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## MODIFICATION OF A DIONEX SYSTEM 12 ION CHROMATOGRAPH FOR SEQUENTIAL DETERMINATION OF THE MAIN COMPONENTS IN ATMOSPHERIC PRECIPITATION

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### SUMMARY

A modification of a Dionex System 12 ion chromatograph is described which enables organic anions (acetate and formate), inorganic cations (ammonium, sodium and potassium) and inorganic anions (chloride, nitrate and sulphate) to be determined sequentially in one measuring procedure. The modified instrument consists of a programmable controller unit, a conductimetric meter, two conductimetric detectors of the Dionex System 12 ion chromatograph, the HPIC-AS4A and HPIC-CS3 modern separation units, AMMS-1 and CMMS-1 micro-membrane suppressor columns, a unique system of valves from Dionex and two dual pumps from Biotronik. The limits of detection are between about 1 and 3  $\mu\text{g/l}$  for chloride, nitrate and sulphate and between about 2 and 10  $\mu\text{g/l}$  for acetate, formate, ammonium, sodium and potassium. The reliability of the method was demonstrated by analysing two NBS simulated rain water Standard Reference Materials. Some examples are given of the application of the method to the sequential determination of the main precipitation components in typical samples from urban and rural regions of the F.R.G. The ion concentrations varied between about 0.02 and 300 mg/l.

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### INTRODUCTION

Industrialization has caused an increase in the release of anthropogenic pollutants into the atmosphere. Sulphuric and nitric acid are atmospheric contaminants resulting to a large extent from the oxidation of sulphur and nitrogen oxides ( $\text{SO}_2$  and  $\text{NO}_x$ )<sup>1,2</sup>. The wet pollutants from the atmosphere and the deposition of toxic substances on the surface of plants, water and soil are therefore topics of interest. For investigating the composition of atmospheric precipitation, ion chromatography is an attractive technique for the determination of ions in solution<sup>3-5</sup>. The determination of inorganic anions, cations and also organic anions such as formate and acetate by ion chromatography has been reported<sup>6-11</sup>. However, the routine determination of the main components in precipitation is associated with several problems:

(1) Negative "dips" or deviations from the baseline can interfere with fluoride and chloride determinations. The addition of the same eluent ion concentration as in

the samples helps to avoid such dip interferences<sup>5</sup>. However, this procedure requires more time for sample preparation.

(2) For a rapid determination of acetate and formate in precipitation samples, the separation column must be automatically cleaned up.

(3) The appropriate columns and eluents must be exchanged between the determination of anions and cations when using one measuring instrument. Then the measuring system must be cleaned to obtain a baseline, which requires a long waiting period.

(4) In contrast to new developments of Dionex ion chromatographic systems, the original Dionex ion chromatograph, Auto Ion<sup>TM</sup>, System 12, equipped with two Type NSI 33-R reciprocating liquid pumps, a P/N 30827 separation column and a P/N 30828 suppressor column, gives unsatisfactory results.

In this paper, a modified Dionex System 12 ion chromatograph is described and routine measurements are reported for the main precipitation components in samples from Schauinsland, Jülich, Berchtesgaden, Essen, Dortmund and Hamburg (F.R.G.). The application of this modified method avoids dip interferences. Moreover, the automatic clean-up of the separation column for the determination of acetate and formate reduces the analysis time.

## EXPERIMENTAL AND RESULTS

### *Apparatus*

The modified ion chromatograph was constructed with the following components: a programmable controller unit and conductivity meter of the Auto<sup>TM</sup> System 12 Analyzer, HPIC-AG4A and HPIC-CG3 guard columns, HPIC-AS4A and HPIC-CS3 separation columns, AMMS-1 and CMMS-1 micro-membrane suppressor columns, Dionex valves, two BT 0512 high-performance liquid chromatographic (HPLC) eluent pump units, an BT 7040 sample injector (Biotronik), an Shimadzu C-R1B integrator, an MGW Lauda RC6 thermostat and two Gilson minipuls 2 tube pumps for the transport of regenerants. Sampling of rain water and snow, free from contamination, is achieved by using an automatic sampler of our own construction, which is now commercially available<sup>12</sup>. The rain water and snow samples were filtered during the sampling in a Satorius Type SM 16511 filtering device through a membrane filter (pore size 0.45  $\mu\text{m}$ ).

### *Chemicals*

An eluent consisting of 3.6 mM NaHCO<sub>3</sub>–4 mM Na<sub>2</sub>CO<sub>3</sub> and 25 mM H<sub>2</sub>SO<sub>4</sub> as regenerant were prepared for the determination of chloride, nitrate and sulphate. For the determination of acetate and formate and for clean-up of the separator, an eluent NaHCO<sub>3</sub> 1 mM and a stronger 10 mM NaHCO<sub>3</sub> eluent, respectively, were used. The eluent and regenerant solutions for determining cations were 70 mM HCl and 40 mM tetramethylammonium hydroxide solution (TMAH), respectively. Before flowing through the columns, the initial concentration of eluent was diluted by a factor of 2 with deionized water or sample. Deionized water (Millipore) and Merck analytical-reagent grade chemicals were used to prepare all solutions.

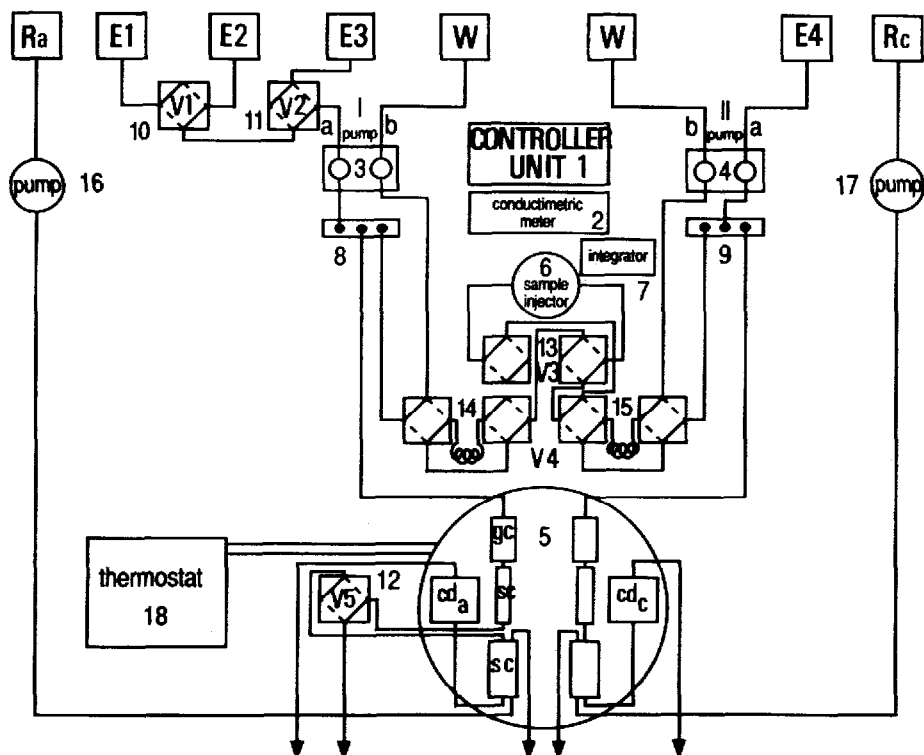


Fig. 1. Flow scheme of modified ion chromatograph.

#### Modification of ion chromatograph

The flow scheme of the modified ion chromatograph is shown in Fig. 1. It consists of one programmable controller unit (1), one conductivity meter (2) from the Dionex System 12, two eluent pumps Biotronik (3, 4), a thermometric box (5) containing the column system and two Dionex conductimetric detectors ( $cd_a$  and  $cd_c$ ), a Biotronik sample injector (6) and a Shimadzu integrator (7). The Biotronik 0512 HPLC pump unit (3, 4) with a dual liquid pump can transport in one pump line (a) a double eluent concentration and in the second pump line (b) the deionized water or sample into a three-way mixer (8, 9) before flowing through the columns. In this instance, the dip interferences can be automatically avoided during the measuring procedure.

The flow path on the left of Fig. 1 with pump I (3) was used to determine acetate, formate, chloride, nitrate and sulphate anions. With the aid of valves V1 (10) and V2 (11) and the programmable controller unit (1), the appropriate eluents 1 mM  $\text{NaHCO}_3$  (E1), 10 mM  $\text{NaHCO}_3$  (E2), 3.6 mM  $\text{NaHCO}_3$ –4 mM  $\text{Na}_2\text{CO}_3$  (E3) were automatically provided for the determination of organic or inorganic anions. By using a stronger eluent, 10 mM  $\text{NaHCO}_3$  (E2), through valves V1 (10) and V5 (12), the separation column can be cleaned up automatically after the analysis cycle of acetate and formate in *ca.* 8 min. Under these conditions, the analysis time was less than 20 min.

At the right hand side of Fig. 1, the analysis scheme for cations is shown. Pump II (4) and suitable eluents and columns were used to perform the determination of ammonium, potassium and sodium cations. By monitoring the programmable controller unit (1), the valve V3 (13) could be switched to bring precipitation samples from the sample injector (6) into the sample loop of 127 or 121  $\mu\text{l}$  (14 or 15). All these processes are automatically achieved by action of the controller unit and valves. Moreover, two Gilson pumps (16 and 17), which deliver a constant volume with time, are used to transport 25 mM  $\text{H}_2\text{SO}_4$  (Ra) and 40 mM TMAH (Rc) regenerant through the micro-membrane suppressors AMMS-1 and CMMS-1. A thermostat (18) regulates the temperature of the contents of the box during the measuring time.

A photograph of the modified ion chromatograph is shown in Fig. 2.

### *Analytical procedure*

A flow chart of the whole analytical procedure is shown in Fig. 3. Standard solutions and filtered precipitation samples are first deposited in the sample injector. Before starting the analytical procedure, three measuring programs for the determination of anions and cations are entered in the program controller of the modified ion chromatograph. The selected measuring parameters were written separately. The program for the determination of acetate and formate is started first. After calibration with a standard solution, the rain water samples are measured and the results calculated automatically by using the Shimadzu integrator. Pump unit II can be switched on manually or automatically before the end of the acetate and formate determination cycle to obtain a constant measuring baseline as required for the determination of  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ . Subsequently, the measurement can be followed by the

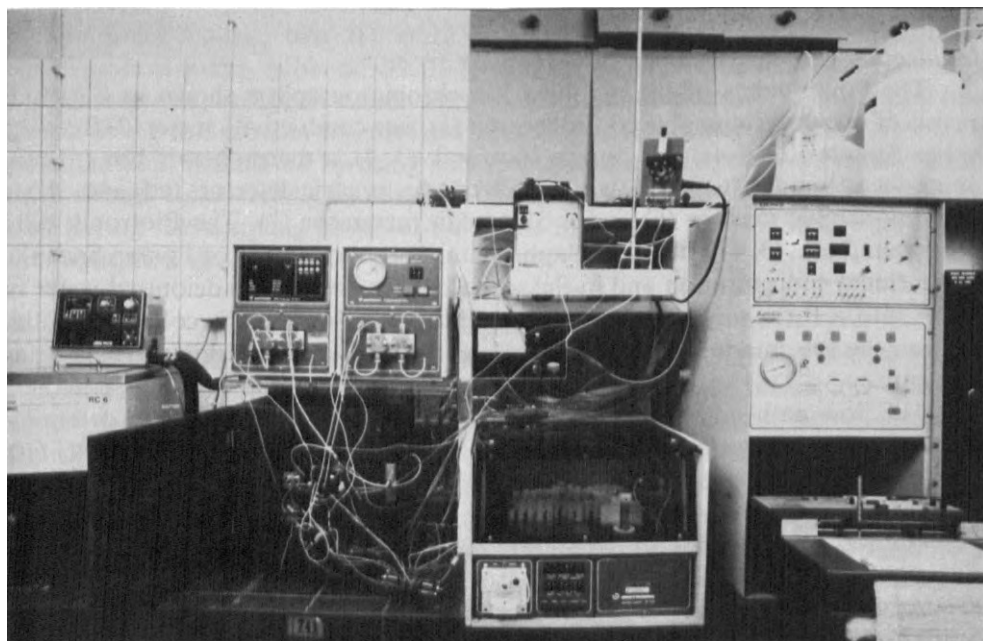


Fig. 2. Modified ion chromatograph system.

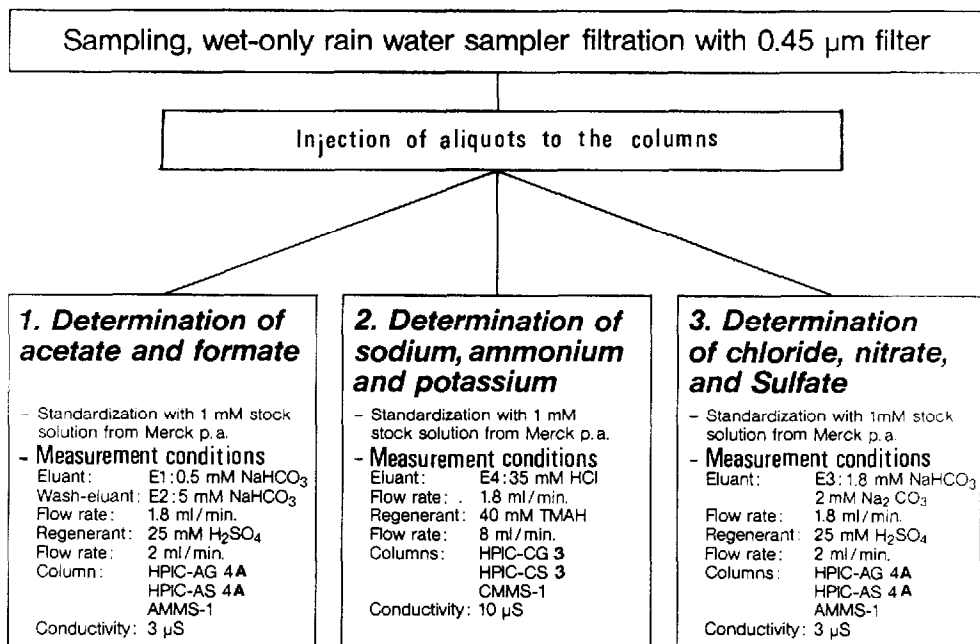


Fig. 3. Flow scheme of the analytical procedure.

controller unit of the ion chromatograph. Finally, in a similar way, the determination of chloride, nitrate and sulphate is automatically performed. In this instance, the sequential determination of main components Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and the organic anions CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup> is possible in one measuring procedure. The limits of detection are 1 µg/l for chloride, 2 µg/l for nitrate and sodium, 3 µg/l for sulphate, 5 µg/l for formate, ammonium and potassium and 10 µg/l for acetate.

*Application of the method to the determination of the main precipitation components*

*Measurement of NBS Standard Reference Material.* The NBS simulated rain water Standard Reference Materials (SRMs) 2694-I and 2694-II were used to test the method. Table I compares results obtained by using the modified ion chromatograph with the NBS certificate values<sup>13</sup>. It can be seen that the agreement is good.

*Measurement of the main components of precipitation samples.* The following examples demonstrate the suitability of the modified ion chromatograph for the sequential analysis of main components in the case of typical precipitation samples collected in the winter of 1988-89 at Schauinsland, Essen, Jülich, Berchtesgaden, Dortmund and Hamburg (F.R.G.).

Fig. 4A shows a typical chromatogram of fluoride, chloride, nitrate and sulphate. It can be seen that the dip interferences have disappeared. Therefore, the peak height of chloride in the chromatogram can be more accurately determined.

The ion concentrations of the precipitation samples varied between about 0.020 and 300 mg/l. The results for the rain water samples from urban and rural regions in

TABLE I  
MEASUREMENT OF THE COMPONENTS OF NBS SRM 2694-I AND SRM 2694-II

$n = 5$ .

SRM	Value (mg/l)	Sodium	Potassium	Fluoride	Chloride	Nitrate	Sulphate	Ammonium
SRM 2694-I	Certified	$0.205 \pm 0.009$	$0.052 \pm 0.007$	$0.054 \pm 0.002$	$(0.24)^{13}$	--	$2.750 \pm 0.050$	--
	Measured	$0.196 \pm 0.005$	$0.050 \pm 0.003$	$0.064 \pm 0.007$	$0.25 \pm 0.050$	--	$2.680 \pm 0.090$	--
SRM 2694-II	Certified	$0.419 \pm 0.015$	$0.106 \pm 0.008$	$0.098 \pm 0.007$	$(1.0)^{13}$	$7.060 \pm 0.150$	$10.90 \pm 0.200$	$(1.00)^{13}$
	Measured	$0.418 \pm 0.030$	$0.118 \pm 0.002$	$0.099 \pm 0.001$	$0.980 \pm 0.060$	$7.150 \pm 0.010$	$10.70 \pm 0.480$	$1.100 \pm 0.080$

TABLE II  
AVERAGE CONCENTRATIONS (mg/l) OF THE MAIN COMPONENTS OF RAIN AND SNOW SAMPLES FROM SIX REGIONS IN THE F.R.G.

Region	Acetate	Formate	Chloride	Nitrate	Sulphate	Ammonium	Sodium	Potassium
Schaunsland, Dec. 1988 ( $n = 3$ )	--	--	0.87	1.79	1.54	0.14	0.48	0.33
Berchtesgaden, Jan. 1989 ( $n = 3$ )	0.10	0.02	1.32	3.79	3.40	1.25	0.95	0.37
Jülich, Jan. 1989 ( $n = 3$ )	0.10	0.01	2.13	4.40	6.57	2.58	0.98	0.16
Essen, Jan. 1989 ( $n = 4$ )	0.21	0.27	1.89	4.06	5.21	1.19	0.72	0.20
Dortmund, Dec. 1988 ( $n = 2$ )	0.07	0.10	3.11	2.08	3.29	0.69	1.33	0.12
Hamburg, Jan. 1989 ( $n = 4$ )	0.22	0.17	6.83	4.27	7.09	0.98	2.91	2.09

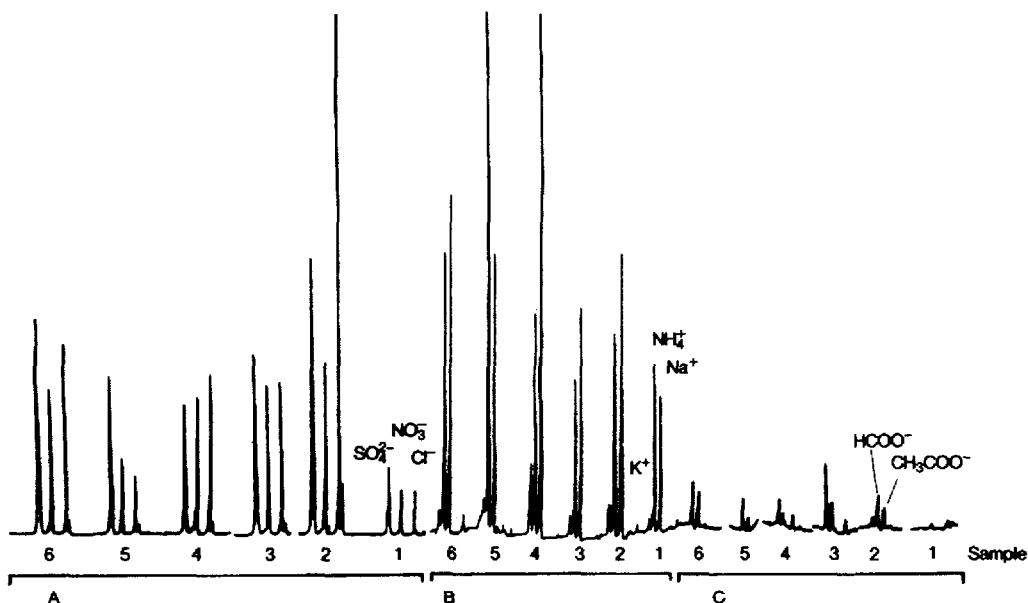


Fig. 4. Typical chromatograms of the main components of precipitation samples from (1) Schauinsland (December 1988), (2) Berchtesgaden (January 1989), (3) Essen (January 1989), (4) Dortmund (December 1988), (5) Jülich (January 1989) and (6) Hamburg (January 1989) (F.R.G.). (A) Determination of chloride, nitrate and sulphate; (B) determination of sodium, ammonium and potassium; (C) determination of acetate and formate.

Table II reveals a difference in the concentrations of the components. High average concentrations were observed in the urban regions (Essen, Dortmund and Hamburg). The lower values from hilly regions (Schauinsland and Berchtesgaden) indicate that the removal of the main precipitation components from the atmosphere by wash-out and rain-out processes depends on the altitude. The amount of precipitation at these sites is in general higher by a factor of 2–2.5. Therefore, the average concentration decreases with the amount of precipitation. It can be seen from Table II that the highest values for chloride, sulphate, sodium and potassium were found in the rain water samples from Hamburg, a typical urban conglomeration with a number of industrial sources. The highest concentration of ammonium, at the Jülich site, is caused by the surrounding agricultural activity of the sampling station. Moreover, a large lignite coal-fired power station of about 2300 MW is located 10 km south-west of the sampling site and also a heavily industrialized area to the west. These two important areas are sources of acid precursors, which explains the high concentrations of nitrate and sulphate in the rain water from the Jülich site. The low concentration of acetate and formate in the samples can be interpreted as resulting from bacterial activity, which destroys most of these organic components during the sampling and storage time under the original conditions. However, this loss of acetate and formate can be avoided if a small amount of chloroform (40  $\mu$ l per 10 ml of sample) is added to the rain water samples, thus stopping bacterial growth<sup>14</sup>.

Table III presents a comparison between the stability of organic anions in treated and untreated samples of rain water sample collected at Jülich. The accuracy

TABLE III

COMPARISON BETWEEN THE STABILITIES OF ORGANIC ANIONS IN TREATED AND UNTREATED ALIQUOTS OF RAIN WATER SAMPLES COLLECTED IN JÜLICH, JANUARY 1989

Storage time (days)	A <sup>a</sup>		B <sup>b</sup>	
	Acetate (mg/l)	Formate (mg/l)	Acetate (mg/l)	Formate (mg/l)
0	0.52	0.40	0.53	0.39
1	0.53	0.39	0.50	0.37
4	0.51	0.37	—	—
5	0.50	0.35	—	—
7	0.50	0.36	—	—
14	0.49	0.35	—	—

<sup>a</sup> A: aliquots treated by adding 40  $\mu$ l of chloroform per 10 ml of rain water sample, stored at +7°C in darkness.

<sup>b</sup> B: untreated aliquots stored at room temperature.

and precision were calculated after replicate analyses of several samples. Table IV shows the results of five measurements of the main components in two rain water samples. As can be seen, the performance of the modified method (with a relative standard deviation less than 8%) is very satisfactory.

With an investment of about US \$2000 for the dual pumps, the modern columns, valves and accessories, the Dionex System 12 ion chromatograph can be modified as described to determine sequentially the main components of precipitation samples in one measuring procedure. By using this automatic ion chromatograph, precipitation samples can be measured continuously.

TABLE IV

USE OF THE MODIFIED ION CHROMATOGRAPHIC SYSTEM FOR THE DETERMINATION OF COMPONENTS IN RAIN WATER

Each sample was analysed five times.

Component	A <sup>a</sup>		B <sup>b</sup>	
	Average concentration (mg/l)	Standard deviation (mg/l)	Average concentration (mg/l)	Standard deviation (mg/l)
Chloride	1.35	0.06	2.78	0.10
Nitrate	1.88	0.07	1.11	0.05
Sulfate	1.25	0.03	1.30	0.06
Ammonium	1.54	0.08	0.99	0.04
Sodium	0.46	0.03	1.21	0.02
Potassium	0.12	0.01	0.13	0.01
Acetate	0.67	0.02	0.42	0.01
Formate	0.72	0.02	0.28	0.02

<sup>a</sup> A: rain water sample from Jülich, January 1989.

<sup>b</sup> B: rain water sample from Dortmund, December 1988.



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