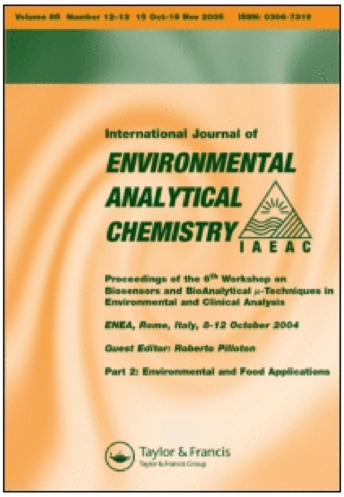

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Capillary GC Determination of Short-Chain Dicarboxylic Acids in Rain, Fog, and Mist†

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A capillary GC and GC-MS method, employing dibutyl esters is described for determining short-chain dicarboxylic acids in rain, fog and mist samples collected in the Los Angeles area. Approximately twenty dicarboxylic acids (C_2–C_{10}) were identified in the water samples, including *cis* (maleic) and *trans* (fumaric) unsaturated, saturated, normal, branched and aromatic. Oxalic acid is the dominant acid, followed by succinic and malonic acids. The total concentrations measured are 2.9–51 μM, 64–66 μM and 12 μM for rain, fog and mist samples, respectively. These diacids are probably produced by photooxidation of anthropogenic and possibly biogenic organic compounds in the atmosphere.

INTRODUCTION

In a previous paper,[1] we detected aliphatic α,ω-dicarboxylic acids (C_4–C_{12}) among ca. 300 organic compounds in Los Angeles rainwater. These compounds are probably washed out from the atmosphere during wet precipitation, as C_3–C_{10} diacids have been reported in aerosols.[2,3,4] These C_3, C_4 and C_5 atmospheric diacids

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and their methyl forms are considered to be produced by photoxidation of cyclic olefins such as cyclohexene and cyclopentene, which are emitted to the atmosphere from gasoline engines.[2] These dicarboxylic acids were analyzed by GC after organic solvent extraction and derivatization to dimethyl esters[1,2,3] or TMS esters.[4] Oxalic acid, however, cannot be separated effectively from samples by solvent extraction techniques and/or may be lost during the subsequent derivatization steps. This is probable because the boiling point of dimethyl oxalic acid is low (164.5°C). The presence of oxalic acid in stratispheric aerosols and rainwater collected in Colorado was detected by Norton[5] using ion chromatography. However, other diacids were not reported in this study.

We describe here a simple and sensitive analytical method for determining short-chain diacids ($\geqq C_2$) in atmospheric water samples as butyl esters using a capillary GC-FID and GC-MS for detection. Samples were concentrated to dryness under basic condition and were derivatized to dibutyl esters. A capillary GC method for the determination of short-chain monocarboxylic acids (C_1–C_7) in rainwater will be presented elsewhere.[6]

EXPERIMENTAL

Sample collection

Rainwater samples were collected on the roof of the Geology Building (UCLA campus) and were stored at 4°C after preservation with $HgCl_2$.[1] Fog water samples were collected on Henninger Flats, San Gabriel Mountains, north of Pasadena, California, using a fog water collector,[7] and were stored at −20°C prior to analysis. The mist water sample was collected at the same location, using a polyethylene sheet[7] and then frozen.

Reagents

Short-chain dicarboxylic acids (C_2–C_{10}), including saturated and unsaturated, normal, branched acids and phthalic acid were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin), and Sigma Chemical Co. (St. Louis, Missouri).

Pure water was obtained by oxidizing impurities in distilled water with $KMnO_4$/KOH, followed by distillation in glass. 1 N KOH solution was prepared after KOH pellets were heated at 500°C for three hours. Fourteen percent BF_3 in butanol was purchased from Applied Science (State College, Pennsylvania). Trifluoroacetic acid anhydride (TFAA) was purchased from Eastman Kodak (Rochester, New York) and Aldrich (Milwaukee, Wisconsin). Methylene chloride and hexane were distilled in an all-glass apparatus prior to use.

Procedure

An approximately 50 ml sample of rainwater was taken in a 200 ml round-bottom flask and concentrated to ca. 2 ml using a rotary evaporator at 50°C under vacuum. The concentrates were transferred into a 10 ml pear-shaped flask and the pH was adjusted to 8.0–9.0 by adding 1 N KOH solution. Fog or mist samples (1 or 2 ml) were taken in a 10 ml pear-shaped flask and were pH-adjusted directly without preconcentration. The samples were then completely dried using the rotary evaporator followed by a nitrogen flow in the pear-shaped flask, to which 0.4 ml of 14% BF_3/n-butanol was added. The flask was then stoppered with a groud-glass stopper and clamp.

The closed flask was first ultra-sonicated for two minutes and then placed in a water bath (100°C) for 30 minutes to form the dibutyl ester derivatives. The reaction mixture was treated with 0.4 ml of TFAA at room temperature for 10 minutes,[8] and washed three times with H_2O (5 ml) in a 20 ml test tube with a Teflon lined cap after adding 5 ml hexane. The organic (hexane) layer was taken to dryness and treated again with 0.2 ml of TFAA in a 7 ml vial with Teflon-lined cap for 10 minutes at 80°C. Excess TFAA was evaporated under N_2 flow. The dibutyl esters in the vial were dissolved in 2 ml CH_2Cl_2, washed with H_2O (2 ml × 3), and volume-adjusted to 50–100 μl in hexane in a 2 ml vial. One μl was then injected into the gas chromatograph.

GC and GC-MS analysis

Dicarboxylic acid dibutyl esters were analyzed on a Hewlett-Packard Model 5840 GC equipped with a FID on a 0.25 mm × 30 m DB-5 fused silica capillary column. A Grob injector was used in a splitless mode. The injection temperature was 250°C. The column temperature was programmed from 40°C (6 min) to 295°C at a rate of 6°C/minute. Peak areas were calculated with a Hewlett-Packard integrator (18850A GC terminal). A Finnigan model 4000 GC-MS with an INCOS 2300 data system was used with the same column described above to obtain the mass spectra of the dibutyl esters. During the GC/MS measurement, the column temperature was programmed from 35°C (6 min) to 280°C at 4°C/min and then from 280°C to 310°C at 2°C/min. E.I. mass spectra were scanned every two seconds.

RESULTS AND DISCUSSION

Derivatization of dibutyl esters

Esterification steps for dicarboxylic acids were examined. Twenty μl of C_2–C_4 diacid standard mixture (in water/methanol, 0.01 μM each) was taken in a 10 ml pear-shaped flask with 10 μl 1 N KOH solution. The diacids were dried under N_2 flow and the butyl esters were synthesized by a procedure described in the Experimental Section. The reaction time was increased from 15 to 60 minutes. The dibutyl esters were diluted in 1 ml hexane and 1 μl was injected into the GC. Figure 1 shows the relative peak area for the esters of C_2–C_4 diacids on gas chromatograms. The yields of the esters reach a plateau in 15 minutes. Thirty minutes was chosen as an optimum esterification time for this procedure.

Gas chromatographic separation and mass spectra of diacid butyl esters

Figure 2 gives the gas chromatogram of authentic dicarboxylic acid dibutyl esters. C_2 to C_{10} α,ω-diacid dibutyl esters are well separated except for C_8, which overlapped with pthalic acid dibutyl esters. Figure 3 shows examples of mass spectra of dibutyl esters for dicarboxylic acids in a fog sample. Their spectra were identical with those of authentic standards. Fragmentation patterns are different depending upon the chain length and structure. Oxalic acid ester gives a base peak at m/e 57, which corresponds to the fragments of

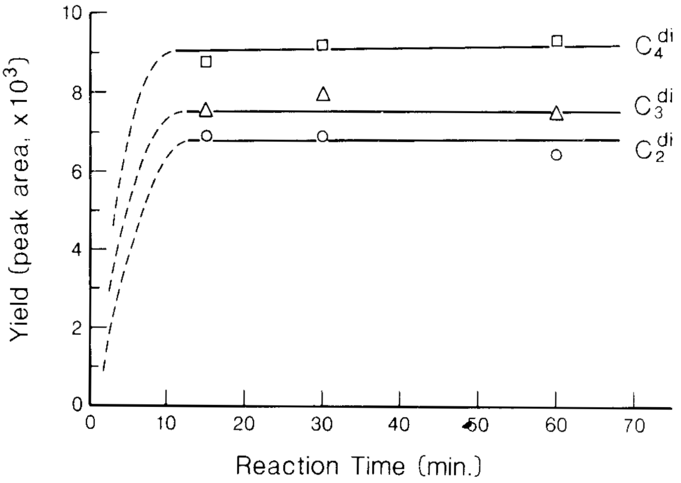

FIGURE 1 Yield of dibutyl esters of C_2–C_4 dicarboxylic acids presented as relative peak area. One μl was injected into the GC from 1 ml of the ester solution in hexane.

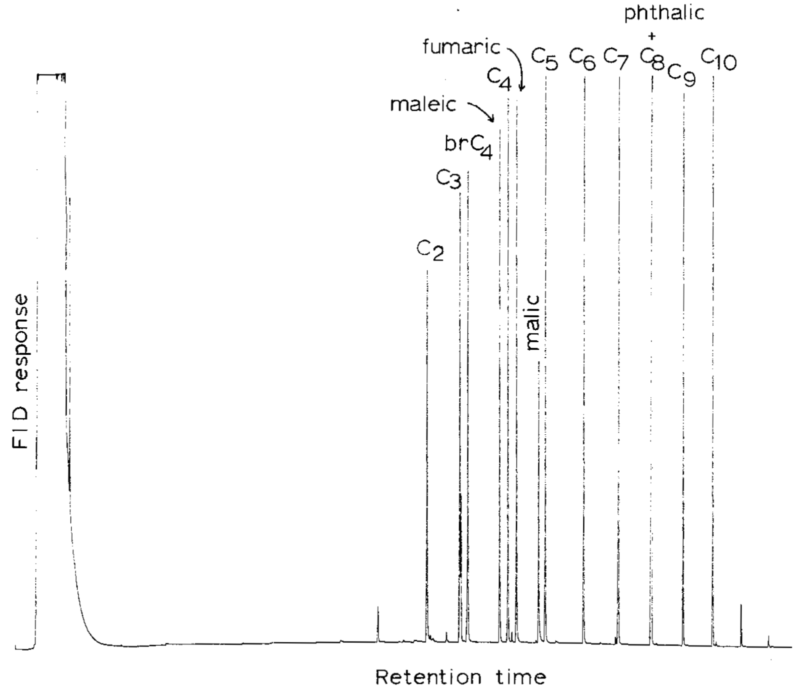

FIGURE 2 Gas chromatogram of dibutyl esters of authentic dicarboxylic acids. One μl was injected from 2 ml of the ester solution in hexane (0.1 n moles/μl each).

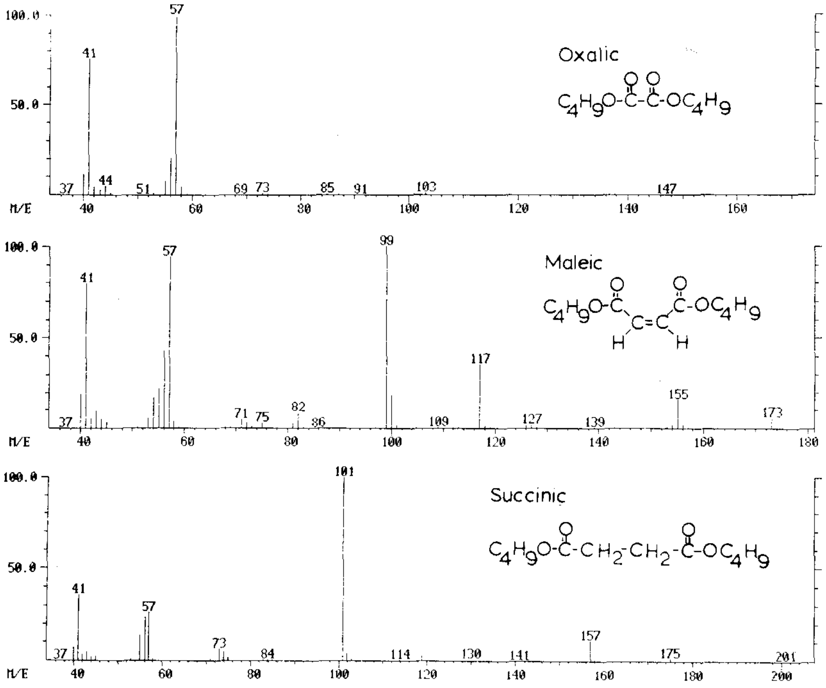

FIGURE 3 Mass spectra of dibutyl esters for oxalic, maleic and succinic acids in a fog sample.

$C_4H_9^+$. Maleic acid dibutyl ester presents a base peak at m/e 99 together with characteristic fragment ion peaks at m/e 117, 155 and 173. Succinic acid dibutyl ester gives a base peak at m/e 101 ($C_4H_9OCO^+$), as well as a characteristic peak at m/e 157 ($C_4H_9OCOCH_2CH_2CO^+$). Table I gives mass spectral data of 24 authentic dicarboxylic acid dibutyl esters.

Recoveries of diacids—Spiked experiment

Recoveries were examined using an 11/1/83 rainwater sample. Fifty ml of the rainwater was taken in a 200 ml flask to which 0, 4, 8 and 12 μl of C_2–C_4 diacid standards (10 n mole/μl each) were spiked. The spiked samples were analyzed for diacid measurements. Figure 4 gives the results of the spiked experiments. The concentrations of the

TABLE I

Mass spectral data of dicarboxylic acid dibutyl esters.

Scan no.	Compounds		M.W. of dibutyl ester	Base peak (m/e)	Major fragmentation peaks in order (m/e)
970	C_2	Oxalic	202	57	41, 56, 40
1049	C_3	Malonic	216	57	41, 105, 56, 87, 143, 161
1068	br C_4	Methylmalonic	230	57	41, 101, 56, 119, 74, 157, 175
1068	br C_5	2,2-Dimethylsuccinic	244	41	88, 57, 59, 115, 171, 70, 143, 189
1149	u C_4	Maleic	228	99	57, 41, 56, 117, 100, 155, 173
1165	C_4	Succinic	230	101	41, 57, 56, 55, 157, 73
1182	br C_5	Methylsuccinic	244	115	41, 57, 43, 41, 56, 87, 171, 73, 189
1185	u C_4	Fumaric	228	56	41, 117, 115, 57, 99, 55, 173, 82
1187	br C_6	2,2-Dimethylsuccinic	258	41	59, 43, 129, 101, 57, 56, 87, 185
1203	br, u–C_5	Methylmaleic	242	113	41, 57, 40, 56, 112, 169, 85, 44, 68, 131, 187
1217	br C_6	Meso-2,3-dimethylsuccinic	258	129	41, 57, 56, 101, 74, 55, 185, 87
1239	OH–C_4	Malic	246	41	89, 57, 44, 56, 71, 117, 145, 99, 155, 173
1256	C_5	Glutaric	244	115	41, 42, 87, 57, 56, 171, 86, 142
1262	br C_6	DL or meso 2,4-dimethylglutaric	258	41	143, 56, 115, 57, 69, 74, 199, 114, 170
1278	br C_6	3-Methylglutaric	258	129	41, 56, 55, 100, 101, 185, 87, 69, 156
1285	br C_6	DL or meso 2,4-dimethylglutaric	258	41	143, 56, 115, 57, 69, 74, 199, 114, 170
1294	br C_7	3,3-Dimethylglutaric	272	143	41, 101, 43, 56, 57, 59, 55, 83, 199, 157, 170, 114, 115, 73, 127
1347	C_6	Adipic acid	258	41	129, 55, 185, 56, 111, 57, 87, 43, 101, 100, 83, 156, 143, 73
1375	br C_7	3-methyladipic	272	41	125, 199, 143, 57, 56, 101, 55, 69, 43, 73, 157, 97, 115, 170
1430	C_7	Pimelic	272	41	125, 55, 56, 57, 143, 101, 199, 69
1507	C_8	Phthalic	278	149	41, 57, 150, 76, 65, 104, 205, 223
1509	C_8	Suberic	286	41	56, 55, 213, 56, 157, 115, 83, 69, 138, 111
1585	C_9	Azelaic	300	41	55, 56, 57, 171, 227, 83, 152, 97, 97, 129, 120, 111, 185
1557	C_{10}	Sebacic	314	41	56, 55, 57, 185, 241, 43, 69, 97, 125, 143

br: branched chain; u: unsaturated; OH: hydroxy.

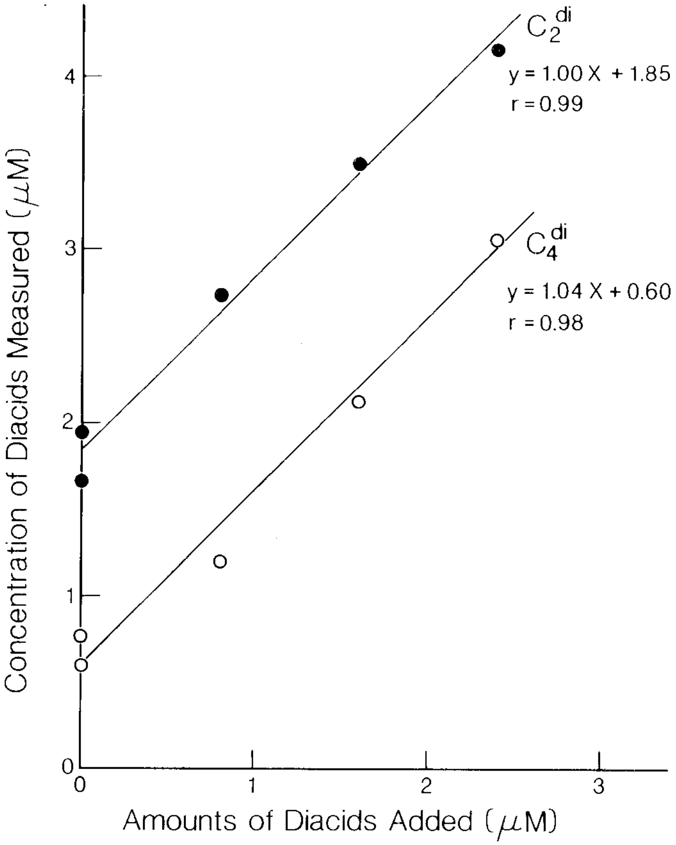

FIGURE 4 A spiked experiment. C_2–C_4 authentic standards (0–2.4 μM) were spiked into 50 ml 11/1/83 rain.

diacids in the spiked rain samples linearly increase with the amounts of the diacids spiked (the slopes are 0.98–0.99). Recoveries of C_2–C_4 diacids at 0.8, 1.6 and 2.4 μM of spiked acids were 65–118%, 91–106% and 97–99%, respectively.

Reproducibility and blank

Table II gives triplicate analyses of 50 ml 11/11–12/83 rain sample, as well as the procedural blank. The relative standard deviations for

TABLE II

Triplicate analyses of 50 ml rain samples (collected 11/11–12, 1983) and procedural blank.

Diacids	Concentration (μM) No. 1	No. 2	No. 3	Mean	RSD[a] (%)	Procedural blank (μM)
Oxalic	1.87	1.84	2.02	1.91	4	0.01
Malonic	0.53	0.46	0.63	0.54	13	n.d.[b]
Methylmalonic	0.23	0.16	0.20	0.20	14	n.d.
Maleic	0.33	0.30	0.33	0.32	4	n.d.
Succinic	0.70	0.74	0.71	0.72	2	n.d.
Methylsuccinic	0.22	0.20	0.20	0.21	4	n.d.
Fumaric	0.17	0.15	0.19	0.17	10	n.d.
Glutaric	0.20	0.18	0.18	0.19	5	n.d.
Adipic	0.13	0.09	0.13	0.12	16	n.d.
Phthalic	0.23	0.23	0.21	0.22	4	n.d.
Azelaic	0.01	0.01	0.01	0.01	0	n.d.

[a] Relative standard deviation.
[b] Not detected.

diacid analysis are within ±16%. The procedural blank was run using 50 ml water. No contamination appeared in the blank except for oxalic acid, where the concentration was less than 1% of that of the rain sample. These results indicate that the present analytical method is reliable.

Distribution of dicarboxylic acids in rain, fog and mist

The following dicarboxylic acids were identified or tentatively identified in the water samples studied, based on comparison of retention times and mass fragmentation patterns of authentic standards: C_2–C_{10} straight-chain saturated α,ω-diacids, C_4–C_7 branched chain saturated α,ω-diacids, C_4–C_6 *cis*- and *trans*-unsaturated α,ω-diacids, and phthalic acids. Table III lists these acids. Malonic, maleic, methylmaleic, fumaric, dimethylmaleic and some branched chain acids have not been reported in atmospheric water samples.

Figure 5 shows a reconstructed ion chromatogram (RIC) of dibutyl esters of dicarboxylic acids in a fog sample. Table IV gives concentrations of diacids in rain, fog and mist samples. In each

TABLE III

Dicarboxylic acids identified in rain, fog and mist samples.

Compounds	Formula
Straight-chain acids	
Oxalic	$C_2H_2O_4$
Malonic	$C_3H_4O_4$
Maleic	$C_4H_4O_4$
Succinic	$C_4H_6O_4$
Fumaric	$C_4H_4O_4$
Glutaric	$C_5H_8O_4$
Adipic	$C_6H_{10}O_4$
Pimelic	$C_7H_{12}O_4$
Suberic	$C_8H_{14}O_4$
Azelaic	$C_9H_{16}O_4$
Sebacic	$C_{10}H_{18}O_4$
Branched-chain acids	
Methylmalonic	$C_4H_6O_4$
Methylsuccinic	$C_5H_8O_4$
Methylmaleic	$C_5H_6O_4$
2,3-Dimethylmaleic[a]	$C_6H_8O_4$
2-Methylglutaric[a]	$C_6H_{10}O_4$
3-Methylglutaric	$C_6H_{10}O_4$
2-Methyladipic	$C_7H_{12}O_4$
Aromatic acids	
Phthalic	$C_8H_6O_4$
3- and 4-Methylphthalic[a]	$C_9H_8O_4$
Dimethylphthalic[a]	$C_{10}H_{10}O_4$

[a] Tentatively identified by mass fragmentation patterns similar to homologous series, for example, methylmaleic acid and dimethylmaleic acid.

sample, oxalic acid was the most abundant dicarboxylic acid followed by succinic acid.

Oxalic acid has been identified in the same samples by HPLC technique which has been developed for α-ketoacids determination in our laboratory.[9] However, the concentration of oxalic acid in this study is 18–48% higher than those obtained by the HPLC technique. There was no difference in measuring authentic oxalic acid between the HPLC and GC techniques. We found that two procedural

TABLE IV

Concentrations of dicarboxylic acids in rain, fog and mist water samples collected in the Los Angeles area (μM).

	Rain				Fog		Mist
Collection date and time	4/28–29/83 1230–0600	8/18/83 1030–1130	9/20/83 1530–1630	11/1/83 1015–1800	6/11/83 0440–0640	6/11/83 0849–1030	6/11/83 1515–1550
volume analyzed (ml)	50	5	5	50	1	1	2
precipitation (mm/h)	0.82	0.15	0.46	1.38			
Oxalic	1.27	25.3	28.3	1.85	25.1	20.0	5.95
Malonic	0.23	4.73	5.55	0.42	8.81	6.86	1.05
Methylmalonic	0.02	0.85	0.76	0.04	0.51	0.73	n.d.
Maleic	0.10	1.77	1.37	0.19	2.83	5.19	1.14
Succinic	0.43	5.36	7.34	0.64	9.73	10.7	1.14
Methylsuccinic	0.14	1.73	1.78	0.16	2.54	3.27	0.48
Fumaric	0.07	2.08	0.73	0.27	1.01	1.41	0.20
Methylmaleic	0.07	0.74	0.62	0.13	3.00	4.46	0.76
Glutaric	0.22	2.38	1.81	0.19	3.63	3.59	0.61
Adipic	0.05	1.22	0.46	0.05	2.57	3.54	n.d.
Pimelic	0.01	n.d.	0.16	n.d.	n.d.	0.18	n.d.
Phthalic	0.22	1.24	1.87	0.23	3.32	4.61	0.85
Azelaic	0.03	n.d.	0.19	0.03	1.43	1.34	n.d.
Total	2.86	47.4	50.94	4.20	64.48	65.88	12.18

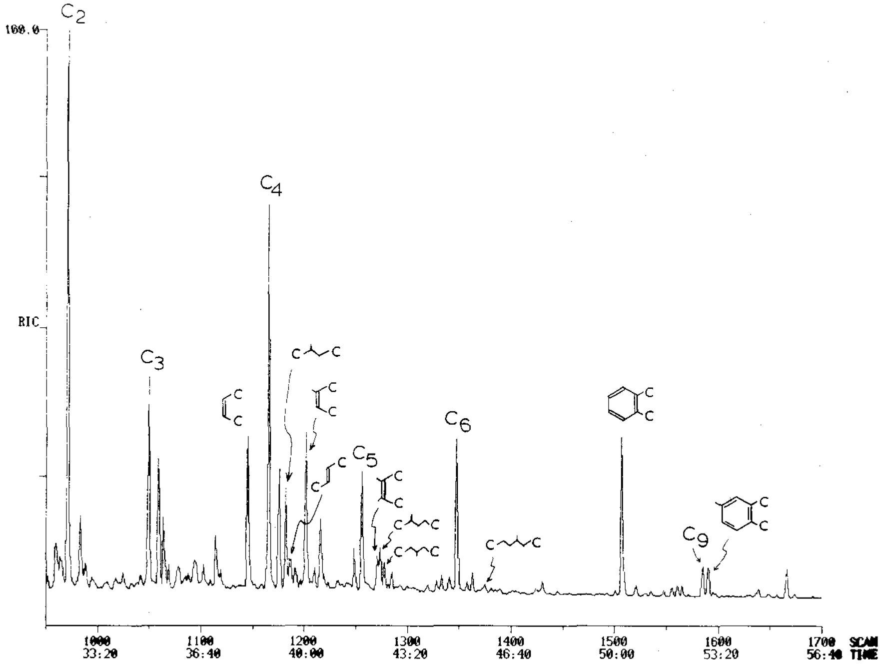

FIGURE 5 Reconstructed ion chromatogram (RIC) of dicarboxylic acid dibutyl esters from a fog sample.

factors are associated with the difference in the concentration of actual samples. First, oxalic acid was found to be present partly in the CH_2Cl_2-extractable fraction (about 20%). This form of oxalic acid may exist as esters or other combined forms in the water samples which are not effectively detected by the HPLC method. Secondly, we found that during the present procedure, formation of oxalic acid from glyoxylic acid had occurred. By using authentic glyoxylic acid, it is estimated that approximately 20% of glyoxylic acid in samples are converted to oxalic acid. Based on the concentration of glyoxylic acid detected in the samples[9] and the conversion rate, contribution of this conversion product to the oxalic acid concentration was calculated as follows: 9–24% for fog and mist samples and less than 3% for rain samples.

C_4–C_7 normal- and branched-chain diacids are probably photooxidation products of cyclic olefines in the atmosphere.[2] Interestingly, *cis*-unsaturated diacids (maleic and methyl maleic) are present in abundance, as well as *trans*-unsaturated (fumaric). These *cis*-unsaturated diacids are not generally present in organisms, which suggests that they are anthropogenic and/or photooxidation products. Benzene and toluene may be the possible precursors. These aromatic hydrocarbons are found in the atmosphere[10] and primarily arise from anthropogenic sources, including gasoline and diesel oils, automobiles, solvent uses, chemical industries, forest fires, etc.[11]

C_9 α,ω-diacid, which is present in low abundance, may primarily originate from biogenic Δ9 unsaturated fatty acids by photooxidation in the atmosphere.[1]

Average concentrations of phthalic acids in the rainwater samples are fairly high (0.89 μM) compared to the measurements of extractable phthalates (average 3 μg/l), from rainwater collected in 1981–1982 at the same location.[1] This indicates that phthalic acids detected in this study are mostly in the free form. They may be formed either by hydrolysis of phthalates or photo-oxidation of naphthalenes. Naphthalenes were detected as major PAHs in the rainwater samples.[12]

Conclusions

A capillary GC method was established to determine short-chain dicarboxylic acids (C_2–C_{10}) in rain, fog and mist water samples. By using this method, ca. 20 diacids were identified; including normal, branched, saturated, unsaturated and aromatic. Four compounds (fumaric acid, maleic acid and its methyl and dimethyl derivatives) have not been reported previously in the atmospheric samples. The distribution of the diacids suggests that most of these acids are produced by oxidation of anthropogenic and possibly some biogenic organic compounds emitted in the atmosphere.

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