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A LIQUID CHROMATOGRAPHY SYSTEM FOR MEASUREMENT OF ORGANIC ACIDS IN PRECIPITATION

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An ion chromatographic system has been developed for routine measurement of carboxylic acids with carbon numbers up to C₈ in precipitation samples. The system combines on-line sample pre-concentration on a low-capacity anion exchange resin with separation by ion exclusion and subsequent detection by UV absorption. Detection limits (peak-to-noise ratio 10:1) of less than 0.4 μmol L⁻¹ are obtained for formic acid and acetic acid. Mineral acids such as sulfuric, nitric and hydrochloric acid, which usually represent the main anions in continental precipitation over the northern hemisphere, do not interfere, since they elute as one peak in the beginning of the chromatogram. The chromatographic system has been tested for overlapping peaks with a variety of C₁-C₈ carboxylic acids, both saturated and unsaturated, substituted and unsubstituted, and with phenol and benzene. Not all organic anions are fully separated: oxalate, maleate, and the anions of various multifunctional organic acids up to tartrate and probably citrate are hidden under the large peak of the strong mineral acids; several other peaks were found to overlap by more than 50%. In many cases, this may not be important, since measurements by other groups and models of tropospheric photochemistry have shown that there are certain acids such as formic and acetic acids which generally predominate in the atmospheric mixture of acidic organic compounds.

KEY WORDS: Organic acids, ion exclusion chromatography, on-line pre-concentration, wet deposition.

INTRODUCTION

In recent years, interest in organic acids in the environment has grown. Organic acids have been identified in organisms, food, beverages and sediments, as well as in marine, terrestrial, and atmospheric water samples.¹⁻⁸ In order to analyze

samples of such a varying degree of complexity, a number of analytical methods have been developed for measurement of organic acids. A rather simple method uses the fact that most carboxylic acids have comparable dissociation constants which are much smaller than those of the strong mineral acids so that one can differentiate between strong and weak acidity using conventional titration techniques.^{9,10} It is obvious that such titration techniques have their limitation when it comes to the determination of individual organic acids. The most sophisticated and sensitive, but also the most expensive analytical method employs gas chromatography—mass spectrometry for the measurement of organic acids in environmental samples.¹¹ Besides the high costs, GC-MS techniques have the disadvantage that the acids need to be pre-separated from an often aqueous matrix and then usually derivatized in order to increase their volatility. For trace amounts of low-molecular-weight acids in particular, the sample clean-up and derivatization procedures are complicated and time-consuming if mass loss and contamination are to be avoided.

High-performance liquid chromatography and ion chromatography are much less expensive and provide a more straightforward way of introducing aqueous samples directly on to a partitioning phase. In the case of reversed-phase HPLC, the partitioning phase is usually a silicate, functionalized as either an octyl or an octadecyl ester. In the case of ion chromatography, a polystyrene-divinylbenzene resin with sulfonic or quaternary ammonium functional groups is frequently employed as the partitioning phase. Partition is achieved by anion exchange as well as by ion-exclusion and ion-pairing techniques. In most cases, the separation of organic acids involves more than one mechanism, and reversed-phase partition phenomena are usually part of the overall separation process. An overview of HPLC/IC methods for the analysis of carboxylic acids was published by Schwarzenbach.¹² Recently, Blake *et al.*³ attempted to separate all organic acids present in sugar cane process juice, employing ion-exclusion chromatography after pre-separation of the organic acids from the process juice by ion exchange.

In the atmosphere, vapor-phase hydrocarbons are degraded in a complex way by photochemical processes to increasingly oxygenated products—ultimately to carbon dioxide and water.^{13–17} Since their polarity and solubility in atmospheric liquid water (cloud, fog, and rain water), tends to increase with increasing degree of oxygenation, the oxygenated intermediates are frequently scavenged by aerosol particles and water droplets and returned to the earth surface by precipitation. Oxidative degradation of intermediates such as the lower aldehydes may also occur in cloud and fog droplets.^{18–20} Precipitation is thus the particular medium in which to look for low-molecular-weight oxygenated intermediates when studying photochemical degradation pathways of atmospheric hydrocarbons. Among the various classes of organic compounds dissolved in rain water, the low-molecular-weight carboxylic acids appear to be very abundant. Earlier measurements by Galloway, Likens, Keene and colleagues^{21–23} have shown that formic and acetic acids are abundant trace constituents of precipitation around the globe. Grosjean *et al.*,²⁴ employing a GC-MS technique, found a range of dicarboxylic acids up to C₁₀ in airborne particulate matter collected in California. Norton and colleagues^{25,26} collected precipitation at a suburban and a rural site in Colorado.

Analysis of these samples by ion chromatographic techniques revealed, besides formic and acetic acids, the presence of relatively large concentrations of the anions of oxalic and other lower dicarboxylic acids. Likens and colleagues²⁷ collected precipitation samples at two rural sites in the Eastern U.S., covering all precipitation events for a whole year. Ion chromatographic analysis of the collected samples showed that there were varying concentrations of anions for a variety of organic acids with formate and acetate as the most abundant species.

Methods for HPLC/IC analysis of carboxylic acids in precipitation employ UV absorbance²⁸ or conductivity²⁹⁻³¹ detection. Since the UV absorptivity of most of the carboxylic acids which occur in precipitation is rather poor, methods have been developed which employ fluorescence detection of carboxylic acids after derivatization with a suitable labelling compound.^{32,33} The disadvantage of this method is similar to that of GC-MS techniques: the manipulative requirements are substantial and the method is time consuming.

A routine method suitable for the analysis of carboxylic acids in larger series of precipitation samples should ideally fulfill the following requirements:

- good separation of the potentially complex organic acid mixture at reasonable retention times (less than one hour per run);
- good sensitivity (detection limits in the lower $\mu\text{mol L}^{-1}$ range);
- good precision and accuracy with reasonable manipulative requirements;
- no interference from other anions;
- no interference from other organic compounds;
- no off-line sample pretreatment;
- reasonable costs.

In the light of these criteria, ion chromatographic techniques appear to be most suited, but among the different ion chromatographic techniques there is no obvious best choice. Classical anion exchange systems may be optimized to separate formic and acetic acids from each other and from other anion peaks, but then the retention times grow rather long. There may also be other problems with resolution. Resin-based ion-exclusion columns (ICE columns) provide much shorter retention times and comparatively good separations for organic acids. There are, however, problems with the separation of relatively strong organic acids such as oxalic acid from the peak of the anions of strong mineral acids. Nevertheless, ion-exclusion chromatography appears to be more suited for the analysis of carboxylic acids in precipitation samples than classical ion-exchange chromatography. As was already mentioned, a general disadvantage of ion chromatography lies in the fact that the sensitivity of available detector systems for fatty acids and nonaromatic di- or multifunctional carboxylic acids is rather poor. At present, the best way to overcome this difficulty is by using on-line sample preconcentration.

Preconcentration methods are widely used in liquid chromatography,³⁴⁻³⁷ but they have never been applied on-line with ion-exclusion chromatography. An additional benefit of employing on-line sample preconcentration is the removal of less polar organic compounds such as fatty alcohols, aldehydes, esters, sugars, and cationic compounds which may accumulate on the analytical column and/or

interfere with peak detection by direct UV absorbance. After experimenting with different systems, we chose a set-up consisting of a short low-capacity on-line anion preconcentration column, two six-port column switching valves, an Aminex HPX-87H ion-exclusion analytical column, a UV/vis detector, and two solvent delivery pumps.

EXPERIMENTAL

Materials

All chemicals used were analytical grade and applied without further purification. Carboxylic acids were purchased from Aldrich (Steinheim, FRG), FLUKA (Buchs, Switzerland), and E. Merck (Darmstadt, FRG). Sulfuric, nitric, and hydrochloric acids as well as sodium hydroxide were purchased from E. Merck (Darmstadt, FRG). The anion-exchange resins for the preconcentration column were obtained from SYKAM (Gauting, FRG) and DIONEX (Idstein, FRG). HPLC water was prepared using an Elgastat UHQ water purification system, obtained from the ELGA group (Lane End, UK).

Apparatus

The preconcentration system consists of a microprocessor-controlled solvent delivery pump (a model 64 HPLC pump, Knauer, Berlin, FRG) and two six-port valves—a Rheodyne 7025 syringe-loaded sample injection valve, equipped with a Tefzel rotor-seal and stainless-steel sample loops with volumes of between 0.1 and 5.0 mL, and a Knauer column-switching valve with the preconcentration column attached. The 23 × 4.3 mm stainless-steel preconcentration column (ACC) is filled with low-capacity anion-exchange resins obtained from SYKAM (special batch) and DIONEX (HPIC-AG1, capacity, 30 $\mu\text{equ g}^{-1}$; particle size, 25 μm), respectively. The ACC is flushed with pure water (HPLC grade) or, for regeneration, with aqueous 0.25 M sodium hydroxide. In both cases, a flow rate of 1.0 mL min^{-1} is maintained.

The components of the ion chromatographic system are: a microprocessor-controlled solvent delivery pump (model S 1000 HPLC pump, SYKAM, Gauting, FRG), a 40 × 4.6 mm BIO-RAD Cation-H guard column, a 300 × 7.8 mm BIO-RAD Aminex HPX-87H ion exclusion column, and an HPLC UV/vis filter photometer (Knauer, Berlin, FRG), equipped with a noise filter (set to 4 sec response time). The UV detector has been set at 220 nm. Diluted aqueous sulfuric acid (10 mM) is used as an eluent at a flow rate of 0.45 mL min^{-1} .

The ion exclusion and guard columns and the UV detector are thermostatted at 40 °C using a Haake F3S thermostat. Chromatograms are recorded by means of a two-channel strip chart recorder (model BD41, Kipp & Zonen, Solingen, FRG).

A schematic of the analytical system is shown in Figure 1. The system is operated in the following way. During the time the sample loop is flushed with

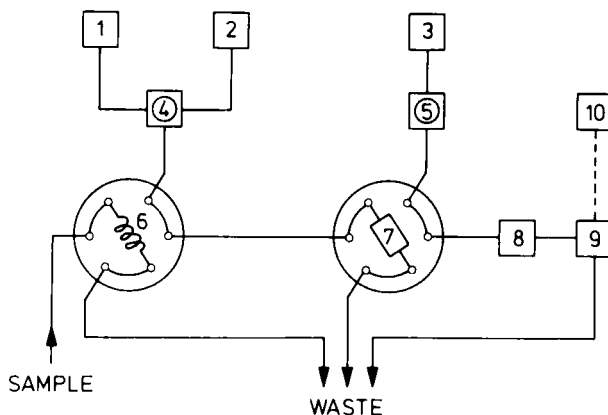


Figure 1 Flow diagram. 1, NaOH; 2, H₂O; 3, H₂SO₄; 4, pump 1; 5, pump 2; 6, valve 1 with sample loop; 7, valve 2 with ACC; 8, analytical column; 9, detector; 10, recorder.

aliquots of sample (at least 3 times the loop volume), HPLC water is pumped through the preconcentration column (ACC) for 2 min by means of pump 1. Then valve 1 is switched in order to transfer the content of the sample loop to the ACC. Depending on the loop volume, HPLC water is allowed to flow through the sample loop and ACC for another 2–15 min (the sample loop should be flushed with at least three volumes of HPLC water). During all this time, valve 2 is in a position which allows the ICE separation column to be flushed by pump 2 with the sulfuric acid mobile phase, while the effluents of the ACC are collected in a waste container. Then valve 2 is actuated to switch the ACC, loaded with sample, into the ICE separation system. After 2 min, the preconcentrated sample has been transferred to the ICE separation column and separation commences. Valve 2 is now switched back for the ACC to be flushed with HPLC water again. After another 2 min, pump 1 is switched to aqueous sodium hydroxide solution in order to regenerate the ACC. Regeneration of the ACC is completed after 30 min. Then pump 1 is switched back to HPLC water. After another 15 min, the chromatographic analysis of the sample is complete, and the next run can be started.

Precipitation samples are collected using PTFE funnels and clean glass bottles with screw caps. If the samples cannot be analyzed immediately after sample collection, which is often the case, precautions have to be taken that the organic acids of the sample do not disappear during sample storage. Adding chloroform to the samples as a biocide, prevents organic acid loss.^{22,23} Since there is a chance that organic acids may be destroyed by non-biological processes as well, we prefer to freeze the samples and keep them refrigerated at -18°C prior to analysis.

RESULTS AND DISCUSSION

With the analytical system described above, blanks were run with HPLC water (sample size 25 mL), using the low-capacity anion-exchange resins from SYKAM

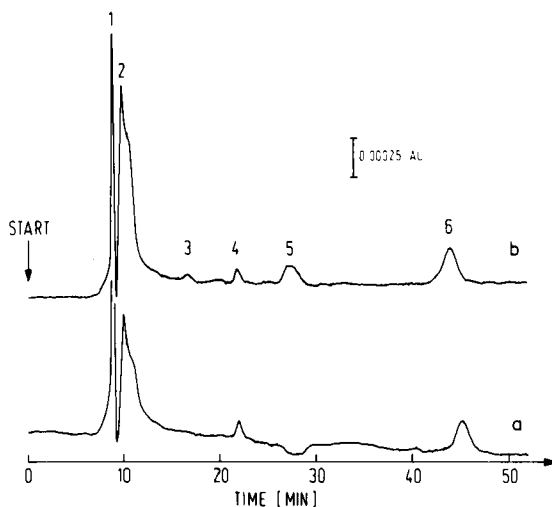


Figure 2 Chromatograms of blank runs. a, Sykam ACC; b, Dionex ACC. 1,2, system peaks; 3,5,6, unknowns; 4, acetic acid. For chromatographic conditions, see text.

and DIONEX for sample preconcentration in the ACC. As shown in Figure 2, the SYKAM resin gave lower blanks and was, therefore, preferred over the resin from DIONEX. Nevertheless, there were still two peaks which had about the same height with both resins (Figure 2, peaks nos. 4 and 6). Blank runs with varying sample volumes suggest that these peaks stem from the HPLC water. Peak 4 in the same chromatogram had the retention time of acetate, but since its height remained reasonably constant from run to run, it could be accounted for by subtraction.

Figure 3 shows a chromatogram obtained from an aqueous standard solution, containing three inorganic and five organic anions which may be expected to occur in precipitation samples. The solution was prepared from the corresponding pure acids or their sodium salts. The total concentration of inorganic anions was 9.2 mM. As may be noted, the inorganic anions form one large peak at the beginning of the chromatogram and the peaks of the organic acid anions are all very well resolved.

Inorganic anions are more strongly retained on anion-exchange resins than organic anions. Thus, although the inorganic anions of a precipitation sample (which are determined by means of a classical ion chromatographic system employing an anion-exchange separation column) do not affect the separation of the organic anions on the ICE column, they limit the size of the sample which can be preconcentrated by blocking the active sites on the ACC. Test runs with aqueous standard solutions showed that as long as the total concentration of inorganic anions did not exceed $140 \mu\text{mol L}^{-1}$, formic and acetic acids were completely retained on the ACC, even with 5 mL samples, and the calibration curves obtained for formic and acetic acids were linear over the range of 0.4–26 and 0.4–10 $\mu\text{mol L}^{-1}$, respectively. Total concentrations of inorganic anions as high as $600 \mu\text{mol L}^{-1}$ are not uncommon in precipitation from polluted air masses,

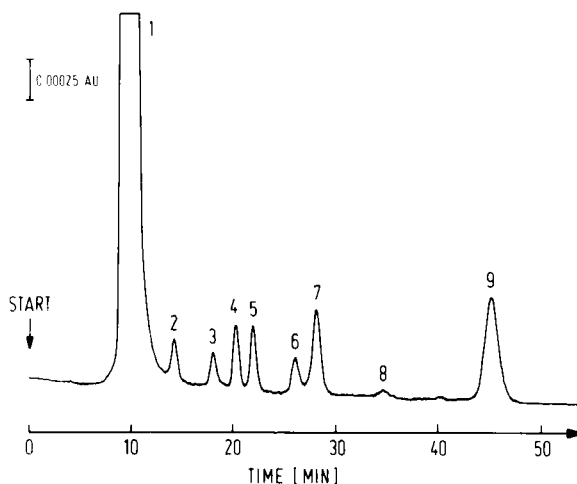


Figure 3 Chromatogram of 4.8 mL of a standard solution concentrated on Sykam ACC. 1, $1.98 \mu\text{mol L}^{-1}$ hydrochloric, $2.74 \mu\text{mol L}^{-1}$ nitric, $4.48 \mu\text{mol L}^{-1}$ sulfuric; 2, $0.30 \mu\text{mol L}^{-1}$ oxoacetic; 3, $0.25 \mu\text{mol L}^{-1}$ hydroxyacetic; 4, $0.43 \mu\text{mol L}^{-1}$ formic; 5, $0.30 \mu\text{mol L}^{-1}$ acetic; 6, $0.23 \mu\text{mol L}^{-1}$ propionic acid; 7, 8, 9, unknowns. For chromatographic conditions, see text.

but whenever high concentrations of inorganic ions were observed in precipitation samples, the organic acid levels were also elevated. In such cases, less sample needs to be preconcentrated so that the total amount of anions can be kept under the critical amounts of $140 \mu\text{mol L}^{-1}$. For cleaner samples a larger volume has to be preconcentrated, but because of potential breakthrough on the ACC never more than 5 mL.

We have obtained (lower) detection limits of less than $0.4 \mu\text{mol L}^{-1}$ for formic and acetic acid by preconcentrating 5 mL of aqueous standard solutions containing no inorganic anions. Since the concentrations of inorganic anions in precipitation are usually low when the organic acids are low, the same detection limits may be assumed for formic and acetic acid in real precipitation samples. Up to concentrations of 33 and $12 \mu\text{mol L}^{-1}$, respectively, calibration curves for formic and acetic acids were linear. The precision of individual determinations was found to be better than 6 and 8%, respectively.

A chromatogram obtained from a precipitation sample is shown in Figure 4. The rain sample was collected at a rural site near Deuselbach/Hunsrück (FRG) on October 20, 1986. An aliquot of 4.8 mL was preconcentrated on the SYKAM low-capacity anion-exchange resin and then chromatographed as described above. After the large composite peak of the strong anions, there eluted a number of peaks, several of which were only poorly resolved.

Table 1 shows results from rain samples taken at a rural site near Wiesbaden (FRG).

In order to test for overlapping peaks, the analytical system was run with various mixtures of carboxylic acids likely to occur in the atmosphere. The results are summarized in Table 2. As may be noted, there are a number of overlapping

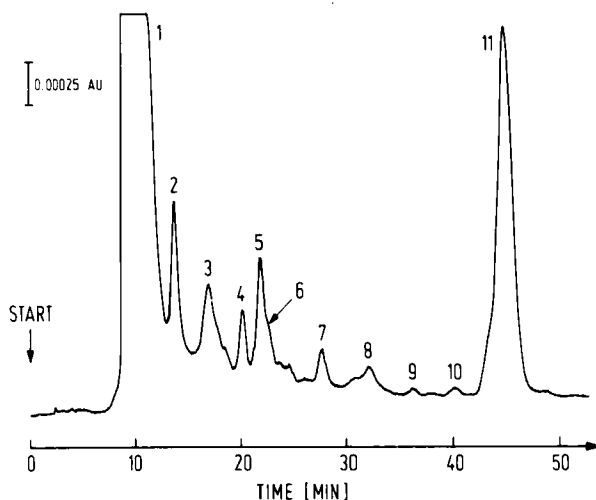


Figure 4 Chromatogram of a rain sample; 4.8 mL concentrated on Sykam ACC. 1, Strong acids; 2,3, unknowns; 4, $0.54 \mu\text{mol L}^{-1}$ formic acid; 5, about $0.25 \mu\text{mol L}^{-1}$ acetic acid; 6–11, unknowns. For chromatographic conditions, see text.

Table 1 Rain samples from Presberg (Taunus, FRG)

Date	Sample no.	Conductivity [μS]	pH	Formate Acetate	
				[$\mu\text{mol L}^{-1}$]	
12/18/84	3	9	4.6	0.70	0.45
	4	11	4.5	0.28	0.45
	5	11	4.4	1.52	0.97
06/20/85	2	118	3.4	27.68	8.77
	3	139	3.2	10.65	5.22
06/26/85	1	31	3.6	9.07	4.17
	2	29	3.7	8.07	3.75
	3	23	3.8	4.78	2.68
	4	23	3.7	4.02	2.60
	5	20	3.9	5.41	1.88
	6	32	3.7	6.07	2.53
	7	24	3.9	6.46	3.07
07/31/85	1	22	3.9	4.35	1.88
	2	18	3.9	4.04	1.37
	3	15	4.0	2.63	1.17
	4	34	3.5	5.35	3.20

peaks. Judging from Figure 4, the first eight acids listed in Table 2 will hardly be resolved from the usually large inorganic anions peak to be expected from precipitation samples collected in Central Europe. The resolution may be better with tropical precipitation samples which usually contain much less inorganic relative to organic anions.^{21,22} In a precipitation sample, there may also be a

Table 2 Retention times of various C₁–C₈ carboxylic acids on ICE column, listed in order of increasing capacity factors.

Acid	<i>k</i> ^{a,b}	Formula	Retention time [min]	<i>pK</i> _a ^d
1. oxalic	0.08	HO ₂ CCO ₂ H	9.5 + 11.0 ^c	{ 1.27 4.27
2. dihydroxymalonic	0.14	(HO) ₂ C(CO ₂ H) ₂	10.0	—
3. hydroxymalonic	0.25	HOCH(CO ₂ H) ₂	11.0 + 12.0 ^c	—
4. maleic	0.36	HO ₂ CCH=CHCO ₂ H	12.0 + 13.0 ^c	{ 1.83 6.07
5. 2-ketoglutaric	0.40	HO ₂ C(CH ₂) ₂ COCO ₂ H	12.3 + 12.9 ^c	—
6. 2-ketosuccinic	0.42	HO ₂ CCH ₂ COCO ₂ H	12.5 + 14.5 ^c	2.56
7. tartaric	0.45	HO ₂ CCH(OH)CH(OH)CO ₂ H	12.8	{ 3.04 4.37
8. citric	0.48	HOC(CH ₂ CO ₂ H) ₂ CO ₂ H	13.0	{ 3.14 4.77
9. oxoacetic	0.59	HCOCO ₂ H	14.0	—
10. pyruvic	0.60	CH ₃ COCO ₂ H	14.1	2.49
11. malic	0.65	HO ₂ CCH(OH)CH ₂ CO ₂ H	14.5	{ 3.40 5.11
12. malonic	0.65	HO ₂ CCH ₂ CO ₂ H	14.5	{ 2.83 5.69
13. 3-ketoglutaric	0.73	HO ₂ CCH ₂ COCH ₂ CO ₂ H	15.2	3.30
14. 2-ketobutyric	0.82	CH ₃ CH ₂ COCO ₂ H	16.0	—
15. succinic	0.93	HO ₂ C(CH ₂) ₂ CO ₂ H	17.0	{ 4.16 5.61
16. hydroxyacetic	1.05	HOCH ₂ CO ₂ H	18.0	3.83
17. methylmalonic	1.05	CH ₃ CH(CO ₂ H) ₂	18.0	{ 3.07 5.76
18. lactic	1.10	CH ₃ CH(OH)CO ₂ H	18.5	3.08
19. formic	1.27	HCO ₂ H	20.0	3.77
20. 3-hydroxybutyric	1.27	CH ₃ CH(OH)CH ₂ CO ₂ H	20.0	4.41
21. glutaric	1.33	HO ₂ C(CH ₂) ₃ CO ₂ H	20.5	{ 4.31 5.41
22. acetoacetic	1.36	CH ₃ COCH ₂ CO ₂ H	20.8	3.58
23. 2-hydroxybutyric	1.44	CH ₃ CH ₂ CH(OH)CO ₂ H	21.5 + 37.0 + 41.0 ^c	3.65
24. acetic	1.50	CH ₃ CO ₂ H	22.0	4.76
25. fumaric	1.53	HO ₂ CCH=CHCO ₂ H	22.3	{ 3.03 4.44
26. adipic	1.78	HO ₂ C(CH ₂) ₄ CO ₂ H	24.5	{ 4.43 5.41
27. propionic	1.95	CH ₃ CH ₂ CO ₂ H	26.0	4.88
28. n-butyric	2.64	CH ₃ (CH ₂) ₂ CO ₂ H	32.0	4.82
29. pimelic	2.91	HO ₂ C(CH ₂) ₅ CO ₂ H	34.4	{ 4.50 5.42
30. methacrylic	3.15	CH ₂ =C(CH ₃)CO ₂ H	36.5	—
31. transmuconic	3.49	HO ₂ CCH=(CH) ₂ =CHCO ₂ H	39.5	—
32. n-valeric	4.28	CH ₃ (CH ₂) ₃ CO ₂ H	46.5	5.05
33. phenol	8.77	C ₆ H ₅ OH	86.0	9.89
34. benzene	13.77	C ₆ H ₆	130.0	—

^a*k*' = *t*_R - *t*₀/*t*₀.^bCalculated only for the main peak.^cTwo or more peaks appeared; main one assumed to be associated with acid (first number in column); smaller peaks probably due to impurities.^d*pK*_a values obtained from several handbooks; conditions not always indicated.

problem with the resolution of oxoacetic and pyruvic acids. Based on retention times, Peak 2 in Figure 4 may be pyruvate or oxoacetate or a mixture of both. Malate and malonate, if present, would also be only poorly resolved from the former two. Peak 3 in Figure 4 may consist of succinate, hydroxyacetate, and methylmalonate. The small shoulder of Peak 3 may be lactate. Peak 4 is formate, with a potential contribution by 3-hydroxybutyrate; however, available information on atmospheric concentrations suggest that 3-hydroxybutyrate does not contribute significantly. Glutarate, if present in significant concentrations, should be at least partially resolved from formate. Acetate and fumarate present another problem. Although acetate would mostly predominate, if the data on atmospheric abundances are correct, fumarate may form a shoulder as in Figure 4 (Peaks 5/6). The small peak which elutes just before Peak 7 is propanoate according to retention time. The identities of Peaks 8–11 in Figure 4 are still unknown. Attempts will be made to isolate the substances producing the unknown peaks for subsequent identification by spectroscopic methods.

Some general conclusions can be drawn from the data listed in Table 2. Introduction of a keto or hydroxy group into the molecule of a carboxylic acid leads to a shorter retention time on the ICE column. The same holds for the introduction of a second or third carboxylic group. The effect increases in the following order: hydroxy < carboxylic < keto group (e.g., 26.0, 18.5, 14.5, and 14.1 min for propanoate, lactate, malonate, and pyruvate). It also increases with increasing separation of the functional groups within the molecule (e.g., 32.0, 21.5, and 20.0 min for n-butyrate, 2-hydroxybutyrate, and 3-hydroxybutyrate).

CONCLUSIONS

An ion chromatographic system has been developed for the routine analysis of organic acids with chain lengths of up to C₈ in precipitation samples. While formic, acetic, and propanoic acids can be determined with reasonable precision and accuracy, the assignment of peaks to other organic acid anions remains ambiguous if there is no additional information on the abundance of organic acids in the samples. Oxalate, maleate, and the anions of various multifunctional organic acids up to tartrate and probably citrate are not sufficiently resolved from the large composite peak of the inorganic anions at concentrations typical for Central European precipitation. With tropical precipitation samples, resolution may be better, since the inorganic anions peak is usually substantially smaller. For the determination of oxalate, IC employing a classical anion exchange column is probably more suited.

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References

1. P. Carlier, H. Hannachi and G. Mouvier, *Atmos. Environ.* **20**, 2079 (1986).
2. W. Distler, *J. Chromatogr.* **192**, 240 (1980).
3. J. D. Blake, M. L. Clarke and G. N. Richards, *J. Chromatogr.* **398**, 265 (1987).
4. E. Mentasti, M. C. Gennaro, C. Sarzanini, C. Baiocchi and M. Savigliano, *J. Chromatogr.* **322**, 177 (1985).
5. M. I. Chicarelli, L. P. Damasceno and J. N. Cardoso, *Org. Geochem.* **6**, 153 (1984).
6. D. J. Kieber and K. Mopper, *Anal. Chim. Acta* **183**, 129 (1986).
7. M. J. Barcelona, H. W. Liljestrand and J. J. Morgan, *Anal. Chem.* **52**, 321 (1980).
8. T. E. Graedel and C. J. Weschler, *Rev. Geophys.* **19**, 505 (1981).
9. G. Gran, *Analyst* **77**, 661 (1952).
10. A. Johansson, *Analyst* **95**, 535 (1970).
11. K. Kawamura and J. R. Kaplan, *Anal. Chem.* **56**, 1616 (1984).
12. R. Schwarzenbach, *J. Chromatogr.* **251**, 330 (1982).
13. R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winter and J. N. Pitts, Jr., *Adv. Photochem.* **11**, 375 (1979).
14. R. Atkinson and A. C. Lloyd, *J. Phys. Chem. Ref. Data* **13**, 315 (1984).
15. J. G. Calvert and W.R. Stockwell, *Environ. Sci. Technol.* **17**, 428A (1983).
16. J. G. Calvert and S. Madronich, *J. Geophys. Res.* **92**, 2211 (1987).
17. D. J. Jacob and S. C. Wofsy, *J. Geophys. Res.* **93**, 1477 (1988).
18. J. G. Calvert, A. Lazrus, G.L. Kok, B. G. Heikes, J. G. Walega, J. Lind and C. A. Cantrell, *Nature* **317**, 27 (1985).
19. W. L. Chameides and D. D. Davis, *Nature* **304**, 427 (1984).
20. W. L. Chameides. In: *Chemistry of Multiphase Atmospheric Systems*, W. Jaeschke (ed.) (Springer-Verlag, Berlin-Heidelberg-New York-Tokyo, 1986) pp. 369-414.
21. J. N. Galloway, G. E. Likens, W. C. Keene and J. M. Miller, *J. Geophys. Res.* **87**, 8771 (1982).
22. W. C. Keene, J. N. Galloway and J. D. Holden, Sr., *J. Geophys. Res.* **88**, 5122 (1983).
23. W. C. Keene and J. N. Galloway, *Atmos. Environ.* **18**, 2491 (1984).
24. D. Grosjean, K. Van Cauwenberghe, J. P. Schmid, P. E. Kelly and J. N. Pitts, Jr., *Environ. Sci. Technol.* **12**, 313 (1978).
25. R. B. Norton, J. M. Roberts and B. J. Huebert, *Geophys. Res. Lett.* **10**, 517 (1983).
26. R. B. Norton, *Geophys. Res. Lett.* **12**, 769 (1985).
27. G. E. Likens, E. S. Edgerton and J. N. Galloway, *Tellus* **35B**, 16 (1983).
28. R. W. Gillett and G. P. Ayers, *Anal. Chim. Acta* **177**, 273 (1985).
29. W. A. Hoffman, Jr. and R. L. Tanner, Report No. BNL 51922 (Denison University, Granville, OH 43023, 1985).
30. M. O. Andreae, R. W. Talbot and S. M. Li, *J. Geophys. Res.* **92**, 6635 (1987).
31. R. Tsitouridou and H. Puxbaum, *Intern. J. Environ. Anal. Chem.* **31**, 11 (1987).
32. A. Nefstel, S. Breitenbach, W. Elbert and J. Hahn, Proceedings of International Conference on Gas-Liquid Chemistry of Natural Waters (Brookhaven, National Laboratory Report No. BNL 51757, 1984).
33. W. Elbert, S. Breitenbach, A. Nefstel and J. Hahn, *J. Chromatogr.* **328**, 111 (1985).
34. A. L. Heckenberg and P. R. Haddad, *J. Chromatogr.* **330**, 95 (1985).
35. P. Daish and I. V. Leonard, *Clin. Chim. Acta* **146**, 87 (1985).
36. T. Takeuchi, Y. Jin and D. Ishii, *J. Chromatogr.* **321**, 159 (1985).
37. P. E. Jackson and P. R. Haddad, *J. Chromatogr.* **389**, 65 (1987).