

## Note

# Analysis of atmospheric precipitation by reversed-phase ion-pair chromatography

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In recent years much effort has been applied to the use of high-performance liquid chromatography (HPLC) for the separation and determination of inorganic anions. The use of a low-capacity anion-exchange column combined with an eluent consisting of a dilute aromatic acid anion solution (*e.g.*, Vydac IC and Hamilton PRP-X100 columns) or with an eluent containing a dilute carbonate-hydrogen-carbonate buffer (*e.g.*, the chemically suppressed Dionex ion chromatography system) for the determination of anions is the most common approach<sup>1–3</sup>. The use of other chromatographic methods, especially in the reversed-phase mode, has also been studied in order to extend the applicability and to permit the use of universal HPLC instrumentation. For the separation of some common inorganic anions, ion-pair chromatography (IPC) or ion-interaction chromatography (IIC) using octadecyl-bonded silica as a non-polar stationary phase has been reported<sup>4,5</sup>. The theoretical dependence of the capacity factor on the mobile phase variables and the optimization of the mobile phase composition has been studied by various workers<sup>6–10</sup> and previously in our laboratory<sup>11,12</sup>.

In this work, a reversed-phase Partisil 10 ODS-3 column was evaluated for the rapid determination of several anions (chloride, nitrite, bromide, nitrate and sulphate) in environmental samples. It was found that a combination of 8 mM tetrabutylammonium iodide (TBAI) and 1 mM potassium hydrogenphthalate (KHP) at pH 6 as the eluent was very suitable for the separation of those anions with this column. The method was applied to rainwater and aerosol samples and the results were compared with those obtained with a PRP-X100 (Hamilton) ion-exchange column. The reproducibility of triplicate measurements ranged between 0.5 and 0.9% for  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The detection limit was 0.1–0.2 ppm with a 100- $\mu\text{l}$  injection sample volume. The results of the field measurements are presented.

## EXPERIMENTAL

### *Sampling*

Single rain event samples and monthly averaged rainwater samples were collected at the roof of the highest university building at the VUB–Oefenplein campus

(an urban site) and simultaneously at the university rooftop and a more rural site (Massart garden) 4 km from the university in a southeast direction. The Massart garden is located at the border of the Zonienwoud (a forest surrounding the southern part of Brussels) and distant from major pollutant sources. Rainwater samples were stored at 4°C until further chemical analysis.

*Single rain event samples.* A wet-only collector was used for the sampling of single rain events. The collection system consisted of a 31-cm diameter polyethylene funnel which was mounted 1 m above the roof of the building of the Science Faculty (Building G), 35 m above the ground level, at the Free University of Brussels. The funnel was attached via a short PTFE tube directly to a fraction collector covered with a Plexiglas box. The funnel was covered between rain events to avoid dry fall-out. The funnel and tubing were rinsed and cleaned with Milli-Q water before a collection sequence was started. The rainwater was collected in glass tubes that had been washed with phosphoric acid and thoroughly rinsed with Milli-Q water. After collecting a volume of 20 ml of subsample, the fraction collector advanced to the next tube. The pH of each of the subsamples was measured shortly after collection.

*Monthly averaged rainwater samples.* During a period of 1 year (April 1986 to March 1987), a total of twelve parallel samplings (at the University rooftop and the Massart garden) of precipitation were carried out. Samples were collected using a rainwater collector. A funnel coupled to a 2-l polyethylene bottle was placed at a height of 1 m.

*Sampling of aerosols.* Total suspended particulates (TSP) were collected on Millipore 0.45- $\mu\text{m}$  HA filters using a high-volume air sampler (CA G004, Contigea Schlumberger SA, Belgium). They also were taken at the top of Building G (VUB-Oefenplein campus). The total sampling time of each sample was 24 h. The sampling rate was 1.05 m<sup>3</sup>/h. Seventeen samples were collected from January 29th to February 24th, 1987. During this sampling period, three snow samples were collected in parallel with the atmospheric aerosol samples. After the total amount of aerosols had been determined, the water-soluble components of the aerosol samples were extracted with 10 ml of Milli-Q water. The sample was shaken overnight in a mechanical shaker and then placed in an ultrasonic bath. The liquid extract was filtered using a low-volume Millipore filtration system (a 15-ml capacity glass funnel; a glass microanalysis frit support, 25 mm; a glass vacuum filtering flask, 125 ml; a Millipore HVLP 02500 filter of 0.45  $\mu\text{m}$  porosity; and a Millipore vacuum pump), and also using an Acrodisc syringe filter (Gelman Sciences; 0.45- $\mu\text{m}$  pore size and 3-mm diameter), and stored in a refrigerator at 4°C until analysis.

#### *Chemicals and apparatus*

The chromatographic technique (equipment, reagents and preparation of eluent) has been described in detail previously<sup>11,12</sup>. In addition, a 1 mM KHP (analytical-reagent grade, R.C.B., Belgium) eluent at pH 5.5 and a 4 mM *p*-hydroxybenzoic acid (analytical-reagent grade, Aldrich-Chemie, F.R.G.) eluent at pH 8.6 were used for the anion-exchange column.

The columns used were a slurry-packed 250 × 4.6 mm I.D. Partisil 10 ODS-3 RP column (Whatman) protected with a 60 × 2.1 mm I.D. guard column with the same packing and a 150 × 3.9 mm I.D. PRP-X100 ion-exchange prepacked column protected with a PRP-X100 Cartridge Guard column (Hamilton). The particle size of the column packings was 10  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

*Evaluation of the retention behaviour of anions on the reversed-phase Partisil 10 ODS-3 column*

*Factors that affect the retention of inorganic anions.* Ion-interaction or ion-pair reversed-phase chromatography carried out with an aqueous eluent containing a quaternary ammonium salt and a phthalate buffer was found to be an efficient system for the separation of various inorganic anions.

The capacity factors ( $k'$ ) of the anions increase with increasing TBAI concentration, reach a maximum and then decrease with further increase in TBAI concentration. A linear relationship was found between  $1/k'$  and the ionic strength of buffer and also the mobile phase pH. An increase in the buffer concentration and/or pH thus results in a decrease in the capacity factor. The relevant figures for the dependence of  $k'$  (or  $1/k'$ ) on the TBAI concentration (or the buffer concentration or the pH of the mobile phase) have been given in a previous paper<sup>11</sup>. The results can be converted into a mathematical model, using the equations

$$1/k'_x = a\{1/[Q^+]_m\} + b[C^-]_m + c[B^-]_m + d[X^-]_m \quad (1)$$

$$1/k'_x = a'\{[(QCA)_s + A_s]/[Q^+]_m\} + b'[B^-]_m + c'[X^-]_m \quad (2)$$

where  $[Q^+]_m$  and  $[C^-]_m$  are the concentrations of the quaternary ammonium ion and the co-anion in the mobile phase, respectively,  $[B^-]_m$  and  $[X^-]_m$  are the concentrations of the buffer anion and sample anion, respectively;  $(QCA)_s$  is the amount of TBAI adsorbed on the stationary phase,  $A_s$  is the number of free sites on the stationary phase and  $a$ ,  $a'$ ,  $b$ ,  $b'$ ,  $c$ ,  $c'$  and  $d$  are constants. Details of the experimental results and discussion have been presented elsewhere<sup>11</sup>.

*Factors controlling the resolution of anion peaks and the peak height.* Experimental evidence demonstrates that the concentration of the ion-interaction reagent (IIR), the buffer concentration and the pH of the eluent are the major factors that affect the retention of anions in the chromatographic process. These factors should therefore also affect the resolution of anion peaks and detection sensitivity of analytes according to the well known resolution and peak-height equations:

$$R_s = \frac{1}{4} \sqrt{N} [k'/(k' + 1)] (\alpha - 1) \quad (3)$$

and

$$h = (4Sm \sqrt{N})/[p \varepsilon_c (k' + 1) L d_c^2 \sqrt{2p}] \quad (4)$$

where  $R_s$  is the resolution,  $N$  is the column plate number,  $k'$  is the mean solute capacity factor of two adjacent peaks in eqn. 3 or the solute capacity factor in eqn. 4,  $\alpha$  is the selectivity factor ( $k'_2/k'_1$ ),  $S$  is the response factor of the detector,  $m$  is the amount of sample injected,  $\varepsilon_c$  is the adsorbent porosity,  $d_c$  is the column diameter and  $L$  is the column length.

As can be understood from eqn. 3, the resolution of an adjacent pair of peaks can be affected and controlled by three parameters,  $N$ ,  $k'$  and  $\alpha$ . The resolution  $R_s$  is

a function of  $\sqrt{N}$ , so that any increase in the plate number results in an increase proportional to the square root of  $N$ . As for a given column the changes in plate number are relatively small with changes in mobile phase conditions<sup>11</sup>, this factor has only a small influence on  $R_S$ . The effect of the term  $k'/(k' + 1)$  on the resolution is also generally minor; if the nominator increases (decreases) by an amount  $\Delta k'$ , the denominator also increases (decreases) by the same amount. The lower the  $k'$  value and the larger the change  $\Delta k'$ , the more important the term  $k'/(k' + 1)$  will be. This term varies by a factor 2 between eluent buffer concentrations of 1 and 4 mM for  $\text{Cl}^- - \text{NO}_2^-$ ,  $\text{Br}^- - \text{NO}_3^-$  and  $\text{NO}_3^- - \text{SO}_4^{2-}$ . The selectivity factor, and hence the capacity factors of the two adjacent peaks, has a major influence on the separation. Previously obtained results showed the dependence of  $R_S$  on the TBAI concentration and mobile phase pH. The large variation of  $R_S(\text{NO}_3^- - \text{SO}_4^{2-})$  with respect to  $R_S(\text{NO}_2^- - \text{Br}^-)$ ,  $R_S(\text{Cl}^- - \text{NO}_2^-)$  and  $R_S(\text{Br}^- - \text{NO}_3^-)$ <sup>12</sup> is primarily due to the change in selectivity ( $\alpha = k'_2/k'_1$ ) as a function of the TBAI concentration or pH.

The peak height or detection sensitivity of analytes is also a function of these factors, as in eqn. 4,  $k'$ ,  $S$  and  $N$  are present. These parameters are affected by the eluent composition (other parameters being constant). The dependence of the peak height on [TBAI] has also been presented previously<sup>12</sup>. The peak height of nitrate and sulphate is considerably increased and that of chloride only slightly with increasing TBAI concentration. This increase should be mainly due to an increasing amount of adsorbed TBA on the stationary phase when the mobile phase concentration of TBA is increased; at higher TBA concentrations,  $k'$  decreases, thus increasing the peak height, but in the low TBA concentration range the plate number or the response factor of the detector must be the peak-height controlling factor.

*Optimum mobile phase composition and column performance.* Based on the above discussion, it is clear that the most important parameter affecting the values of the resolution factor and peak height is the capacity factor. This factor depends on mobile phase variables such as ionic strength, pH and quaternary ammonium salt concentration. Optimization of these mobile phase variables should therefore lead to a well resolved chromatogram and a rapid and sensitive analytical method. A three-factor central composite design with a computer-aided multifactor statistical optimization approach was carried out for the optimization of the mobile phase composition. Unique optimum mobile phase conditions which meet all the requirements (rapid analysis of five anions with adequate resolution and high sensitivity) were to be [TBAI] = 8–8.5 mM, [KHP] = 0.5–1 mM and pH = 6–6.5. These values agree very well with the best results we observed experimentally. Details of the optimization approach have been presented elsewhere<sup>12</sup>.

Laboratory slurry-packed ODS-3 columns and a low-capacity anion-exchange pre-packed PRP-X100 column were used for the performance study. The ODS-3 column gives the highest theoretical plate number when an eluent containing 0.5 mM TBAI and 1 mM KHP was used. Under these conditions, the resolution of the peak pair  $\text{NO}_2^- - \text{Br}^-$  and the peak heights of chloride, nitrate and sulphate, however, were low. If the optimum mobile phase composition of a more concentrated TBAI eluent (8 mM) is used at a higher pH (6), the column gives a lower theoretical plate number, but an adequate resolution for the  $\text{NO}_2^- - \text{Br}^-$  peak pair. In addition, we obtained the highest conductance responses (peak heights) for chloride, nitrate and sulphate, and the shortest overall retention time. The plate numbers and resolutions (see Table II in

ref. 11) show that the efficiency of the ODS-3 column when used with TBAI-KHP eluent is as good as that of the commercially pre-packed PRP-X100 column. If we compare the performances obtained with the ODS-3 column for eluent conditions 8 mM TBAI, 1 mM KHP and pH 6.0 and the Hamilton PRP-X100 column for eluent conditions 1 mM KHP and pH 5.5 in detail, we observe that the numbers of theoretical plates per metre are almost identical, the resolutions of the peak pair  $\text{NO}_2^-$ - $\text{Br}^-$  are identical, the elution times of the last peak ( $\text{SO}_4^{2-}$ ) are very close, the analysis times for five anions are both 8–9 min and the peak height of the anions is much better with the ODS column, especially for nitrate and sulphate.

Two negative system peaks occur at 10 and 20 min with the ODS-3 column for the above-mentioned eluent conditions. If one performs a new injection at the moment of the appearance of the first negative peak (every tenth minute), the system peaks will not interfere with the peaks of the analytes and the total analysis time will not increase. The number of analyses that can be performed on the ODS column without reconditioning the packing amounts to 500 and sometimes up to 1500 injections, depending on the nature of the sample and also on the frequency of analysis. In addition, a column regeneration technique (column repacking) can be used to prolong the lifetime of the column<sup>11,13</sup>.

#### *Application to the determination of anions in precipitation samples*

*Reproducibility of retention time and concentration of anions in a rainwater sample.* Variation of the retention time of the separated anions in a rainwater sample using the reversed-phase column was tested. Table I shows the reproducibility of the retention times of each anion, which is very good. Moreover, the higher the retention time, the better is the relative standard deviation (R.S.D.): chloride has a mean retention time of 233 s and an R.S.D. of 2.85%, whereas sulphate has a retention time of 556 s and an R.S.D. of 1.70%. In addition, concentrations of three major anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) in a given rainwater sample were repeatedly determined after separation (Table II). The S.D.s for the three anions were between 0.37 and 0.41 and the R.S.D.s between 4 and 13%; these are satisfactory results for rainwater analyses on a routine basis.

*Determination of anion concentrations in rainwater and aerosol samples.* Table III compares the results for  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations (ppm) in some aerosol samples. The results were determined by using ion exchange (PRP-X100 column) and reversed-phase (ODS-3 column) chromatographic methods and the agreement of the

TABLE I

REPRODUCIBILITY TEST ON THE RETENTION TIMES OF THE SEPARATED ANIONS IN A RAINWATER SAMPLE WITH THE RP ODS-3 COLUMN

Chromatographic conditions: TBAI, 8 mM; KHP, 1 mM; pH, 5.4; flow-rate, 2 ml/min; sample injection volume, 25  $\mu\text{l}$ .  $n = 10$ .

Parameter	$\text{Cl}^-$	$\text{NO}_2^-$	$\text{Br}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
Mean value (s)	233	303	337	461	556
S.D. (s)	6.65	7.39	7.79	8.46	9.45
R.S.D. (%)	2.85	2.44	2.31	1.84	1.70

TABLE II

## REPRODUCIBILITY TEST ON THE ANION CONCENTRATIONS IN A RAINWATER SAMPLE WITH THE RP ODS-3 COLUMN

Chromatographic conditions: as in Table I.  $n = 9$ .

Parameter	$Cl^-$	$NO_3^-$	$SO_4^{2-}$
Mean value (ppm)	4.61	3.22	8.51
S.D. (ppm)	0.37	0.41	0.34
R.S.D. (%)	8	13	4

results between the two method is satisfactory. Figs. 1 and 2 show an example of a reversed-phase ion-pair chromatogram of some anions in aerosol and rainwater, respectively. Fig. 3 shows the calibration graphs for the determination of  $Cl^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ . Fig. 4 shows the variation in the concentration of anions determined in sequentially collected rainwater samples. These results clearly indicate that the anion concentrations in rain decrease in a hyperbolic way with the amount of precipitation. Similar profiles were observed for trace metals in rainwater above the North Sea<sup>14</sup>. The hyperbolic relationship reflects the fact that in the last stages (sequences) of the rainwater samples, the anion concentration tends to a constant value which corresponds to the initial or cloud vapour concentration. This concentration is a measure of the background concentration of the dissolved anions in raindrops. Also, in the initial stages (sequences) of the rainwater samples, the anion concentration is much higher owing to an additional amount of salts which will be incorporated and solubilized in the raindrops during their fall. This additional amount is thus a measure of the scavenging efficiency of anions from aerosols by the raindrops.

TABLE III

## COMPARISON OF ANALYTICAL RESULTS FOR AEROSOL SAMPLES OBTAINED USING A REVERSED-PHASE COLUMN (ODS-3) AND AN ION-EXCHANGE COLUMN (PRP-X100)

All data represent the average of duplicate runs for each sample. Chromatographic conditions: TBAI, 8 mM; KHP, 1 mM; pH 6 for the ODS-3 column; 4 mM *p*-hydroxybenzoic acid at pH 8.5 for the PRP-X100 column; flow-rate, 2 ml/min; sample injection volume, 50  $\mu$ l.

Sample No.	$Cl^-$ (ppm)		$NO_3^-$ (ppm)		$SO_4^{2-}$ (ppm)	
	ODS-3	PRP-X100	ODS-3	PRP-X100	ODS-3	PRP-X100
1	0.5	0.4	0.9	1.0	4.3	4.5
2	37.8	40.6	8.3	10.0	21.7	20.0
3	59.2	60.8	25.2	27.8	18.4	18.8
4	6.2	5.3	4.4	5.5	17.8	17.3
5	1.2	1.2	5.6	5.5	14.9	15.3
6	0.9	0.9	0.5	—	20.5	21.8
7	9.5	8.7	11.2	12.1	7.6	7.9
8	22.4	22.4	20.6	21.6	5.4	—
9	6.6	5.7	5.6	6.3	5.4	—

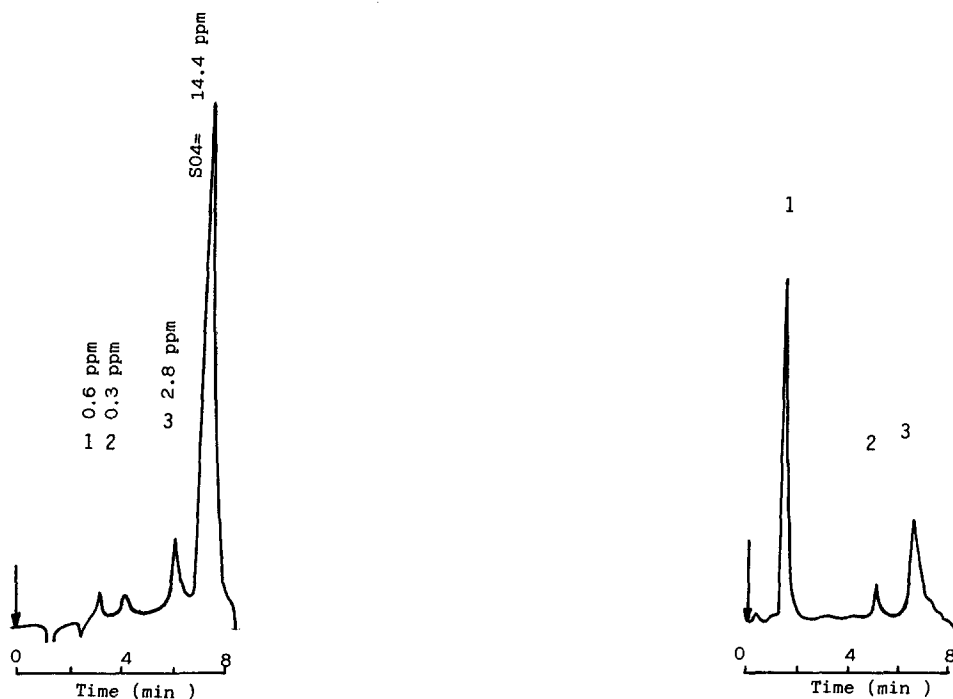


Fig. 1. Example of a reversed-phase ion chromatogram for an aerosol sample. Chromatographic conditions: TBAI, 8 mM; KHP, 1 mM; pH, 6; flow-rate, 2.5 ml/min; sample injection volume, 50  $\mu$ l. Peaks: 1 =  $\text{Cl}^-$ ; 2 =  $\text{NO}_2^-$ ; 3 =  $\text{NO}_3^-$ .

Fig. 2. Example of a reversed-phase ion chromatogram for rainwater. Chromatographic conditions: pH, 5.4; sample injection volume, 25  $\mu$ l; other conditions as in Fig. 1. Peaks: 1 =  $\text{Cl}^-$ ; 2 =  $\text{NO}_3^-$ ; 3 =  $\text{SO}_4^{2-}$ .

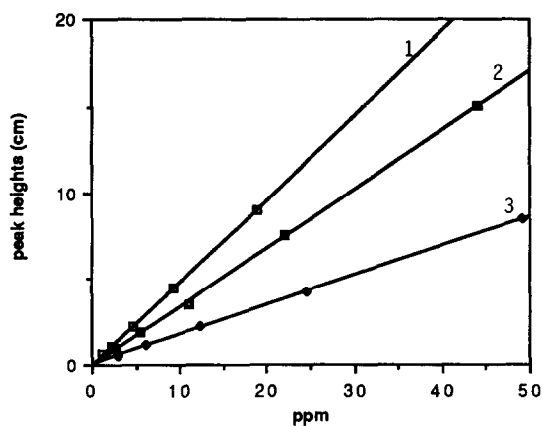


Fig. 3. Calibration graphs for (1)  $\text{Cl}^-$ , (2)  $\text{SO}_4^{2-}$  and (3)  $\text{NO}_3^-$  for the determination of sample anions in atmospheric precipitation. Chromatographic conditions: TBAI, 8 mM; KHP, 1 mM; pH, 5.4; flow-rate, 2.0 ml/min; injection of standard, 25  $\mu$ l.

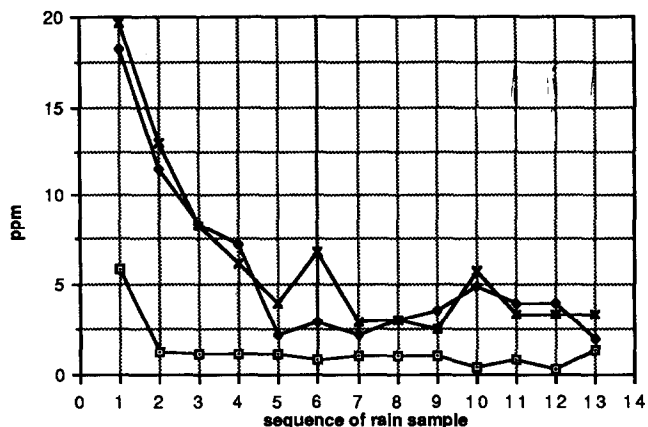


Fig. 4. Diagram showing the variation of anion concentrations in rainwater, determined in sequentially collected rainwater samples (determined on each 20 ml from the start of raining; sampled on June 1st, 1986 at Building G, VUB-Oefenplein, Brussels). Chromatographic conditions: TBAI, 8 mM; KHP, 1 mM; pH, 6; flow-rate, 2.0 ml/min. □ = Cl<sup>-</sup>; ● = NO<sub>3</sub><sup>-</sup>; × = SO<sub>4</sub><sup>2-</sup>.

Environmental atmospheric samples such as wet precipitation (rainwater or snow) and aerosols were also regularly collected. Fig. 5 shows an example of the variation of the sulphate concentration with monthly collected rainwater. In January 1987 high sulphate concentrations were observed. That month the temperature was very low, leading to an increased consumption of fuel and an increased output of sulphate. The SO<sub>4</sub><sup>2-</sup> concentrations in the samples that were collected at the urban site were generally slightly higher than those collected at the rural site.

Typical inorganic anion compositions of some aerosol samples are shown in Table IV. Using an injection volume of 100 μl a limit of detection of about 0.1 mg/l and a linear calibration range up to 60 mg/l for the anions are obtained.

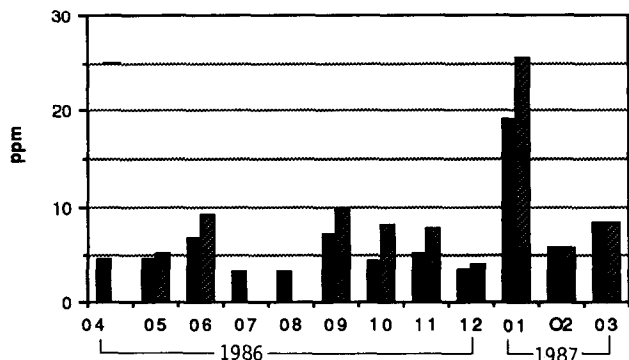


Fig. 5. Example of the variation of the sulphate concentration collected rainwater samples and comparison between two sampling sites: black boxes = more rural; hatched boxes = urban.



TABLE IV  
TYPICAL INORGANIC ANION COMPOSITION OF AEROSOL SAMPLES

Sampling date (Feb. 1987)	Air volume (m <sup>3</sup> )	Concentration (nequiv./m <sup>3</sup> )				
		Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	Br <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
2-3	24.10	155.8	1.81	0.52	293.4	311.8
6-7	25.03	147.3	0.52	1.50	82.3	347.3
11-12	24.65	135.7	1.41	1.02	116.6	233.4
19-20	25.71	62.5	1.18	0.24	152.0	227.1
22-23	25.00	181.6	0.61	1.50	124.1	283.5
23-24	25.41	172.4	1.54	2.46	117.3	184.9

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