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DETERMINATION OF ORGANIC AND INORGANIC ACIDS IN PRECIPITATION SAMPLES

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SUMMARY

This paper describes an ion chromatographic method for simultanous analysis of major organic and inorganic acids (formic, acetic, nitric, sulfuric, hydrochloric and hydrofluoric) in precipitation samples. The method can also determine several other acids commonly cited in literature on precipitation-related samples; namely, propionic, glycolic, butyric, methanesulfonic, nitrous, hydroxymethylsulfonic, oxalic, phosphoric and citric acids. The method can be adapted for routine analysis of these acids, which are resolved in less than 10 min. Three types of natural waters were used and 60 recoveries made giving a percent recovery range of 100 ± 10%.

INTRODUCTION

While inorganic acids (as Cl^-, SO_4^{2-}, NO_3^-) continue to be very important constituents in acid rain studies, organic acids are becoming more and more a prerequisite for proper accounting of atmospheric chemistry processes and precipitation ionic balances[1–5]. In fact, Grosjean *et al.*[6] very recently showed that in Los Angeles smogs, acetic and formic acids (the major components of organic acids) are present in greater quantity than nitric and hydrochloric acid combined. Likewise, Solomon *et al.*[7] reported high gas phase formic acid concentration compared to HNO_3, HCl and HF in Los Angeles area. Keene and Galloway[1] reported the two organic acids contributed 16% of free acidity in central Virginia precipitation, whereas Backman and Peden[3] reported 8% total acidity in central Illinois rainwater. The ionic balances of Ferek *et al.*[5], which did not include organic acids, consistently showed anion deficit with an 8% average. Thus organic acids particularly formic and acetic are important constituents to study.

Fluoride is an interesting element to study also because F^- in rain samples partially originate from the notorious ozone-depleting chlorofluorocarbons (CFCs) and it is required for accurate ionic balance calculations. Since atomic F has a much smaller ozone depletion potential than Cl following decomposition reactions of CFCs in the stratosphere, F does not readily enter in the ozone-depletion mechanism and is therefore more available to form HF. The latter finds its way back to earth surface, because once formed HF is a permanent "reservoir" molecule, remaining chemically unchanged until it diffuses into the troposphere and is removed by rain[8,9].

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Fluoride is commonly analysed by ion-selective electrode or by ion chromatography (using the Dionex workhorse column HPIC-AS4A with CO_3^{2-}/HCO_3^- eluent), that relies on matrix matching technique. But the technique, though adequate for eliminating the water dip interference, is an additional step of a method and it lessens the potential to simultanously analyse the anions and certain monovalent cations[10]. Furthermore, these conditions will result in F^-/acetate/formate co-elution.

While F^-, acetate and formate can be simultanously determined using HPIC-AS4-B_4O_7 conditions[11], most peaks of other anions of interest are unacceptably long and broad. Similarly, the three ions can be acceptably resolved[12] using HPIC-AS6-B_4O_7, but at the expense of the other important inorganic ions. The two organic acids and others can also be adequately determined by ion-exclusion chromatography[11,13], but again the major inorganic ions cannot be obtained in the same run.

Rocklin *et al.*[14] published a gradient elution chromatogram of 36 organic and inorganic parameters which were resolved in 30 min. A good deal of the parameters, however, are not of interest to current acid rain studies. To a routine laboratory, which supports precipitation projects requesting for major ions (acetate, formate, F^-, Cl^-, NO_3^-, SO_4^{2-}), both time and analyte constraints (<30 min, <36 parameters) must be tailored to increase cost-effectiveness.

It would be desirable for a routine laboratory to have a method capable of simultanously analysing the major organic and inorganic anions within a reasonably short time. This paper describes such a method, which in 10 min resolves the major as well as other acids commonly reported in the precipitation-related samples. Table I lists the organic acids cited in several recent publications and studied here.

EXPERIMENTAL

Chemicals

Milli-Q water (18 MΩ) was used. High-purity chemicals used were 50% NaOH, LiOH, NH_4OH, H_2SO_4, butyric acid, sodium and potassium salts: carbonate,

TABLE I

ORGANIC ACIDS CITED IN SOME RECENT LITERATURE FOR PRECIPITATION-RELATED SAMPLES

Acids	*Formula*	*Refs.*
Formic	HCOOH	1–4, 6, 7, 15–18
Acetic	CH_3COOH	1–4, 6, 15–18
Oxalic	HOOCCOOH	4, 6
Gylcolic	$HOCH_2COOH$	16
Propionic	CH_3CH_2COOH	16, 17
Lactic	$CH_3CHOHCOOH$	16
Butyric	$CH_3CH_2CH_2COOH$	16, 18
Succinic[a]	$HOOCCH_2CH_2COOH$	19
Citric	$HOOC(CH_2COOH)_2COOH$	3
Methanesulfonic	CH_3SO_3H	15
Hydroxymethylsulfonic	$HOCH_2SO_3H$	16

[a] Not cited in these samples, but is an important component of natural organic matter (see discussion).

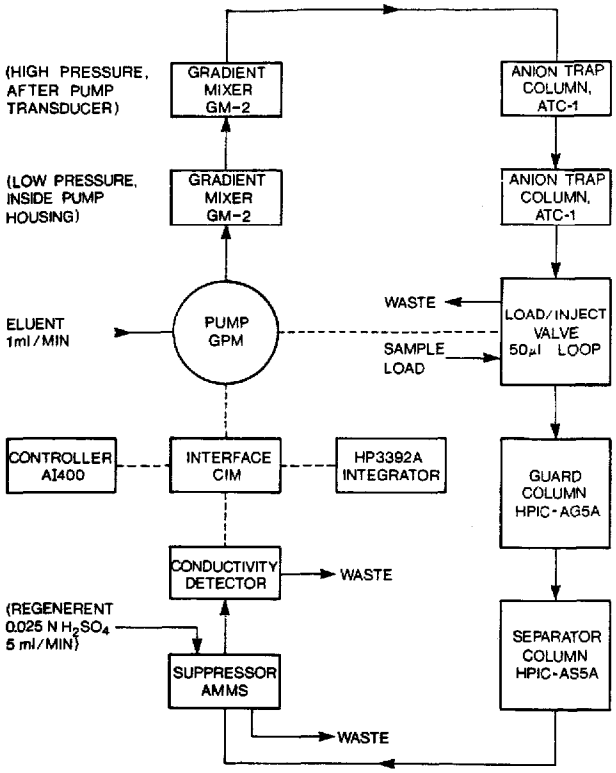

Fig. 1. System schematic (AMMS = anion micromembrane suppressor).

bicarbonate, fluoride, acetate, propionate, formate, methanesulfonate, chloride, nitrite, succinate, sulfate, oxalate, phosphate, nitrate, citrate, borate and hydroxymethylsulfonate. A stock solution of 1000 ppm (mg/l) of each acid was prepared, the organic acids being preserved with 0.2% HPLC-grade chloroform.

Equipment and operation conditions

The system comprises Dionex's gradient pump, columns, conductivity detector CDM-1, autoion 400 and is schematized in Fig. 1. The two ATC columns were used to minimize background contaminants. An eluent profile and main steps of a run are shown in Table II. To avoid CO_2 pickup by eluents, at the beginning of each week, the eluents were carefully prepared using helium-degassed water and 50% NaOH, which was pipetted from the middle of the bottle, and the He atmosphere constantly applied over the eluents until the end of the week. The eluent flow-rate is 1.0 ml/min, and the regenerent (0.025 N H_2SO_4) flow-rate about 5 ml/min throughout.

RESULTS AND DISCUSSION

Common acids in precipitation samples

Based on some recent publications, the common acids comprise the major ones (SO_4^{2-}, NO_3^-, F^-, Cl^-, formate and acetate) and propionate, lactate, glycolate,

butyrate, methanesulfonate, hydroxymethylsulfonate, nitrite, oxalate, phosphate, and citrate. Although succinate is not commonly reported (Table I), the acid is a controversial one vis-a-vis its inherent part of natural organic matters and has recently been identified to be one of the important acids in the make-up of humic and fulvic acids[17]; we therefore chose to include it in this study.

Optimization

Using a standard containing most of the above acids, several potential eluents including LiOH, NaOH, $Na_2B_4O_7$, NH_4OH, Na_2CO_3, $NaHCO_3$ and some combinations of them were tested on three different separation columns, HPIC-AS4A, -AS5A and -AS6A. The NaOH-AS5A combination was found to be most effective in resolving the mono-, di- and trivalent analytes of interest.

Experiments showed that 0.75 m*M* NaOH eluent as used by Rocklin *et al.* [14] was not always effective in resolving the weakly retained monovalent acids, possibly due to the difficulty in maintaining a CO_2-free eluent or a constant CO_2 content in the eluent, or the slight variability of the AMMS-suppressing capacity, resulting in variable background conductivity, μ_0. After each weekly change of eluent, μ_0 is not always the same, which can result in poor resolution of monovalents; a slight change in eluent concentration was necessary to achieve a better resolution. This can be best realized using a water eluent (E_1) in conjunction with a 10 m*M* NaOH eluent (E_2) to quickly find the effective concentration at the beginning of each week (Table II). Thus, instead of a fixed concentration of NaOH, a small range (0.5–2.5 m*M*) was found suitable to resolve the monovalents, the 80:20 (2 m*M*) and 90:10 (1 m*M*) combinations of E_1–E_2 being more often used. The chromatogram from formate peak to the last peak is negligibly affected by this weak eluent concentration range.

For the more strongly retained analytes, a stronger eluent is needed, which is made up of E_1 (water) and E_3 (200 m*M* NaOH) (Table II). A fixed concentration of NaOH was not always effective in resolving two neighboring peaks with markedly different concentrations, for example a small PO_4^{3-} peak shouldering a large NO_3^- peak, or a small oxalate shouldering a large SO_4^{2-}. As in the weak-eluent case, an effective concentration can be easily found by simply varying E_1 (and subsequently E_3). A range of 88–96 m*M* NaOH was found effective in achieving a better resolution of such peaks (small peaks shouldering large ones), and the concentration most often used was 90 m*M* (E_1–E_3 = 55:45) or 94 m*M* (E_1–E_3 = 53:47).

TABLE II
AN ELUENT PROFILE AND MAIN STEPS OF A RUN

Time (min)	*% E_1 (Milli-Q water)*	*% E_2 (10 mM NaOH)*	*% E_3 (200 mM NaOH)*	*Load/inject (valve)*
0.0	85	15	0	Load
0.1	85	15	0	Inject
1.0	53	0	47	Inject
3.0	53	0	47	Load
4.5	53	0	47	Load
4.6	85	15	0	Load
15.0	85	15	0	Load

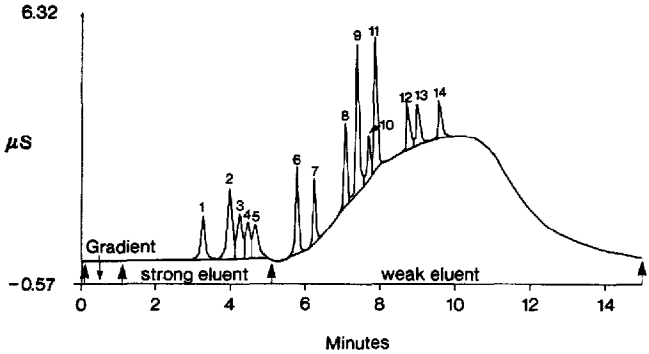

Fig. 2. Chromatogram showing each eluent spatial interval. Peaks: 1 = F^-, 0.1 ppm; 2 = acetate, 1.0 ppm; 3 = propionate, 1.0 ppm; 4 = glycolate, 0.5 ppm; 5 = butyrate, 1.0 ppm; 6 = formate, 0.5 ppm; 7 = methanesulfonate, 0.5 ppm; 8 = Cl^-, 0.2 ppm; 9 = NO_2^-, 0.2 ppm; 10 = succinate, 0.5 ppm; 11 = SO_4^{2-}, 0.5 ppm; 12 = phosphate, 0.2 ppm; 13 = NO_3^-, 0.08 ppm; 14 = citrate, 0.5 ppm.

Basically then, it is a two-eluent system, a weak and a strong one as shown in Fig. 2. The small gradient step (0.1–1 min) helps to smooth out the transition. (A similar two-eluent system was previously used for cations[10]). To maintain optimum operating conditions, a daily system cleaning with 200 m*M* NaOH for 10 min was used.

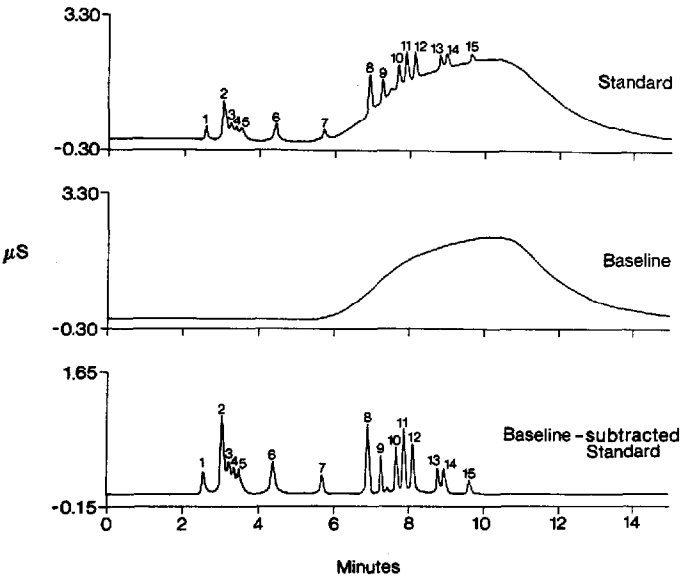

Fig. 3. Baseline-subtracted chromatogram of a standard. Peaks: 1 = F^-, 0.025 ppm; ; 2 = acetate, 0.25 ppm; 3 = propionate, 0.25 ppm; 4 = glycolate, 0.125 ppm; 5 = butyrate, 0.25 ppm; 6 = formate, 0.125 ppm; 7 = methanesulfonate, 0.125 ppm; 8 = Cl^-, 0.05 ppm; 9 = nitrite, 0.025 ppm; 10 = succinate, 0.25 ppm; 11 = sulfate, 0.125 ppm; 12 = oxalate, 0.125 ppm; 13 = phosphate, 0.05 ppm; 14 = NO_3^-, 0.018 ppm; 15 = citrate, 0.125 ppm.

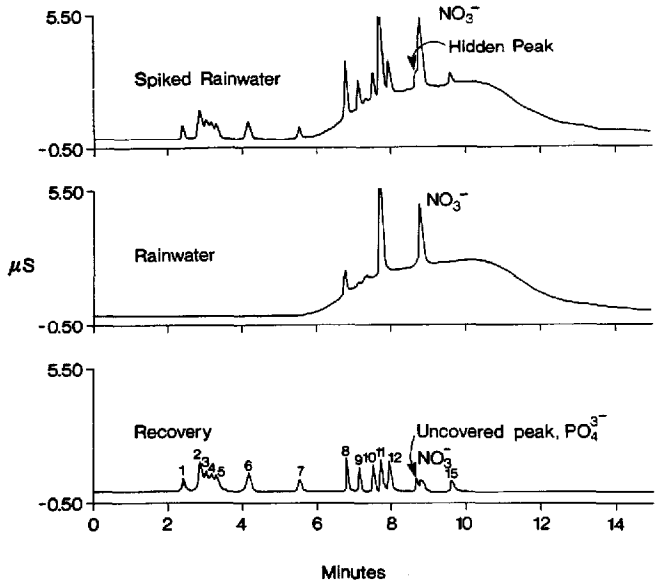

Fig. 4. Uncovering of hidden peak by background-subtraction technique. Peaks as in Fig. 3.

Baseline

Although the actual baseline is shaped as in Fig. 2, the quantitation can be carried out in the usual manner. However, the baseline-subtraction technique can be useful in checking the proper behavior of baseline (Fig. 3) or in recovery studies to uncover or sharpen hidden peaks (Fig. 4), hence facilitating identification and quantitation.

The use of mannitol–boric acid combination[13] to flatten out the baseline was tested and found to affect three things negatively: the baseline, the separator retaining capacity, and possibly the suppressor suppressing capacity. The baseline rise due to the strong eluent kept increasing to ≈ 10 μS instead of ≈ 2.5 μS as seen in Figs. 2–4. To lower the baseline back down, the two ATC columns had to be cleaned with 1 *M* NaOH for 2 h along with the whole-system cleaning. The separator retaining capacity seemed to have slightly decreased as evidenced by the early F^- elution (Figs. 3 and 4) observed after, compared to the late F^- elution (Fig. 2) observed before the mannitol–boric acid use. In these three figures the background conductivity were practically the same, ≈ 2.6 μS. Soon after, the AMMS was plugged and had to be cleaned thoroughly with NaOH, H_2SO_4, and 5% acetonitrile. The suppressor suppressing capacity slightly decreased as μ_0 increased from 2.6 to 3.6 μS, which subsequently required a more dilute weak eluent for satisfactory resolution of monovalents. The mannitol–boric acid use was abandoned.

Interferences

Of the seventeen potentially present acids, lactate coelutes with acetate, and hydroxymethylsulfonate with succinate. Fortunately, succinate is not a commonly present acid as indicated earlier, whereas lactate is found infrequently and at very low

concentration compared to acetate[20]. In general the concentration interference can occur when two analytes with close retention times have markedly different concentration levels. Nitrate and phosphate are an example as NO_3^- is often much more concentrated than PO_4^{3-}. But as explained above resolution can be achieved by using an effective E_1–E_3 ratio or background-subtracting technique.

Sensitivity

Sensitivity has been defined and redefined by many authors as, for example: the concentration giving a signal-to-noise ratio of 2 (ref. 21); the minimum detectable concentration[22]; the response (or signal change) per unit concentration[23,24]; the ability to discern the difference between very small amounts of a substance[25]; or a measure of the effectiveness of a detector to respond to compounds entering it[26]. Based on many of these definitions, the method sensitivity is depicted here as the response in function of concentration (Fig. 5). For each acid at three to four low concentration levels of interest a line was manually drawn and the regression parameters were calculated and shown in the legend. If sensitivity is taken as the response per unit concentration, it may be equated to the slope of each line, and the sensitivities for the various acids can be easily compared as shown in Table III and Fig. 5. It is seen that the inorganic responses, particularly of the monovalent ions, are greater (more sensitive) than the organic ones, except oxalate. The response of the latter ions is close to that of sulfate and phosphate.

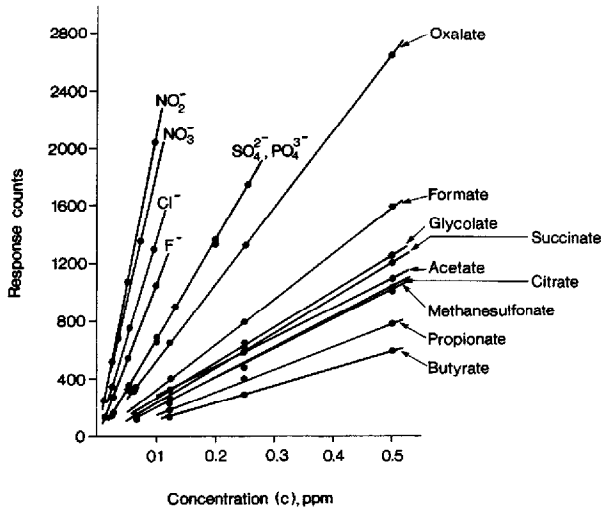

Fig. 5. Sensitivity of the fifteen acids studied. Regression parameters of equations $R = a + bc$ (r = correlation coefficient) for the acids: NO_2^- = 11.1 + 20 516c (r = 1.000); NO_3^- = −9.1 + 18 937c (r = 1.000); Cl^- = 108.7 + 11 790c (r = 0.998); F^- = 8.0 + 10 368c (r = 1.000); SO_4^{2-} = −52.4 + 7 120c (r = 0.999); PO_4^{3-} = −1.0 + 6728c (r = 1.000); oxalate = −13.2 + 5344c (r = 1.000); formate = 0.2 + 3200c (r = 1.000); glycolate = −10.3 + 2550c (r = 1.000); succinate = −23.5 + 2470c (r = 1.000); acetate = 94.0 + 2007c (r = 0.999); citrate = −19.7 + 2117c (r = 0.999); methanesulfonate = −12.3 + 2058c (r = 1.000); propionate = −11.0 + 1590c (r = 0.999); butyrate = −10.0 + 1200c (r = 1.000).

TABLE III
METHOD SENSITIVITIES FOR THE VARIOUS ACIDS (RESPONSE COUNTS/ppm)

Acid	*Sensitivity*	*Acid*	*Sensitivity*
Nitrite	20 516	Glycolate	2550
Nitrate	18 937	Succinate	2470
Chloride	11 790	Acetate	2007
Fluoride	10 368	Citrate	2117
Sulfate	7120	Methanesulfonate	2058
Phosphate	6728	Propionate	1590
Oxalate	5344	Butyrate	1200
Formate	3200		

Performance characteristics

Three types of waters were studied: a rain sample from Sibley collected by the surveillance and monitoring group, a Eulerian quality control sample (EU-ANI-1, a composite rain sample), and a rain–snow mixture collected from Burlington, which was immediately preserved with 0.2% $CHCl_3$. All samples were filtered through a 0.45-μm membrane filter. The first two samples were originally unpreserved as dictated by their protocol, but were preserved when used in recovery studies. The recovery data are presented in Tables IV–VI, showing good precision (small standard deviation of five replicate analyses) and a range of 100 $\pm$ 10% recoveries.

Table VII shows the reproducibility of retention times at two concentration levels of interest. The retenton times were obtained from spiked Milli-Q water and

TABLE IV
RECOVERY DATA FOR SIBLEY RAIN WATER, IN ppm (mg/l) AND %

Acid	*Sibley water (mg/l $\pm$ S.D., n=5)*	*Spike level 1*		*Spike level 2*	
		Recovery		*Recovery*	
		mg/l $\pm$ S.D. (n=5)	*%*	*mg/l $\pm$ S.D. (n=5)*	*%*
Fluoride	–	0.025 $\pm$ 0.001	100	0.106 $\pm$ 0.003	106
Acetate	–	0.246 $\pm$ 0.013	98	1.033 $\pm$ 0.020	103
Propionate	–	0.241 $\pm$ 0.004	96	1.056 $\pm$ 0.031	106
Glycolate	–	0.122 $\pm$ 0.003	98	0.490 $\pm$ 0.013	98
Butyrate	–	0.240 $\pm$ 0.005	96	1.027 $\pm$ 0.039	103
Formate	–	0.124 $\pm$ 0.009	99	0.470 $\pm$ 0.060	94
Methanesulfonate	–	0.130 $\pm$ 0.005	104	0.538 $\pm$ 0.021	108
Chloride	0.090 $\pm$ 0.003	0.147 $\pm$ 0.009	106	0.294 $\pm$ 0.008	105
Nitrite	0.005[a]	0.031 $\pm$ 0.004	104	0.111 $\pm$ 0.004	106
Succinate	–	0.259 $\pm$ 0.011	104	1.045 $\pm$ 0.030	104
Sulfate	1.140 $\pm$ 0.039	1.246 $\pm$ 0.032	101	1.504 $\pm$ 0.025	99
Oxalate	–	0.126 $\pm$ 0.001	101	0.541 $\pm$ 0.013	108
Phosphate, PO_4–P	–	0.053 $\pm$ 0.002	106	0.209 $\pm$ 0.005	104
Nitrate, NO_3–N	0.155 $\pm$ 0.011	0.174 $\pm$ 0.001	103	0.211 $\pm$ 0.004	100
Citrate	–	0.125 $\pm$ 0.004	100	0.531 $\pm$ 0.015	106

[a] Estimated from small peaks.

TABLE V

RECOVERY DATA FOR A EULERIAN QUALITY CONTROL SAMPLE, EU-ANI-1, IN ppm (mg/l) AND %

Acid	*EU-ANI-1*		*Spiked EU-ANI-1*	
	Found (mg/l ± S.D., n=5)	*Design value (mg/l)*	*Recovery*	
			(mg/l ± S.D., n=5)	*%*
Fluoride	–	–	0.055 ± 0.004	110
Acetate	–	–	0.481 ± 0.052	96
Propionate	–	–	0.529 ± 0.053	106
Glycolate	–	–	0.258 ± 0.025	103
Butyrate	–	–	0.511 ± 0.035	102
Formate	–	–	0.234 ± 0.019	94
Methanesulfonate	–	–	0.252 ± 0.009	101
Chloride	0.025 ± 0.001	0.02	0.131 ± 0.008	105
Nitrite	–	–	0.052 ± 0.001	104
Succinate	–	–	0.992 ± 0.021	99
Sulfate	0.063 ± 0.012	0.056	0.311 ± 0.006	99
Oxalate	–	–	0.250 ± 0.006	100
Phosphate, PO_4–P	–	–	0.099 ± 0.003	99
Nitrate, NO_3–N	0.029 ± 0.001	0.03	0.060 ± 0.001	95
Citrate	–	–	0.250 ± 0.005	100

TABLE VI

RECOVERY DATA FOR A BURLINGTON RAIN-SNOW SAMPLE, IN ppm (mg/l) AND %

Acid	*Burlington rain–snow, found (mg/l ± S.D., n=5)*	*Spiked Burlington rain–snow*		
		Expected (mg/l)	*Recovered*	
			mg/l ± S.D., n=5	*%*
Fluoride	0.064 ± 0.019	0.158	0.157 ± 0.040	99
Acetate	0.856 ± 0.006	1.770	1.691 ± 0.011	96
Propionate	–	1.000	1.055 ± 0.076	106
Glycolate	0.529 ± 0.006	0.976	0.944 ± 0.048	97
Butyrate	–	1.000	1.037 ± 0.077	104
Formate	4.716 ± 0.336	4.705	4.871 ± 0.133	104
Methanesulfonate	–	0.500	0.512 ± 0.106	102
Chloride	0.910 ± 0.023	1.019	1.043 ± 0.045	102
Nitrite	0.013 ± 0.003	0.112	0.104 ± 0.008	93
Succinate	0.227 ± 0.024	1.204	1.263 ± 0.035	105
Sulfate	8.302 ± 0.066	7.971	8.267 ± 0.048	104
Oxalate	0.280 ± 0.010	0.752	0.724 ± 0.025	96
Phosphate, PO_4–P	0.333 ± 0.016	0.500	0.533 ± 0.040	107
Nitrate, NO_3–N	1.249 ± 0.031	1.196	1.229 ± 0.032	103
Citrate	0.060 ± 0.003	0.554	0.511 ± 0.020	92

TABLE VII
REPRODUCIBILITY OF RETENTION TIMES

Acid	*Concentration level 1*		*Concentration level 2*	
	Spike 1 (ppm)	*Average retention time ± S.D. (min)*[a]	*Spike 2 (ppm)*	*Average retention time ± S.D. (min)*[b]
Fluoride	0.10	2.51 ± 0.02	0.025	2.51 ± 0.03
Acetate	1.00	2.99 ± 0.03	0.25	2.99 ± 0.03
Propionate	1.00	3.16 ± 0.03	0.25	3.16 ± 0.03
Glycolate	0.50	3.29 ± 0.03	0.125	3.29 ± 0.04
Butyrate	1.00	3.43 ± 0.03	0.25	3.43 ± 0.03
Formate	0.50	4.32 ± 0.04	0.125	4.32 ± 0.04
Methanesulfonate	0.50	5.67 ± 0.05	0.125	5.69 ± 0.05
Chloride	0.20	6.90 ± 0.04	0.05	6.92 ± 0.03
Nitrite	0.10	7.25 ± 0.03	0.025	7.27 ± 0.03
Succinate	1.00	7.63 ± 0.03	0.25	7.64 ± 0.03
Sulfate	0.50	7.81 ± 0.03	0.125	7.82 ± 0.03
Oxalate	0.50	8.04 ± 0.03	0.125	8.06 ± 0.03
Phosphate	0.20	8.64 ± 0.05	0.05	8.65 ± 0.05
Nitrate	0.072	8.85 ± 0.05	0.018	8.87 ± 0.06
Citrate	0.50	9.37 ± 0.04	0.125	9.41 ± 0.08

[a] Average of 15 retention times (9 of spiked Milli-Q water and 6 of spiked natural water), over a 15-day perod.

[b] Average of 12 retention times (6 of spiked Milli-Q water and 6 of spiked natural water), over a 15-day period.

spiked natural water samples over a 15-day period. As can be seen, the precision for all analytes is quite good (very small standard deviation) and the calculations indicate that the largest coefficient of variation is only 1.1%.

As with sensitivity, the detection limit has been abundantly written about in the literature. For example, it is often defined in terms of signal-to-noise ratio[22], standard deviation of short-term noise[24], or standard deviation of several replicate analyses of a sample containing a low level of analyte, usually 1–10 times the concentration of the estimated detection limit[27,28]. The detection limits listed in Table VIII were obtained following the last type of definition; they were equated to twice the standard deviation

TABLE VIII
DETECTION LIMIT OF THE ACIDS, IN ppm (mg/l)

Acid	*Detection limit (ppm)*	*Acid*	*Detection limit (ppm)*
Fluoride	0.010	Nitrite	0.011
Acetate	0.059	Succinate	0.080
Propionate	0.057	Sulfate	0.040
Glycolate	0.040	Oxalate	0.067
Butyrate	0.074	Phosphate	0.028
Formate	0.040	Nitrate	0.012
Methanesulfonate	0.053	Citrate	0.071
Chloride	0.022		

of eight replicate analyses of a sample containing analytes with concentration equal to eight times the estimated detection limit. The latter was estimated as the concentration giving a signal equal to 2–3 times that of the noise. It is expected that these detection limits (Table VIII) would be lower if a concentrator or a better detector featuring the temperature-controlled multielectrode flow cell are used. It was unnecessary to study the upper limits as the precipitation samples do not contain very high concentrations of these acids to surpass the column capacity.

Preservation

Tables IV–VI indicate two things: (1) the two unpreserved samples do not contain any organic acids as opposed to the preserved one (Table VI), which seems to confirm the need to preserve samples[1,3] if organics are to be accountable; and (2) F^- analyses by AS4- or AS4A-CO_3^{2-}/HCO_3^- on the two unpreserved samples (or possibly on any unpreserved sample after 62 days storage in a 4°C room[1]) would be free from acetate–formate interference.

When $CHCl_3$ is used, the analysis for Cl^- may be affected[3]. Furthermore, although $CHCl_3$ prolongs the holding time or may prevent some preferential conversion between organic acids[29], it may produce some decomposition products; for example, an extra peak between nitrite (peak 9) and succinate (peak 10) appeared in the preserved standard (Fig. 3), but not in the preserved Milli-Q water.

While it is best to analyse immediately after sample collection, such practice is hardly a practical reality. Some form of preservation is required. A detailed study using $CHCl_3$ or some other biocides seems necessary.

CONCLUSION

A method has been developed for routine analysis of major inorganic and organic acids as well as several other acids commonly cited in the literature on precipitation samples.

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