

Note

Determination of organic and inorganic acid species in the atmosphere and in rain-water by ion chromatography

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The determination of organic acids, in addition to the other inorganic acid species more commonly measured, is of great importance for a complete understanding of the nature of acidity in the dry (sedimentation of particles and gases) and wet (rain and snow) deposition. Organic acids constitute approximately 30% of the ether-extractable compounds in the atmospheric aerosol¹. Recently, organic compounds have been found in rain and snow samples and one study estimated that organic acids contributed 16–35% of the free acidity². Formic and acetic acids have been found to be the most abundant of atmospheric organic acids and they are major sources of free acidity in precipitation in remote regions or in unpolluted areas³. These acids probably originate from both anthropogenic and biogenic sources as well as in photochemical oxidation of organic compounds in the atmosphere. Motor exhausts were suggested as one major source of atmospheric organic acids. Organic acids together with other carbonyl compounds (aldehydes and ketones) are produced in ozone–olefin reactions and also formed in free radical oxidations during the degradation of hydrocarbons. Formic acids is an interesting minor product of the photochemistry, but apparently does not play an important part in the atmospheric chemistry.

Only a limited number of sampling and analytical methods have been suggested for determination of organic acids, and these are based on the use of spectrochemical techniques⁴, liquid chromatography⁵ and gas chromatography (GC). Ion chromatography has also been used for measuring formic and acetic acids in the atmosphere, but the sampling method with water film is unable to distinguish between the free acids and other gaseous compounds that hydrolyze or oxidize to the acids upon collection or analysis. Air moves in laminar flow past the film of water and the atmospheric constituents are collected by diffusion⁶. A capillary GC method has been applied to the measurement of organic acids (C₁–C₁₀) in the atmosphere and motor exhausts, and involves their esterification to *p*-bromophenacyl esters⁷. The methods cited are expensive or impractical for routine monitoring and furthermore they do not detect other gaseous compounds that are of particular interest for acid deposition.

This paper presents an accurate and sensitive method for the simultaneous determination of volatile organic acids and gaseous inorganic species in the atmo-

sphere and rain-water. Air samples were collected on potassium hydroxide impregnated cellulose filters, and aqueous extracts were directly analyzed by ion chromatography. The rain samples were analyzed with the same procedure.

EXPERIMENTAL

The experiments were performed at a rural site located on the Area della Ricerca of C.N.R. about 30 km east of Rome. The monitoring station operates within the ambit of the EMEP project (Co-operative program for monitoring and evaluation of the long range transmission of air pollutants in Europe).

Apparatus

The sampling assembly consisted of two filters which were set in series in a multiple filter holder for the collection of particles and of gaseous species. Air was drawn through the filters with a membrane pump (Gast) at a flow-rate of 12.5 l/min; the flow was kept constant with a flow controller and was continually recorded. The atmospheric sampling was carried out on a 24-h basis for an air volume of 18 m³. The pump, the flow controller and the recorder were placed in an air-conditioned van. The filter holder was protected from rain and sunlight by an inverted plastic funnel. It consists of a polyethylene tube, the outside wall of which was covered with aluminium foil.

To separate particulate and gaseous phases, a cellulose triacetate or PTFE membrane filter was used together with an alkaline filter. The cellulose triacetate and PTFE filters were considered to be the most suitable for the preservation of the sample composition since they show the lowest degree of ambient gas retention. Volatile organic acids and all gaseous inorganic acids were collected on the second filter which was impregnated with potassium hydroxide. Along with organic acids, chloride, nitrite, nitrate and sulphate, were found in the extracts from the impregnated filters. The chloride is due to environmental hydrochloric acid and hydrochloric acid liberated from chlorides by reaction with strong acids deposited on the particulate filter. The nitrite is due to nitrous acid present in the atmosphere. The nitrate may be due to gaseous nitric acid and to volatilization of ammonium nitrate which may dissociate into ammonia and nitric acid specially at higher sampling temperatures. In the determination of NO₂⁻ and NO₃⁻, nitrogen dioxide might interfere, since a small fraction of it absorbed by the potassium hydroxide impregnated filter will be converted into nitrite and nitrate. Such interferences can reasonably be considered to be negligible in rural areas. Sulphate is formed by oxidation of sulphur dioxide in solution.

The precipitation samples were collected on a daily basis using a wet/dry collector which exposes separate containers during wet (rain) and dry (sedimentation of particles) periods. Additional details of collector characteristics are given elsewhere⁸.

Preparation of filters

Whatman 41 cellulose filters (diameter 47 mm) were rinsed in aqueous 1 M potassium hydroxide solution and dried under vacuum over silica gel. The filters were stored in polyethylene containers in the dryer. To avoid contamination, the assembly of the filters must be made in a short time. After the sampling the filters were placed in polyethylene containers and stored in the dryer.

Metrical or PTFE membrane filters (diameters 47 mm; Gelman GA-4, 0.8 μm or TF1000, 1 μm) were used to collect particulate matter. Particulate water-soluble chloride, nitrate, sulphate and hydronium can be determined.

Analytical procedures

The impregnated filters used for collection of the gaseous compounds were each extracted with 10 ml of deionized water in a 15-ml glass bottle. The bottle was shaken for a few minutes.

The filter extracts and precipitation samples were analyzed for organic acids and for Cl^- , NO_2^- , NO_3^- and SO_4^{2-} . Two procedures were applied: ion chromatography (IC) for the simultaneous determination of inorganic anions and C_1 – C_2 organic acids in a single injection, and ion exclusion chromatography (IEC) coupled with IC for the determination of all volatile organic acids⁹. The former procedure gives a good separation of inorganic anions but it does not adequately resolve all organic acids that can be subject to matrix interferences. The IC method does not detect organic acids longer than C_2 that should be present in the atmosphere. A typical chromatogram showing the separation of HCOO^- , CH_3COO^- , Cl^- , NO_2^- , NO_3^- and SO_4^{2-} is presented in Fig. 1. The use of IEC eliminates matrix interferences and provides a simple and an effective way to separate all organic acids. Fig. 2 shows a typical chromatogram of C_1 – C_3 acids in the atmosphere.

The conditions for IC analyses were: separator system, two guard columns containing HPIC-AG-3 (50 \times 4 mm I.D.) and an analytical column containing HPIC-AS3 (250 \times 4 mm I.D.); an anion fibre suppressor AFS-1; eluent, 2 mM sodium bicarbonate–1.67 mM sodium carbonate; flow-rate, 0.50 ml/min; regenerant of AFS-1, 0.025 N sulphuric acid, flow rate, 1.50 ml/min; injection volume, 50 μl .

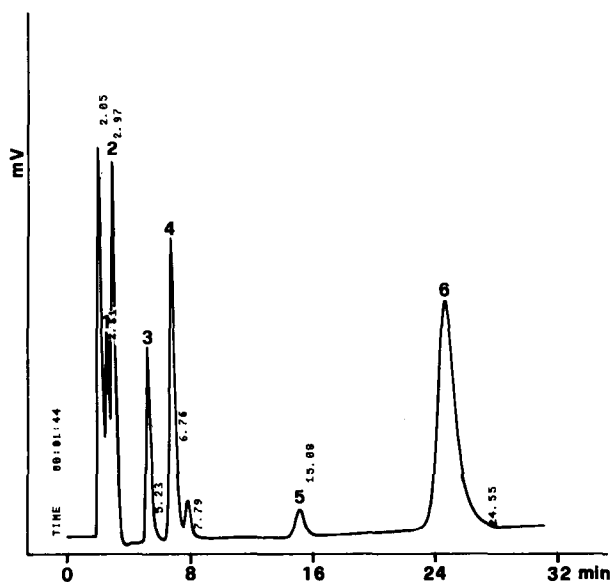


Fig. 1. Typical chromatogram of an extract from a potassium hydroxide-impregnated filter. Peaks: 1 = CH_3COO^- (3.6 ppm); 2 = HCOO^- (1.9 ppm); 3 = Cl^- (1.1 ppm); 4 = NO_2^- (3.0 ppm); 5 = NO_3^- (1.2 ppm); 6 = SO_4^{2-} (10.4 ppm).

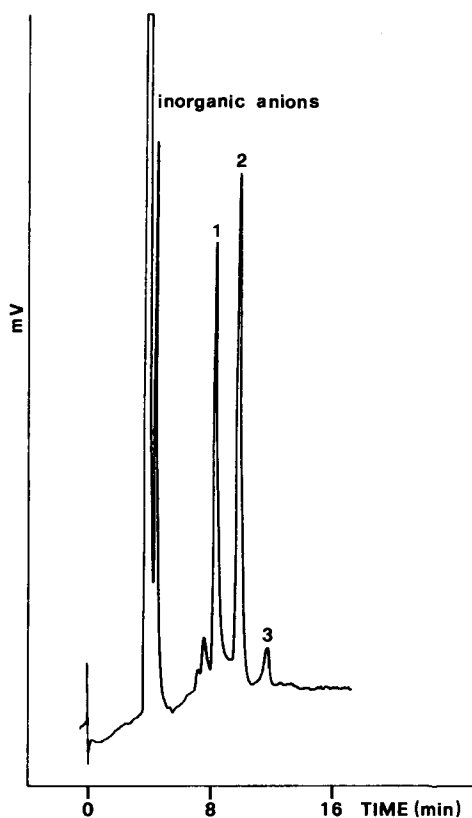


Fig. 2. Typical chromatogram of volatile organic acids in the atmosphere and unresolved inorganic anions. Peaks: 1 = HCOO^- (3.8 ppm); 2 = CH_3COO^- (12.6 ppm); 3 = $\text{CH}_3\text{CH}_2\text{COO}^-$ (0.9 ppm).

The conditions for IEC analyses were: separator column contains HPICE - AS2 (250 \times 4 mm I.D.); anion fibre suppressor AFS-2; eluent, 1 mM TDFHA (tridecafluoroheptanoic acid, Fluka) + 1% isopropanol for high-performance liquid chromatography; flow-rate 0.8 ml/min; regenerant for AFS-2, 10 mM TBA-OH (40% tetrabutylammonium hydroxide in water; Aldrich Chemie); flow-rate 1.8 ml/min; injection volume 50 μl . The separator columns and the anion fibre suppressors were obtained from Dionex^{10,11}.

A Dionex ion chromatograph (QIC Ionchrom Analyzer) equipped with a conductivity detector was used.

The organic acids in the samples were identified and quantitated by comparison with standards. The detection limits for formic and acetic acids for an air samples of volume 1 m^3 were 0.05 and 0.15 μg respectively. These detection limits could be lowered by a particular care in storing and handling of filters in order to avoid any contamination.

Upon collection, the pH of precipitation samples was determined using an Orion Model 601 pH meter.

TABLE I

BLANK VALUES (μg per filter) FOR C_1 , C_2 ORGANIC ACIDS ON CELLULOSE FILTERS

	C_1	C_2
Mean	0.36	0.56
S.D.	0.85	0.87
N	10	10

RESULTS AND DISCUSSION

In order to examine the efficiency of the potassium hydroxide impregnated filters to collect volatile organic acids, air samples were drawn through three filters in series assembled in a combined filter holder. The first filter was used to collect particulate matter, the second and third were impregnated filters.

The first and third showed very low concentrations of particulate organic acids, whereas the second filter adsorbed almost all of the organic acids. The mean concentrations of C_1 and C_2 organic acids on the first filter were less than 2% of the total recovered acids. The percentage of organic acids trapped on the third filter was less than 3%. Recoveries of C_1 and C_2 acids from the second potassium hydroxide impregnated filters were 96–98% after 24 h (18 m^3), 94–96% after 32 h (24 m^3) and 90–92% after 56 h (42 m^3). The recoveries of inorganic anions from the potassium hydroxide impregnated filters were 95–98% at 24 h¹².

These results indicate first that the C_1 , C_2 and C_3 acids and inorganic species in the atmosphere are trapped mostly on a single potassium hydroxide impregnated filter after 24 h of sampling. This finding is consistent with what has been observed by other authors¹³. Secondly, the formic and acetic acids in the atmosphere are mostly present in the vapour phase. However, the vapour phase to particulate ratio of organic acids is dependent on the atmospheric conditions.

Blanks were run together with the samples. Blank analyses of the filters are

TABLE II

CONCENTRATIONS ($\mu\text{g}/\text{m}^3$) OF HCOO^- , CH_3COO^- , $\text{CH}_3\text{CH}_2\text{COO}^-$, Cl^- , NO_2^- , NO_3^- AND SO_2 IN THE ATMOSPHERESampling time: 24 h. Air volume sampled: 18 m^3 . N.D. = not determinable.

Sampling day	HCOO^-	CH_3COO^-	$\text{CH}_3\text{CH}_2\text{COO}^-$	Cl^-	NO_2^-	NO_3^-	SO_2
9/1/86	0.80	3.34	0.15	0.45	1.71	0.52	2.72
15/1	1.03	3.62	0.10	0.49	1.12	0.37	3.25
16/1	1.16	4.08	0.15	0.60	1.12	0.59	4.24
20/1	0.80	3.34	0.05	0.55	0.91	0.35	1.29
21/1	1.00	2.98	0.05	0.72	2.07	0.53	3.79
22/1	0.34	—	N.D.	0.60	1.14	0.41	3.60
23/1	0.46	0.44	N.D.	0.61	0.69	0.33	4.65
29/1	0.73	3.90	N.D.	0.42	0.79	0.38	2.21
30/1	0.74	2.01	N.D.	0.34	0.29	0.28	2.29
31/1	0.02	0.33	N.D.	0.78	0.35	0.57	2.10

TABLE III

THE CONCENTRATIONS (mg/l) OF HCOO^- , CH_3COO^- , Cl^- , NO_3^- and SO_4^{2-} IN RAIN SAMPLES

Sampling day	Sample size (mm)	pH	HCOO^-	CH_3COO^-	Cl^-	NO_3^-	SO_4^{2-}
28/1/86	16	5.6	0.10	N.D.	0.35	0.28	0.58
29/1	20	5.2	0.20	N.D.	1.62	0.42	0.87
30/1	24	6.6	0.52	2.31	7.20	1.17	23.35
31/1	14	5.9	0.22	2.08	2.63	0.62	4.40
3/2	94	6.0	0.23	N.D.	4.46	1.25	3.05
12/2	90	4.2	0.25	1.14	3.05	2.56	4.05
17/2	40	4.8	0.28	N.D.	0.13	0.64	0.57
18/2	3	4.8	1.11	1.48	6.07	2.50	4.49
19/2	20	3.5	0.30	1.27	12.10	2.43	4.24
24/2	13	5.1	0.32	N.D.	2.95	1.39	1.37

presented in Table I as the mean, standard deviation (S.D.) and number of filters tested, N . The mean blank values have been subtracted from the values reported for C_1 and C_2 acids.

Table II shows the concentrations of formic, acetic and propionic acids and inorganic anions: formic and acetic acids were determined by means of IC and IEC, propionic acid by IEC. Acetic acid was the most abundant organic species, followed by formic acid. The concentrations of formic and acetic acids ranged from 0.1 to 1.8 $\mu\text{g}/\text{m}^3$ and from 0.2 to 5.5 $\mu\text{g}/\text{m}^3$ respectively. Propionic acid was found in some samples in very low concentrations. The results reveal that SO_2 is the prevalent inorganic species. The data compare well with those obtained at other unpolluted sites⁶.

Table III shows data for rain samples analyzed for SO_4^{2-} , NO_3^- , Cl^- , CH_3COO^- and HCOO^- with the IC method described. The measurements of pH and the analyses were carried out immediately after sample collection in order to minimize the organic acidity changes. The results indicate a temporal variability and are not very representative of the average composition of the acidic component of precipitation because they coverably a brief period.

CONCLUSIONS

This study represents the first attempt to characterize the volatile organic acids in the atmosphere in Italy. We haven't enough data to assign a specific source to these compounds and to estimate the RCOO^- (CH_3COO^- and HCOO^-) contribution to the acidity of precipitations. Future studies will focus on the temporal variation and the source of the organic acids in air and rain.

The analytical procedure developed is suitable for determining low concentrations in rural and remote sites, and for the study of the long range transportation and transformation of these species. The simplicity of the sampling equipment makes this method useful also for monitoring stations manned by non-technical personnel.

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