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Determination of low-molecular-mass organic acids in fogwater by ion-exchange chromatography with automatic column switching

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Abstract

An analytical method for low-molecular-mass organic acids ($C_{n<6}$) in fogwater, which contains chloride, nitrate and sulfate abundantly, was developed using isocratic ion chromatography with automatic column switching. Nitrate and sulfate ions were allowed to separate from the organic acids by fast elution with a backward flow of eluent through the precolumn. Part of the chloride passed through the precolumn together with the organic acids at the specified switching time. Two types of connected columns were examined for the chromatographic separation of 20 species of organic acids. Lactate, acetate, isobutyrate, *n*-butyrate and methacrylate were separated with AG4A-SC+AS4A-SC+AS11 columns (method A), and lactate, acetate, glycolate isobutyrate, pyruvate and crotonate with AS11+AS11 columns (method B). The determination of pyruvate was free from interfering crotonate even though they were incompletely separated by method A. By method B, formate was also free from interfering *n*-butyrate. The analysis times for the methods were 18 and 23 min, respectively. Lactate, glycolate, formate and pyruvate were detected in fog samples. This method is suitable for routine analysis of fogwater samples due to its procedural and instrumental simplicity. © 1997 Elsevier Science B.V.

Keywords: Column switching; Water analysis; Environmental analysis; Organic acids; Inorganic anions

1. Introduction

Organic acids are important materials in atmospheric chemistry processes. While the low-molecular-mass organic acids are produced by photochemical oxidation of biogenic hydrocarbons [1,2], these acids, in particular formic acid and acetic acid, are generated from motor exhaust [3] and have been found abundantly in the urban atmosphere [4]. In the atmospheric chemistry of the organic acids, their incorporation into fog [5] is one of the interesting processes from the standpoint of their influence on the acidification of fog. For example, organic acids in fogwater are known to play an important role in suppressing Fe-catalyzed S(IV) oxidation [6].

Low-molecular-mass organic acids in the atmosphere are usually determined by gas chromatography [7] and ion chromatography with an ion-exclusion column [8–11]. For conductometric detection in ion-exclusion chromatography, suppression of the background conductivity [12] and concentration techniques [9–11] have been devised to improve the detection sensitivity. Ion-exchange chromatography is widely used for the analysis of inorganic acids. When organic acids are analyzed together with inorganic acids, gradient elution is occasionally used [13,14]. This method has obvious superiority in that both organic and inorganic acids can be analyzed simultaneously. However, when a fog sample is analyzed, modification of the detection sensitivities

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may be required during an analysis because inorganic anions (e.g., SO_4^{2-}, NO_3^-, Cl^-) are often present at 10–100 times the amount of organic acids. Furthermore, the gradient elution needs extra time because the column used must be restored to its initial state.

Column switching was used for the concentration of analytes [10,11,15] and for removal of interferences [16,17]. Umile et al. [18] have studied isocratic ion chromatography with column switching for the simultaneous separation of low-molecular-mass organic acids and inorganic anions. The technique can be performed with a single pump and is suitable for routine analysis. This paper describes a method for the rapid and selective analysis of low-molecular-mass organic acids using the technique. The method is based on fast elution of inorganic anions using a column switching which can automatically create a reversible eluent flow through a precolumn in an isocratic elution mode. The chromatographic separation of $C_{n<6}$ monocarboxylic acids, including α,β-unsaturated ones, was studied by using connected columns. The developed method was applied to analysis of fogwater.

2. Experimental

2.1. Apparatus

A Model DX-AQ 1100 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with an electrical conductivity detector and an anion self-regenerating suppressor ASRS-I was used for the analysis. The instrument was modified by joining two additional pneumatic quadri-port switching valves (Dionex) to the eluent flow system (Fig. 1). The switching valve works automatically. An automatic sample injector (Model DAS-80, Dionex) was used. The AG11 column was used as the precolumn. The separation columns used were AG4A-SC+AS4A-SC+AS11 (method A) and AS11+AS11 (method B). The AG11 was also operated as a separation column. Their physical and chemical properties are shown in Table 1. A Model C-R6A chromatogram recorder (Shimazu, Kyoto, Japan) was used. Concentrations of chloride, nitrate and sulfate ions contained in fogwater were determined with a Model 2000 i/sp ion chromatograph (Dionex) (eluent: 2 m*M* Na_2CO_3+1 m*M* $NaHCO_3$, column: AG4A-SC+AS4A-SC). A Model FWG-400F fog sampler (Usui Industrial Laboratory, Tokyo, Japan) was used for fogwater collection.

2.2. Reagents

The reagents used were of the highest purity available from Wako (Osaka, Japan), Aldrich (Milwaukee, USA) and Sigma (St. Louis, USA). Standard stock solutions (1000 μg ml^{-1}) of organic acids were prepared by dissolution of the acids or of the

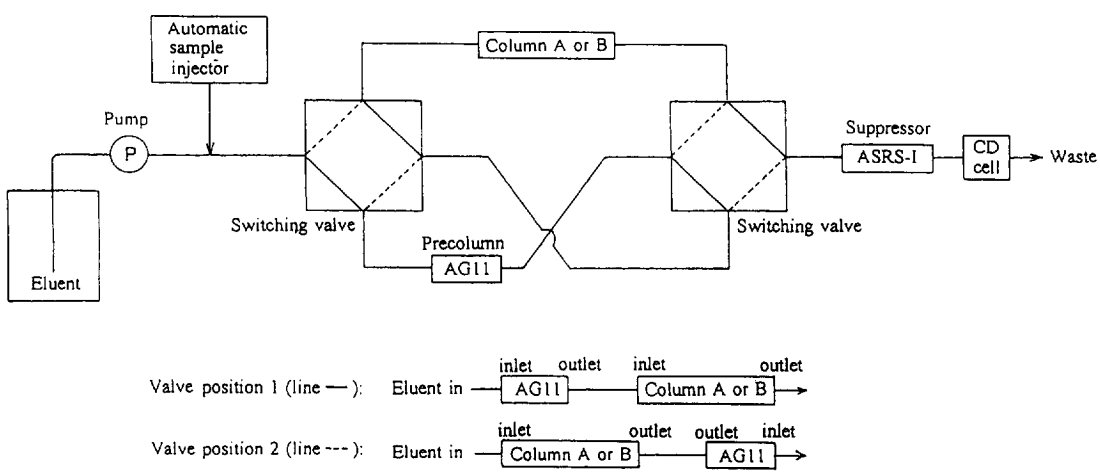

Fig. 1. Column switching device in ion chromatograph. Two switching valves in the upper figure work simultaneously. The lower figure: eluent paths through columns at two positions of the switching valve. Column A, AG4A-SC+AS4A-SC+AS11; Column B, AS11+AS11.

Table 1
The properties of materials in the columns

Property	AS4A-SC/ AG4A-SC	AS11/ AG11
Support	Ethylvinylbenzene crosslinked with 55% divinylbenzene	
Diameter	13 μm	
Layer	Latex	
Diameter	160 nm	85 nm
Cross-link	0.5%	6%
Functional group	Alkanol quaternary ammonium	
Ion-exchange capacity	20 μequiv.	45 μequiv.
Column dimensions	AS4A-SC: 250 mm×4 mm I.D. AG4A-SC: 50 mm×4 mm I.D.	AS11: 250 mm×4 mm I.D. AG11: 50 mm×4 mm I.D.

salts with deionized water (18 MΩ) obtained by double distillation of ion-exchanged water. Standard solutions were prepared by appropriate dilution of the standard stock solutions with the deionized water. The eluent, 5 m*M* $Na_2B_4O_7$ solution, was prepared by dissolving 1.90 g of $Na_2B_4O_7 \cdot 10H_2O$ in deionized water.

2.3. Procedure

A fogwater sample was collected in a 50-ml PTFE bottle for 20 min. The sample was stored in a refrigerator (2°C) and analyzed in a day. One ml of the sample was transferred to a plastic bottle (1.5 ml volume) for the automatic sample injector of the ion chromatograph and then was sent to the injector. The injection volume was 100 μl. The detection sensitivity of the ion chromatograph was set to 10 or 3 μS full scale. Flow-rates of the eluent in methods A and B were 1.5 and 1.0 ml min^{-1}, respectively. In the initial step of the analytical procedure, the switching valve was set at position 1 in Fig. 1. Counting of the switching time was started at the time the sample was injected. In method A, the first column switching was done after 70 s (the valve was changed to position 2). After 13 min, the valve was restored to position 1. The analysis was carried out for 18 min. The first and second switchings in method B were 90 s and 16 min, respectively and the analysis time was 23 min. The calibration curves (peak height and concentration) were prepared in the same manner as the samples.

3. Results and discussion

3.1. Column switching sequence

Fig. 1 shows schematically the principle of the column switching devised. A mixture of organic acids and inorganic anions (fluoride, chloride, nitrate and sulfate) is injected into the ion chromatograph and separated by the AG11 precolumn. The organic acids and fluoride ion elute from it prior to other inorganic anions (elution order: fluoride and organic acids>chloride>nitrate ≫ sulfate). Chloride (large part), nitrate and sulfate ions were allowed to reach the detector faster than the organic acids with the first column switching which connects the precolumn to the separation column outlet just when fluoride and the organic acids completely enter the separation column. In this step, it is required to connect the precolumn outlet to that of the separation column because fast elution of nitrate and sulfate ions is accomplished only by the backward flow of eluent through the precolumn. If the precolumn inlet is connected to the separation column outlet, about 50 min (flow-rate of the eluent=1.5 ml min^{-1}) were necessary for sulfate elution from the precolumn.

3.2. Switching time

Two factors which determine the first switching time were evaluated. One is the time when the organic acids completely enter the separation column. If the switching time is short, some or all of the organic acids remain in the precolumn and elute with the inorganic anions. The time when the entire

amount of the organic acids tested can be recovered through the separation column was determined. For method A, *n*-valerate, methacrylate and crotonate were incompletely recovered at a 50-s switching time, whereas all compounds tested were completely recovered at 70 s. For method B, 90 s were required for complete recoveries. Another factor is the time the chloride ion elutes from the precolumn after the organic acid. It is desirable to prevent chloride ion passage through the precolumn to shorten the analysis time. Chloride ion (10 $\mu g\,ml^{-1}$) did not pass through the precolumn at <50 and 80 s switching times in methods A and B, respectively. However, part of the chloride (method A, 4.2%; method B, 0.2%) passed through the precolumn at the time corresponding to the complete recoveries of the organic acids in both methods. Hence, the second column switching was made prior to elution of chloride from the separation column; thereby, the switching valve was restored to position 1 in Fig. 1. This column switching shortened the analysis time by 1–2 min. The retention times of the chloride passing through the precolumn were 16 and 21 min in the methods A and B, respectively (Fig. 2).

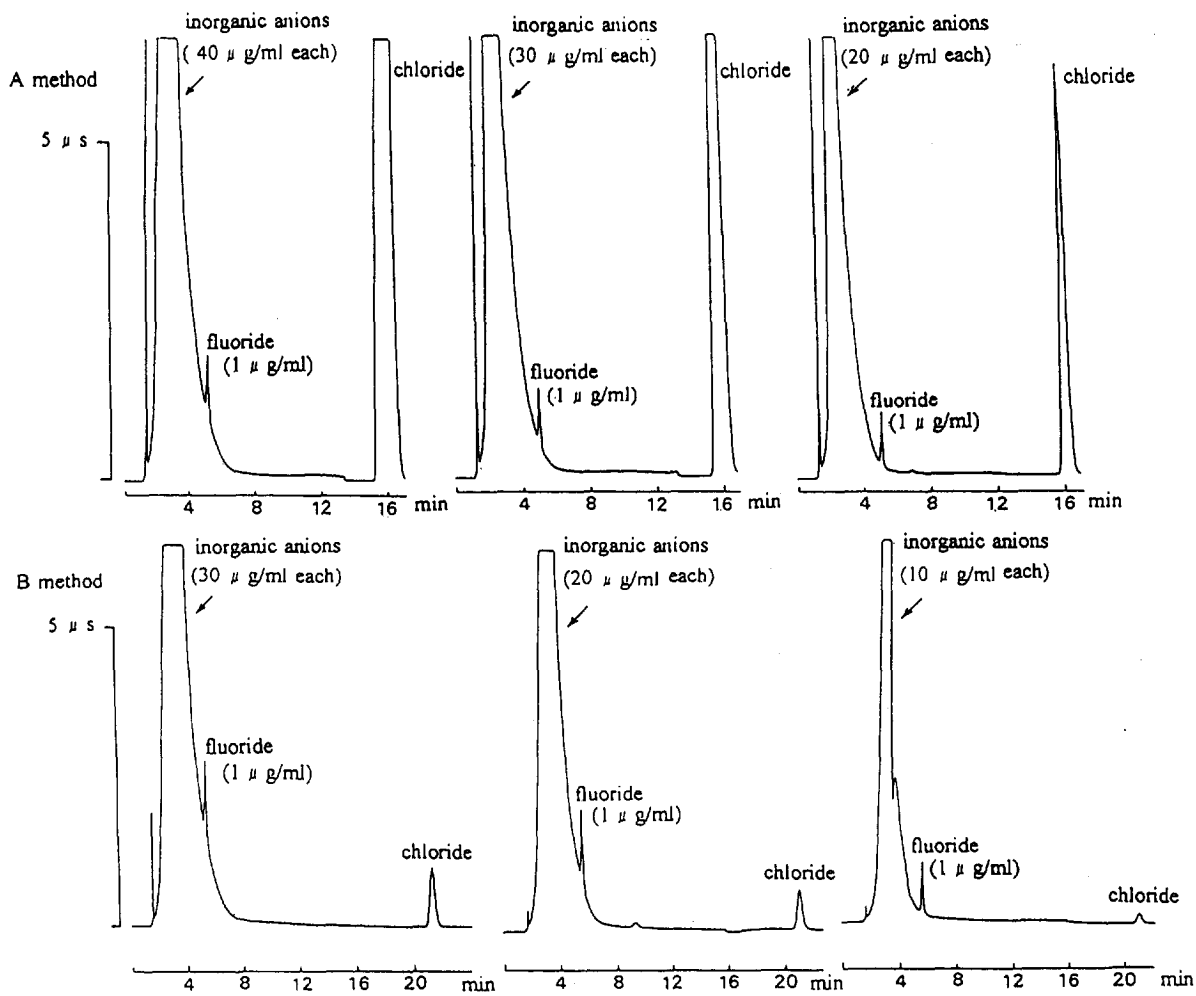

Fig. 2. Influence of inorganic anion concentration on the separation of fluoride ion. Inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) were tested in the same concentration in a sample solution.

3.3. Chromatographic separation of fluoride from other inorganic anions

Complete separation of fluoride from other inorganic anions is important for the analysis of organic acids because the retention time of fluoride is close to that of several organic acids. Chromatograms of fluoride and other inorganic anions (chloride, nitrate and sulfate were mixed in the same concentration) are shown in Fig. 2. The fluoride peak (1 $\mu g\ ml^{-1}$) appeared at the tail of the large peak of chloride, nitrate and sulfate mixture when the concentration of these anions was beyond 20 and 10 $\mu g\ ml^{-1}$ in methods A and B, respectively. The separation of fluoride and the other inorganic anions was mainly influenced by sulfate and nitrate concentrations. Nitrate and sulfate up to 50 and 25 $\mu g\ ml^{-1}$ were completely separated from fluoride in method A, respectively and up to 30 and 10 $\mu g\ ml^{-1}$ in method B. When the concentrations of nitrate and sulfate ions contained in a fog sample are very high, sample dilution or low-volume sample injection should be carried out. The flow-rate of the eluent adopted for B method was 1.0 $ml\ min^{-1}$. If the rate was 1.5 $ml\ min^{-1}$, fluoride could not be separated from other inorganic anions because the retention time of fluoride became shorter [retention time (t_R)=3.6 min]. Therefore, some of the organic acids whose peaks appear close to that of fluoride will be undetectable. The AS4A-SC column slowed down the elution of organic acids more than AS11 at the same flow-rate of the eluent. This is effective for separating the organic acids from inorganic anions.

3.4. Chromatographic characteristics of organic acids

Table 2 shows the retention times of the organic acids (20 compounds) prepared by the two specified methods. The retention times of the acids having the same number of carbon atoms were approximately in the order hydroxyalkanoic acids>alkanoic acids> alkenoic acids in both methods. The alkanoic acids eluted more slowly with an increase of their carbon number except for formate in both methods. The formate peak was situated between those of isobutyrate and *n*-butyrate in the chromatogram of method B; whereas, it overlapped that of isovalerate for method A because formate was more strongly retained by AS4A-SC.

The combination of the AS4A-SC and AS11 columns worsened the separation of 2-hydroxybutyrate and glycolate and that of vinylacetate and acrylate because the retention time order of the two compounds in each group for the AS11 column was opposite to that for the AS4A-SC column. The chromatographic separability of 20 mixed compounds in both methods is compared in Fig. 3. 3-Hydroxybutyrate, 4-hydroxybutyrate and 2-hydroxyisobutyrate were inseparable in both methods. For method A, lactate, acetate, isobutyrate, *n*-butyrate and methacrylate were separated and for

Table 2
The retention time of the organic acids

Alkanoic acid	t_R [a] (min)		Hydroxyalkanoic acid	t_R [a] (min)		Alkenoic acid	t_R [a] (min)	
	A[b]	B[c]		A[b]	B[c]		A[b]	B[c]
Acetate	5.62	6.30	3-Hydroxybutyrate	5.12	5.49	Vinylacetate	7.74	10.03
Propionate	6.00	7.10	4-Hydroxybutyrate	5.19	5.47	Acrylate	7.85	9.81
Isobutyrate	6.31	7.98	2-Hydroxyisobutyrate	5.29	5.49	Crotonate	9.19	12.67
n-Butyrate	6.71	8.70	Lactate	5.43	5.93	Methacrylate	9.64	13.73
2-Methylbutyrate	6.99	9.73	2-Hydroxybutyrate	5.92	6.89			
Isovalerate	7.33	10.33	Glycolate	5.92	6.51			
Formate	7.35	8.40	2-Hydroxyvalerate	7.21	9.59			
n-Valerate	9.08	14.06	(α-ketoalkenoic acid)					
			Pyruvate	8.88	10.93			

[a] t_R: retention time.
[b] A: Method A, t_R of fluoride=5.05 min.
[c] B: Method B, t_R of fluoride=5.60 min.

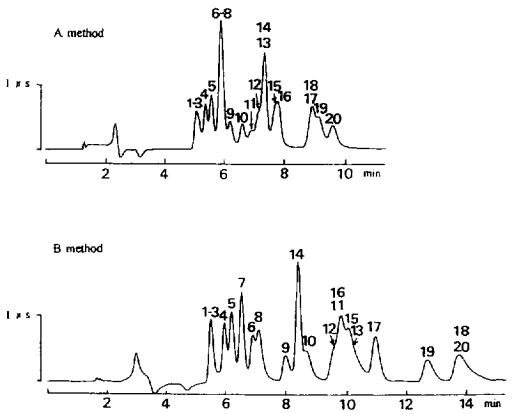

Fig. 3. Comparison of the chromatographic separability of method A with that of method B. Concentration of each compound was 1.0 μg ml^{-1}. 1=3-hydroxybutyrate, 2=4-hydroxybutyrate, 3=2-hydroxyisobutyrate, 4=lactate, 5=acetate, 6=2-hydroxybutyrate, 7=glycolate, 8=propionate, 9=isobutyrate, 10=*n*-butyrate, 11=2-methylbutyrate, 12=2-hydroxyvalerate, 13=isovalerate, 14=formate, 15=vinylacetate, 16=acrylate, 17=pyruvate, 18=*n*-valerate, 19=crotonate, 20=methacrylate.

method B, lactate, acetate, glycolate, isobutyrate, pyruvate and crotonate were separated.

3.5. Determination of incompletely separated compounds

In both methods A and B, several pairs of the compounds were incompletely separated. 2-Hydroxybutyrate and propionate, formate and *n*-butyrate and acrylate and vinylacetate with method B, and pyruvate and crotonate with method A were examined regarding the possibilities of their determination (Table 3). The recoveries were calculated using peak height which gave better results than those by peak area. The recovery was strongly influenced by ratio of analyte concentration to interfering one and improved with increase of the ratio. The determination of formate was free from *n*-butyrate interference at a concentration ratio of formate to *n*-butyrate larger than 1/2 in method B. The same result was obtained for the determination of pyruvate in the presence of crotonate by method A. Propionate did not interfere with the determination of 2-hydroxybutyrate with method B when the concentration of 2-hydroxybutyrate was the same as or above that of propionate. However, the recoveries of propionate, *n*-butyrate, acrylate, vinylacetate in method B and that of crotonate in method A were increased by over ~10% by the incompletely separated compound. For the tested fog samples, pairs of these incompletely separated compounds were not observed. Therefore, no interference will be present in fog analysis.

3.6. Analysis of fog samples

Ten fogwater samples were collected successively

Table 3
Recovery in the presence of incompletely separated compound

Compounds		Analyte	Recovery in the presence of both α and β[b] (%)		
α	β		Concentration ratio (α/β)[a]		
			1/2	2/2	2/1
2-Hydroxybutyrate	Propionate	α	ND[d]	101±2	100±4
		β	108±3	110±3	ND[d]
Formate	*n*-Butyrate	α	100±2	100±4	101±2
		β	109±5	ND[d]	ND[d]
Acrylate	Vinylacetate	α	ND[d]	111±4	108±4
		β	108±1	114±3	ND[d]
Pyruvate[c]	Crotonate[c]	α	103±5	102±5	103±3
		β	103±2	108±3	116±5

[a] The concentration used was 1 or 2 μg ml^{-1}.
[b] The recovery was obtained from the ratio of the peak height in the presence of incompletely separated compound to that in its absence and is shown as the average and the standard deviation (n=3).
[c] These compounds were analyzed by method A and the others by method B.
[d] ND=not detected. This result was caused by the complete overlap of both peaks.

for 20 min each at the top of Mt. Maya on 26 August 1996. Six to 15 ml of fogwater was obtained by 20-min sampling. Chromatograms of a sample prepared by methods A and B are shown in Fig. 4. Both methods detected lactate, formate and pyruvate. Further, glycolate could be detected by method B. The concentrations of these acids obtained by method B were shown in Table 4. The calibration curves of the acids were linear at concentrations ranging from 0.05 to 2.5 μg ml^{-1}. Therefore, their detection limits in Table 4 were set at 0.05 μg ml^{-1}. The 2-hydroxybutyrate concentration could not be determined because it was below the detection limit. Acetate, whose peak is observed between those of lactate and glycolate in the chromatogram of standard solution, was not detected in the samples. An unknown peak (t_R=8.2 min) observed by method A was separated into 2 peaks (t_R=10.1 and 10.4 min) by method B. The retention time of the unknown peak (the first peak) in method B agreed very closely with that of vinylacetate. However, no peak was observed at the retention time of vinylacetate in method A. In order to elucidate the role of the organic acids in the acidification of fogwater, I plan to study the organic acids (particularly acetic acid) reaction in fogwater and to identify these unknown compounds in the near future.

4. Conclusions

A rapid analysis of low-molecular-mass organic acids using column switching was studied. The column switching technique allowed rapid separation of organic acids from inorganic anions. This separation was accomplished using two types of connected columns. The AS4A-SC column was effective for this separation due to its stronger affinity for the organic acids. The use of two connected AS11 columns was effective for the separation of organic

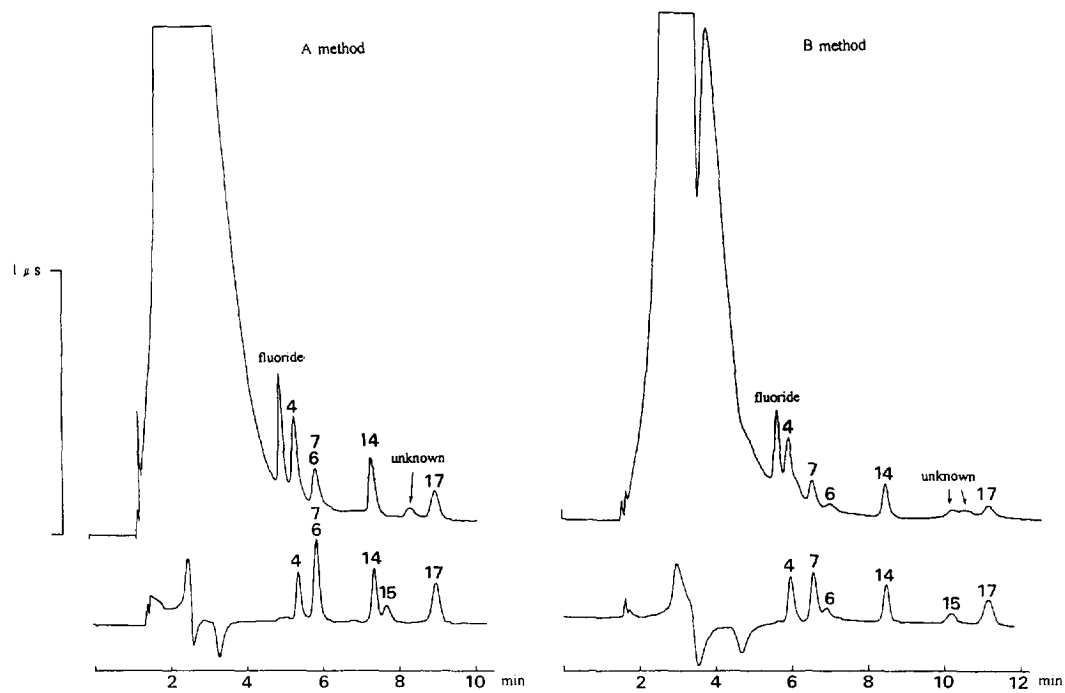

Fig. 4. Chromatograms of a fogwater sample. Upper figure: chromatograms of a fogwater sample collected at the top of Mt. Maya on 26 August 1996. Lower figure: Those of a standard solution containing 0.2 μg ml^{-1} lactate (4), 0.2 μg ml^{-1} glycolate (7), 0.2 μg ml^{-1} formate (14), 0.2 μg ml^{-1} pyruvate (17), 0.1 μg ml^{-1} 2-hydroxybutyrate (6) and 0.1 μg ml^{-1} vinylacetate (15). For method B, the sample solution diluted to 1/2 concentration with deionized water was used for the analysis in order to separate the organic acid peaks from those of the inorganic anions. The concentrations of chloride, nitrate and sulfate ions in the sample solution were 6.2, 17.0 and 20.7 μg ml^{-1}, respectively.

Table 4
Analytical results of fogwater obtained by method B

Sample no.	Lactate ($\mu g\ ml^{-1}$)	Glycolate ($\mu g\ ml^{-1}$)	Formate ($\mu g\ ml^{-1}$)	Pyruvate ($\mu g\ ml^{-1}$)	Cl^- [b] ($\mu g\ ml^{-1}$)	NO_3^- [b] ($\mu g\ ml^{-1}$)	SO_4^{2-} [b] ($\mu g\ ml^{-1}$)
1	0.25	0.05	0.13	0.08	3.8	9.5	17.2
2	0.19	ND[a]	ND[a]	ND[a]	3.8	10.2	15.9
3	0.24	0.09	0.16	0.14	6.4	15.6	21.9
4	0.26	0.14	0.34	0.21	8.1	21.2	26.6
5	0.26	0.10	0.28	0.17	6.2	17.0	20.7
6	0.17	0.06	0.08	0.10	4.8	15.7	16.5
7	0.20	0.07	0.16	0.15	5.2	16.2	15.5
8	0.19	0.08	0.09	0.18	6.0	20.3	16.0
9	0.46	0.07	0.14	0.17	6.7	23.9	18.1
10	0.23	0.05	0.19	0.17	5.7	22.8	16.7

Fogwater samples were collected successively for 20 min each at the top of Mt. Maya on 26 August 1996.
[a] ND: not detected (detection limit: set to 0.05 $\mu g\ ml^{-1}$).
[b] Cl^-, NO_3^- and SO_4^{2-} were analyzed using a Model 2000 i/sp ion chromatograph.

acids. Lactate, formate and pyruvate, the major compounds in fogwater, could be determined with both connected columns. This method is simple because it is free from concentration and precolumn clean-up procedures. Further, the single pump separation system presents easy construction and no expensive apparatus. Therefore, this method is suitable for routine analysis and could be applicable to trace analysis of low-molecular-mass organic acids in aqueous samples containing relatively large amounts of inorganic anions.

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