH_2PO_4 and $NaNO_2$ (Fluka) were used to prepare stock standard anion solutions (1000 mg/l). Orion 951007 1000 mg/l $N-NH_4$ standard solution was used as the NH_4^+ stock standard solution. Carlo Erba 1000 mg/l atomic absorption stock standard cation solutions were used.

Sodium carbonate and sodium hydrogencarbonate (Merck) were used for preparation of the eluent for IC anion determinations and methanesulphonic acid (Fluka) for that for cation determinations.

2.2. Instrumentation

A modified Dionex 2000i ion chromatograph with a Dionex gradient pump, eluent degassing module and conductivity detector was used. Anions were separated on an AS4A-SC ion-exchange column (4 mm I.D.), with an AG4A-SC guard column, and detected after suppression with an ASRS1 anion electrical self-regenerating suppressor. Cations were separated on a CS12 ion-exchange column (4 mm I.D.), with a CG-12 guard column, and detected after suppression with CSRS1 cation electrical self-regenerating suppressor. Switching from the anion to the cation column was effected using a PC remote-driven dual stack nitrogen-actuated Dionex valve. Acquisition of data and chromatograms and remote control of instrumentation were performed with Dionex AI450 software on a PC station.

For comparison, a Spectroflame ICP atomic emission spectrometer was used for Na^+, Ca^{2+} and Mg^{2+} determination, a Pye Unicam flame atomic emission spectrometer was used for K^+ determination and a Lachat flow-injection instrument for NH_4^+ determination by the indophenol spectrophotometric method.

2.3. Anion-exchange chromatographic analysis

The anions Cl^-, NO_3^-, NO_2^-, PO_4^{3-} and SO_4^{2-} were eluted using eluent 1 (4 mM $NaCO_3$ + 2.4 mM $NaHCO_3$) and eluent 2 (Milli-Q-purified water) with a linear gradient programme from eluent 1–eluent 2 = 40:60 initially to pure eluent 1 after 12 min, at a flow-rate of 1 ml/min.

The injection volume was 100 μl, the run time was set to 12 min, the cycle time was 15 min per analysis and the conductivity detector full-scale was 30 μS.

2.4. Cation-exchange chromatographic analysis

Isocratic elution was used for Na^+, Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ determination with 20 mM methanesulphonic acid as eluent (1 ml/min). The injection volume was 100 μl, the run time was set to 12 min, the cycle time was 15 min per analysis and the conductivity detector full-scale was 3 μS.

3. Results and discussion

3.1. Anion determination

A typical chromatogram is reported in Fig. 1, showing retention times for the various anions. With the actual operating conditions a good correlation for the calibration graph was obtained for all anions ($r^2 \approx 0.99$) in the range 1–20 mg/l (1–5 mg/l for nitrite). A quadratic fit was employed because of the behavior of high-concentration standard solutions: a positive deviation was observed, probably due to ageing of the column. This effect (mostly evident for sulphate and phosphate) was not studied further.
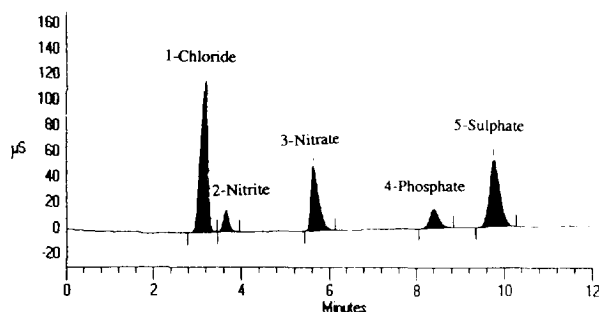
Fig. 1. Typical anion chromatogram for standard solution (4 mg/l NO_2^-, 10 mg/l other anions). Column. Dionex AS4A; injection volume, 100 μl; conductivity detector full-scale, 30 μS; gradient elution with carbonate eluent as described in the text.

The relative standard deviation was less than 1% at the 5 mg/l concentration level and between 0.7 and 3% at the 1 mg/l concentration level (Table 1).

A practical detection limit for the proposed method was calculated considering that during routine analysis a lower limit of integration is imposed corresponding to an area of 1500. Including also the effect of error in instrumental determination at low concentration, detection limits of 30 μg/l for chloride, 50 μg/l for nitrite, 60 μg/l for nitrite, 200 μg/l for phosphate and 40 μg/l for sulphate were obtained.

Table 1
Precision data for ion chromatographic determination of anions

Anion	R.S.D. (%)	
	1 mg/l[a]	5 mg/l[b]
Chloride	3.0	0.6
Nitrite	1.1	
Nitrate	0.7	0.6
Phosphate	2.0	0.8
Sulphate	1.2	0.6

Injection volume, 100 μl; detector full-scale, 30 μS.
[a] Sample size: 11.
[b] Sample size: 5.

3.2. Cation determination

Vial contamination

Two types of autosampler vials for standards and samples were tested for background contamination. Contamination from plastic and glass vials was checked before use. Whereas the contamination levels in glass vials for K^+, Mg^{2+} and NH_4^- were below the detection limit, the levels for Na^+ and Ca^{2+} were higher (about 25 μg/l) and it was not possible to reduce them below the detection limit. Plastic autosampler vials showed a greater contamination problem. Even after repeated washings with nitric acid and Milli-Q-purified water in an ultrasonic bath the levels remained unchanged. The best results were obtained using new glass vials cleaned with Milli-Q-purified water in an ultrasonic bath six times for at least 10 min. Samples and standards were transferred directly to the vials, in order to avoid other sources of contamination. Glass vials not conditioned with acids are highly recommended, because the same vials can be used for anion analysis, thus saving time for complete analysis.

It must be remembered that cation concentrations in real fog water samples (see Table 5) are much higher than the contamination levels for Ca^{2+} and Na^+.

Linearity

Five standard solutions with increasing concentrations (0.2, 0.5, 1, 2 and 5 mg/l) were used for calibration for cation determinations (Ca^{2+}, Na^+, K^+, Mg^{2+} and NH_4^+). The calibration was linear for Ca^{2+} ($y = 85260x + 472.5$; $r^2 = 0.9998$), Na^+ ($y = 73670x = 680.5$; $r^2 = 0.9998$), K^+ ($y = 47220x - 1331$; $r^2 = 0.9998$) and Mg^{2+} ($y = 136800x - 1907$; $r^2 = 0.9998$), whereas the best fit for ammonium was a quadratic type ($x = 4.15^{-11}y^2 + 1.31^{-5}y - 0.09149$). For ammonium a negative deviation from linearity was observed, probably due to the decrease in mobility with increasing concentration. Interferences from the other cations were excluded because the same effect was observed for solutions containing NH_4^+ only at concentrations up to 20 mg N/l.
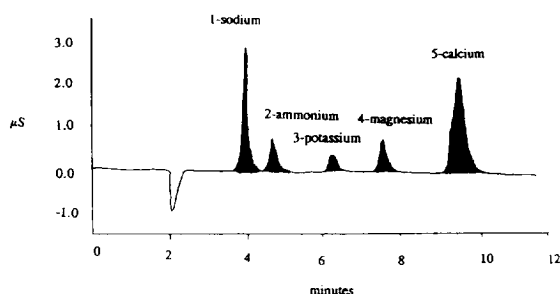
Fig. 2. Typical cation chromatogram for standard solution (2 mg/l all cations). Column, Dionex CS-12; injection volume, 100 μl; conductivity detector full-scale, 3 μS; elution with 20 mM methanesulphonic acid as described in the text.

Linearity was checked up to 20 mg/l using single-element standard solutions. From the practical point of view a quadratic fit must be used if ammonium is to be determined; if not, both types of fit can be used.

A typical chromatogram obtained for a standard solution is shown in Fig. 2.

Interferences

Possible interferences between alkali and alkaline earth metals were checked on single-element standard solutions by adding different concentrations of other alkali or alkaline earth metals and recording the value of the integrated areas. Preliminary results showed that some interferences between elements that elute close together are likely to exist, even if the data are

sometimes contradictory; further studies are necessary.

Precision

The precision of the analysis of real samples was calculated at two concentration levels, as found into two fog water samples collected in the Po valley (Northern Italy). From Table 2 it can be seen that the relative standard deviation (R.S.D.) ranges from 0.67 to 5.03% for higher concentrations and from 1.57 to 3.32% for lower concentrations.

Accuracy

As internal reference materials for checking the accuracy of cation determinations, two artificial fog water samples were prepared and analysed with the proposed method. The results obtained were compared with the average data resulting from an intercomparison exercise on samples organized with other laboratories. As shown in Table 3, good accuracy can be obtained for all the parameters, recoveries ranging from 89.5 to 113%.

Detection limit

As for anion determinations, a practical detection limit for the proposed method was calculated considering a lower limit for area integration of 500. The calculated detection limits were

Table 2
Precision data for ion chromatographic determination of cations

Cation	Concentration (mg/l)	R.S.D. (%)	Concentration (mg/l)	R.S.D. (%)
Na$^+$	0.31	4.2 (1.0[a])	2.4	5 (0.5[a])
NH$_4^+$	2.73	1.6 (2.0[b])	27.02	2.4 (1.5[b])
K$^+$	0.21	4.8 (3.9[c])	1.77	4 (0.4[c])
Mg^{2+}	0.17	2.3 (0.4[a])	1.48	0.7 (0.3[a])
Ca^{2+}	0.52	3.3 (0.8[a])	4.26	0.9 (0.2[a])

Injection volume, 100 μl; detector full-scale, 3 μS; sample size, 10.
[a] By ICP-AES.
[b] By indophenol FIA spectrophotometric method.
[c] By FAES.

Table 3
Comparison between reference and found values for artificial fog water samples

Cation	Reference value[b] (mg/l)	Found (mg/l)	Difference (%)
Solution A[a]			
NH_4^+	200.9 ± 3.5	179	−11
Ca^{2+}	7.34 ± 0.15	7.27	−1
Mg^{2+}	4.27 ± 0.09	4.50	+5
Na^+	3.86 ± 0.10	4.02	+4
K^+	3.89 ± 0.03	4.02	+3
Solution B[a]			
NH_4^+	25.8 ± 0.3	24.7	−4
Ca^{2+}	0.97 ± 0.02	1.00	+3
Mg^{2+}	0.57 ± 0.01	0.62	+9
Na^+	0.48 ± 0.02	0.53	+10
K^+	0.51 ± 0.01	0.56	+10

[a] Solution A, high level; solution B, low level.
[b] Reference values ±95% confidence interval ($n = 9$).

6, 15, 40, 20, and 12 μg/l for Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}, respectively.

Comparison with other commonly used techniques

Comparison with spectroscopic techniques for Na^+, Ca^{2+}, Mg^{2+} and K^+ determination and the indophenol FIA spectrophotometric procedure for ammonium determination was carried out on the basis of precision, sensitivity and practical considerations on time and cost of analysis.

In our laboratory Na^+, Ca^{2+} and Mg^{2+} are normally determined using ICP-AES and K^+ by FAES. Detection limits for these elements are 10, 5, 2 and 10 μg/l for Na^+, Ca^{2+}, Mg^{2+} and K^+, respectively.

Except for Mg^{2+}, these limits are better than those previously reported for IC analysis; however, the latter are more than sufficient for cation determination in fog water samples. It must be remembered also that the calculated IC detection limits are practical limits for the method proposed in this work; the theoretical limits are lower.

The detection limit for ammonium is lower than that for the indophenol method (25 μg/l).

Precision data for cation determinations by spectroscopic and FIA techniques are reported in Table 3; the values range from 0.2 to 1.5% for higher concentration levels and from 0.4 to 3.9% for lower concentration levels. As shown, the results for ammonium are similar for both techniques, whereas for the other elements the spectroscopic precision is better than that for the IC technique, although in the latter case the R.S.D. is less than 5% and therefore suitable for fog water samples analysis.

The results show that for fog water analysis, the IC, spectroscopic and FIA methods have similar analytical performances and can be used for routine laboratory analysis. From the practical point of view it must be stressed, however, that with only the one IC instrumentation with the switching technique described in this work both cation and anion determinations can be performed in two successive runs in the same autosampler vials. Otherwise, three different analytical techniques must be used, with time and cost penalties.

In Table 4, data obtained from the IC analysis of real fog water samples are compared with results from spectroscopic techniques for calcium, sodium, potassium and magnesium. The agreement between the two series of data is acceptable for most of the samples; some of the differences can be explained by the fact that

Table 4
Comparison between ion chromatographic and atomic spectroscopic results for cation determination in fog water samples

Sample	ICP-AES			FAES	IC			
	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
MI14-93	4.09	0.49	1.81	1.61	3.82	0.49	1.61	1.87
MI15-93	4.26	0.34	1.36	1.79	4.11	0.40	1.03	1.86
MI16-93	2.03	0.34	0.76	1.21	1.85	0.35	0.72	1.36
MI17-93	4.87	0.48	1.09	1.57	4.61	0.50	0.98	1.59
MI19-93	4.32	0.44	1.39	1.57	4.05	0.46	1.24	1.76
MI21-93	2.89	0.31	1.20	1.60	2.69	0.34	1.11	1.97
MI01-94	4.29	0.62	3.02	2.14	4.39	0.71	3.13	2.54
MI02-94	2.37	0.19	1.32	0.65	2.67	0.33	1.44	1.03
MI03-94	3.28	0.36	2.34	1.61	3.33	0.48	2.27	2.29
MI04-94	N.D.	N.D.	N.D.	5.20	15.90	2.20	4.23	6.28
MI05-94	6.16	1.27	2.46	2.52	6.13	1.38	2.68	3.00
VE24-93	1.55	0.17	0.47	1.02	1.43	0.17	0.48	1.08
VE25-93	3.99	0.43	1.94	2.60	3.73	0.41	1.89	2.73
VE26-93	2.81	0.21	1.88	1.53	2.53	0.22	1.80	1.62
VE27-93	4.69	1.59	2.51	1.68	4.31	1.47	2.30	1.79
VE28-93	3.28	0.51	1.49	1.93	3.06	0.53	1.29	2.21
VE29-93	7.07	0.93	1.51	5.30	6.62	1.01	1.52	5.70
VE30-93	4.26	0.47	0.80	2.86	4.19	0.58	0.95	3.18
VE31-93	17.04	0.71	1.65	1.93	15.40	0.79	1.61	2.20
VE33-93	3.35	0.61	4.85	2.13	3.14	0.70	4.46	2.30
VE34-93	2.79	0.47	2.12	1.37	2.63	0.58	2.09	1.60
VE01-94	1.82	0.48	2.53	0.73	1.90	0.58	2.45	0.98
VE02-94	2.08	0.35	2.27	1.50	2.26	0.45	2.30	1.78
VE04-94	1.21	0.29	0.78	0.53	1.07	0.29	0.67	0.59

Samples were collected in the Po Valley (Northern Italy) during the winter season 1993–1994.

practical reasons led to a time delay between chromatographic and spectroscopic analyses.

Application to real samples

The proposed IC method was applied to the determination of major cations and anions in fog water samples collected in the Po valley (Northern Italy) during the winter season 1993–1994. Samples were collected by using an automatic sampler with a PTFE impactor; an automatic optical device allowed differentiation between fog and rain.

In Table 5, complete analytical results are reported. NO_3^- and SO_4^{2-} are the species that make the largest contribution to acidity, while NH_4^- is the principal neutralizing compound, in

particular in highly industrialized urban area [Milan (MI)].

4. Conclusions

The proposed IC two-columns switching technique is suitable for the rapid, precise and accurate determination of major cations and anions in fog water samples. Acceptable detection limits are obtained for all the ions. The time of analysis is significantly shortened as only one ion chromatograph is used, without the need for atomic spectroscopic and spectrophotometric (manual or automatic) instrumentation, thus lowering operational costs.

Environmental problems related to waste dis-

Table 5
Results of the analysis of fog water samples using the method described in this work

Sample	Cl (mg/l)	NO_2 (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	NH_4 (mg/l)
MI14-93	9.92	<0.05	47	97	3.82	0.49	1.61	1.87	46.7
MI15-93	0.54	<0.05	<0.06	<0.04	4.11	0.40	1.03	1.86	155.1
MI16-93	6.52	<0.05	35	61	1.85	0.35	0.72	1.36	27
MI17-93	21.9	<0.05	83	149	4.61	0.50	0.98	1.59	88.1
MI19-93	14.9	<0.05	57	117	4.05	0.46	1.24	1.76	59.2
MI21-93	15.5	<0.05	71	115	2.69	0.34	1.11	1.97	67.7
MI01-94	28.3	<0.05	111	338	4.39	0.71	3.13	2.54	149.3
MI02-94	10.0	0.2	12	41	2.67	0.33	1.44	1.03	26.6
MI03-94	9.25	<0.05	103	95	3.33	0.48	2.27	2.29	57.1
MI04-94					15.90	2.20	4.23	6.28	141.1
MI05-94	12.6	33.5	370	200	6.13	1.38	2.68	3.00	163.7
VE24-93	2.60	3.4	28	36	1.43	0.17	0.48	1.08	21.8
VE25-93	12.4	1.3	20	28	3.73	0.41	1.89	2.73	15
VE26-93	2.78	4.8	46	31	2.53	0.22	1.80	1.62	23.9
VE27-93	10.4	3.5	50	37	4.31	1.47	2.30	1.79	26.7
VE28-93	11.8	3.0	44	130	3.06	0.53	1.29	2.21	66.1
VE29-93	13.4	5.5	77	141	6.62	1.01	1.52	5.70	73.4
VE30-93	5.33	7.7	44	42	4.19	0.58	0.95	3.18	37.3
VE31-93	8.51	6.8	68	123	15.40	0.79	1.61	2.20	59.2
VE33-93	9.34	3.6	38	110	3.14	0.70	4.46	2.30	47.2
VE34-93	9.02	<0.05	39	42	2.63	0.58	2.09	1.60	33.4
VE01-94	11.1	2.1	10	34	1.90	0.58	2.45	0.98	18.9
VE02-94	5.63	2.5	22	95	2.26	0.45	2.30	1.78	42.1
VE04-94	2.84	<0.05	155	34	1.07	0.29	0.67	0.59	45.7

Samples were collected in the Po Valley (Northern Italy) during winter season 1993–1994.

charge of potentially dangerous tetrabutylammonium hydroxide regenerant for suppression are avoided with the use of an electrical self-regenerating suppressor.

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