Determination of malic acid and other C₄ dicarboxylic acids in atmospheric aerosol samples

Andreas Röhr1,2, Gerhard Lammel 1,3,*

1 Max-Planck-Institut für Meteorologie, Bundesstraße 55, D-20146 Hamburg, Germany
2 Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Germany
3 Meteorologisches Institut, Universität Hamburg, Germany

Received 2 January 2001; received in revised form 7 September 2001; accepted 17 October 2001

Abstract

An ion chromatographic method was developed which is able to separate five unsubstituted and hydroxy C₄ dicarboxylic acids, succinic, malic, tartaric, maleic and fumaric acid, besides the other unsubstituted C₂–C₅ dicarboxylic acids, oxalic, malonic and glutaric acids, as well as inorganic ions in samples extracted from atmospheric particulate matter. By the application of this method it was found for both rural and urban sites and for various types of air masses that in the summer-time malic acid is the most prominent C₄ diacid (64 ng m⁻³ by average), exceeding succinic acid concentration (28 ng m⁻³ by average) considerably. In winter-time considerably less, a factor of 4–15, C₄ acids occurred and succinic acid was more concentrated than malic acid. Tartaric, fumaric and maleic acids were less concentrated (5.1, 5.0 and 4.5 ng m⁻³ by average, respectively). Tartaric acid was observed for the first time in ambient air.

The results indicate that in particular anthropogenic sources are important for the precursors of succinic, maleic and fumaric acids. Biogenic sources seem to influence the occurrence of malic acid significantly. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atmospheric aerosol; Dicarboxylic acids; Malic acid; Particulate organic matter

1. Introduction

Being late products in the photochemistry of aliphatic and aromatic hydrocarbons and due to the low vapour pressure being almost entirely partitioning to the particulate phase, the dicarboxylic acids constitute an important fraction of the water soluble part of particulate organic matter (POM) in atmospheric aerosol particles at remote (Kawamura and Usukura, 1993; Limbeck and Puxbaum, 1999), rural (Röhr and Lammel, 2001) and urban (Sempéré and Kawamura, 1994; Limbeck and Puxbaum, 1999; Röhr and Lammel, 2001) sites. Mostly the unsubstituted dicarboxylic acids have been addressed by determinations based on gas chromatographic and ion chromatographic methods (Dabek-Zlotorzynska and McGrath, 2000), whereas no adequate method for the determination of the hydroxy acids is at hand.

Oxalic acid is by far the most abundant dicarboxylic acid in ambient air. Little is known so far on the photochemical degradation paths of biogenic and anthropogenic volatile organic compounds: based on laboratory studies (Dumdei et al., 1988; Kleindienst et al., 1999), it is likely that C₄ degradation products are important intermediates in the atmospheric chemistry of simple anthropogenic aromatic hydrocarbons. Their incomplete oxidation would lead to substituted and unsubstituted intermediates, saturated and unsaturated C₄ diacids. Most biogenic volatile organic compounds are considered not to form POM. The most significant terrestrial biospheric precursors of POM are certainly the terpenes with trees
as the predominant emitting species (Griffin et al., 1999). C₄ fragments could be formed in terpene photochemistry, but no low-molecular (<C₆) products could be identified so far.

The aim of the present study was to develop a reliable chromatographic method by which the most important low-molecular unsubstituted and substituted C₂–C₅ dicarboxylic acids could be separated from each other in aqueous extracts of atmospheric aerosol samples and also quantitated. It covered the acids succinic (butanedioic), malic (monohydroxybutanedioic), tartaric (2,3-dihydroxybutanedioic), maleic (cis-butenedioic), fumaric (trans-butenedioic), oxalic (ethanedioic), malonic (propanedioic) and glutaric acid (pentanedioic acid). Ion chromatography was preferred, because the sample preparation procedure does not need any organic solvent, possible analyte losses in extraction steps would be minimized and the target ions can be determined together with the major inorganic ions present (Cl⁻, NO₃⁻, SO₄²⁻) in one separation.

2. Experimental

The standard mixtures were aqueous solutions (Seralpur) of the carboxylic acids. These reagents were used as received (p.a.; Merck). The eluents were composed of aqueous solutions of inorganic salts and methanol (HPLC gradient grade; Malinckrodt Baker).

2.1. Separation

For analyses we used an ion chromatography system consisting of guard and separation columns (Dionex, AG11-HC and AS11-HC, 250 x 4.6 mm ID, both maintained at constant temperature, 30°C), anion suppression system (Dionex, ASRS-ultra) and conductivity detector. Several eluent compositions containing sodium hydroxide and methanol were tested in eluent gradient programmes. A methanol-free gradient (henceforth called eluent A), with increasing NaOH (Merck, p.a.; 0.5–16.2 mmol l⁻¹ during minutes 5–35 of the separation; modified but similar as used earlier; Kerminen et al., 1999), proved adequate for the determination of oxalic, glutaric, pyruvic, and maleic acid. The corresponding peaks did not show interferences with other anions including the inorganic ions Cl⁻, NO₃⁻ and SO₄²⁻ (Fig. 1(a)). However, the malonic and succinic acids coelute with tartaric and maleic acid anions, respectively, such that the peaks represent the sums of two acids each. A gradient programme sweeping from 0.5 to 18 mmol l⁻¹ NaOH and from 0% to 20% methanol (eluent B; cf. Table 1) proved to meet the aim best. The addition of methanol to the eluent allows for the satisfactory separation of succinic and maleic acids and the separation of the peaks which correspond to the malic and tartaric acid anions (Fig. 1(b)) together with other mono- and di-carboxylic acid anions (and some inorganic anions). The latter pair of diacid anions remain incompletely separated but their presence and relative importance can be judged from the chromatograms. With regard to the application of the method to atmospheric aerosol samples, this limitation appeared
to be acceptable as in all samples we analysed it was found that the ratio of the peak heights was >5 and the concentration of tartaric acid was below detection limit (see below).

Species recovery based on multiple standard mixture application on filter membranes were 103.7 ± 5.3%, 100.4 ± 4.0%, 100.2 ± 7.0%, 100.9 ± 6.0% and 105.1 ± 3.9% for the C$_4$ DCAs succinic, malic, tartaric, maleic and fumaric acids, respectively, at concentrations corresponding to atmospheric concentrations of ca. 10 ng m$^{-2}$, and better at higher concentrations. Recovery upon addition to the matrix were determined for succinic acid using standard reference material (‘urban aerosol’ SRM1649a, NIST) and found to be 104%.

**Precision of analyses:** Based on multiple standard mixture determination the uncertainty related to the recommended chromatographic determination is estimated to be <4% for malic, <6% for succinic, maleic and glutaric, <10% for malonic and tartaric, <15% for oxalic acid (in the 1–10 ng l$^{-1}$ range, based on 2$sigma$). Peak identification was based on a match of retention times between standard samples and was confirmed by addition of authentic standard substances to selected samples.

Detection limits achieved corresponded to 10–50 ng for the acids investigated. They were determined as the mean ±3 S.D. of the field blank value or, if higher, the level corresponding to S/N = 10 in chromatograms.

**2.2. Application to samples of atmospheric origin: sampling and sample treatment**

Table 1

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Vol% H$_2$O</th>
<th>Vol% NaOH (5 mmol l$^{-1}$)</th>
<th>Vol% NaOH (60 mmol l$^{-1}$)</th>
<th>Vol% CH$_3$OH</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>Isocratic phase</td>
</tr>
<tr>
<td>8</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>Start gradient</td>
</tr>
<tr>
<td>18</td>
<td>65</td>
<td>0</td>
<td>15</td>
<td>20</td>
<td>Maximum CH$_3$OH achieved</td>
</tr>
<tr>
<td>28</td>
<td>50</td>
<td>0</td>
<td>30</td>
<td>20</td>
<td>Maximum NaOH achieved</td>
</tr>
<tr>
<td>38</td>
<td>70</td>
<td>0</td>
<td>30</td>
<td>0</td>
<td>Stop gradient</td>
</tr>
<tr>
<td>38.1</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>Return to starting conditions</td>
</tr>
<tr>
<td>45</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>End of run</td>
</tr>
</tbody>
</table>

Samples were taken from five inland sites in Germany: three rural sites during summer-time (Falkenberg, 52°13’N/14°08’E, July–August 1998) and winter-time (Merseburg, 51°21’N/11°58’E, and Eningen, 48°24’N/9°15’E, November–December 1999 and March 2000, respectively) and two urban sites in the summer-time (Eichstädt at the rim of the Berlin conurbation, 52°42’N/13°08’E, and Leipzig, 51°19’N/12°25’E, July–August 1998 and July–August 1999, respectively). During the summer campaigns the weather was almost dry with very few light precipitation events. During the winter-time campaigns rain and snow fall occurred frequently. The most abundant C$_4$ diacids were malic and succinic acid with 42 and 20 ng m$^{-2}$, by average, respectively. The concentrations were significantly above detection limit in all except one sample. Tartaric, fumaric and maleic acids, were less concentrated (5.1, 5.0

2.3. Application to samples of atmospheric origin: data analysis

We classified the samples according to the air mass origin and trajectory based on 72 h near-ground back-trajectories analysed with state-of-the-art weather forecast models of German Weather Service (DWD; Europa-Modell) and National Oceanic and Atmospheric Administration (NOAA; HYSPLIT). The samples were grouped into two categories: Marine air masses which underwent only little influence from the continent and, in particular, had not passed industrialized regions (northern sector, henceforth called “marine”) and marine air masses which experienced continental influence during rapid transport from the Atlantic over parts of western Europe or when residing over western, southern or central Europe for considerable time (“marine-continental”). Samples associated with trajectories covering more than one sector are considered ambiguous and not attributed to one of the classes.

3. Results and discussion

The most abundant C$_4$ diacids were malic and succinic acid with 42 and 20 ng m$^{-2}$, by average, respectively. The concentrations were significantly above detection limit in all except one sample. Tartaric, fumaric and maleic acids, were less concentrated (5.1, 5.0
and 4.5 ng m$^{-3}$, by average, respectively) and found below detection limits in 33%, 53% and 51%, respectively, of all analysed samples. To our knowledge this is the first observation of tartaric acid in the atmosphere. The 5 C$_4$ diacids determined accounted for 0.37% of the total suspended particulate matter and for 28% of the low-molecular weight diacids: In the same samples the concentrations of oxalic, malonic and glutaric acids were 188, 40 and 12 ng m$^{-3}$. Obviously higher concentrations of the C$_4$ diacids were observed at the urban sites with highest ratios for succinic and maleic acids, $c_\text{urban}/c_\text{rural} = 2$.

The analysis of the samples grouped according to air mass class and season (Table 2) shows that malic and succinic acids are enriched in air when transported over the European continent: $c_\text{marine-continental}/c_\text{marine} = 38/12 \approx 3$ for malic acid and and $c_\text{marine-continental}/c_\text{marine} = 18/8.8 \approx 2$ for succinic acid. Summer-time concentrations are much higher than winter-time ($c_\text{summer}/c_\text{winter} = 15$ and 4, respectively). The latter ratios reflect the seasonalities of emission patterns and photo-chemical activity. Of course, the concentration ranges at different sites vary. This variability is small, however, when data sets from the same season are considered (Table 2).

What are the sources of the acids, primary emissions or emissions of photochemical precursors? Primary sources are unknown. In principle, any emission of volatile organic compounds (VOC) must be considered as a potential precursor emission. Road traffic is the most prominent emitter of non-methane volatile organic compounds in Europe while nature ranks second (EEA – European Environment Agency, 1998). Biogenic emissions are much stronger in summer than in winter in the cool and cold temperate climate zones in Europe and in the neighbouring ocean areas (Simpson et al., 1994) in the literature to compare with: 40 ng m$^{-3}$ of oxyacids are formed.

Table 2

<p>| C$_4$ acid concentrations (ng m$^{-3}$) and concentration ratios malic/succinic (mol/mol) for all samples, site types (rural and urban), individual sites, seasons and classes of air mass origin |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Succinic acid (ng m$^{-3}$)</th>
<th>Malic acid (ng m$^{-3}$)</th>
<th>Tartaric acid (ng m$^{-3}$)</th>
<th>Maleic acid (ng m$^{-3}$)</th>
<th>Fumaric acid (ng m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>20 (1.5–70)</td>
<td>42 (0.5–194)</td>
<td>5.1 (&lt;0.2–40)</td>
<td>4.5 (&lt;1.2–13)</td>
</tr>
<tr>
<td>Site type</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rural</td>
<td>14 (&lt;2.5–70)</td>
<td>34 (&lt;2.5–194)</td>
<td>4.0 (&lt;0.2–23)</td>
<td>3.2 (&lt;0.2–13)</td>
</tr>
<tr>
<td>Urban</td>
<td>30 (&lt;9.1–68)</td>
<td>54 (&lt;7.3–129)</td>
<td>6.7 (&lt;1.0–40)</td>
<td>6.2 (&lt;1.2–14)</td>
</tr>
<tr>
<td>Season</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter</td>
<td>7.2 (&lt;2.5–25)</td>
<td>4.4 (&lt;2.5–19)</td>
<td>1.1 (&lt;0.2–6.54)</td>
<td>1.1 (&lt;0.2–4.5)</td>
</tr>
<tr>
<td>Summer</td>
<td>28 (&lt;7.2–70)</td>
<td>64 (&lt;7.3–194)</td>
<td>5.8 (&lt;1.0–40)</td>
<td>4.9 (&lt;1.2–14)</td>
</tr>
<tr>
<td>Air mass class</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marine</td>
<td>8.8 (3.4–14)</td>
<td>12 (1.4–20)</td>
<td>0.6 (&lt;1.6–0.8)</td>
<td>1.8 (&lt;1.8–2.3)</td>
</tr>
<tr>
<td>Marine-continental</td>
<td>18 (&lt;5.2–61)</td>
<td>38 (&lt;5.2–129)</td>
<td>4.6 (&lt;0.2–23)</td>
<td>3.9 (&lt;0.2–14)</td>
</tr>
</tbody>
</table>

Concentration data listed as: time-weighted means (minimum–maximum). Concentration ratios listed as: Time-weighted means ± standard deviation. $n$ is the number of samples, $t$ is the total sampling time (h). For derivation of means of data subsets which include values below the detection limit, these were set equal to half the detection limit.
maleic acid and 170 ng m\(^{-3}\) of succinic acid have been determined in Tokyo air (by average, 4 samples) using a gas-chromatographic method after derivatization of the dried samples to the butyl esters and organic extraction (\(n\)-hexane). By this method the hydroxyl groups are not derivatized and the recovery of polar substances should be limited due to significant partitioning to the polar phase (which was not quantified by Sempère and Kawamura, 1994). Therefore, a systematic underestimation of hydroxy acids could result.

We observed maleic and fumaric acids at 3.2 and 4.8 ng m\(^{-3}\), respectively, at the rural sites and 6.4 and 5.5 ng m\(^{-3}\), respectively, at the urban sites (mean values, cf. Table 2). Higher concentrations were reported from Tokyo, 28 and 17 ng m\(^{-3}\) (Sempère and Kawamura, 1994). Anthropogenic sources, namely toluene emissions (from vehicle exhaust, besides other), can be considered as a significant source of maleic and fumaric acids: Laboratory experiments (Dumdei et al., 1988; Bierbach et al., 1994; Kleindienst et al., 1999) showed that toluene photochemistry leads to \(\text{cis}\)-butenedial as a major product which is then oxidized to maleic acid. (In these experiments, the anhydride of maleic acid was observed only, which supposedly resulted from the relatively dry conditions applied in these experiments.) Through isomerization fumaric acid might be formed in a subsequent step and, as it is the thermodynamically favoured isomer and if no other paths of formation are possible, the ratio of fumaric acid over maleic acid has increased from the sources the concentrations have decreased and at rural sites, more distant to the sources the concentrations are higher, and the ratio of fumaric acid over maleic acid has increased (\(c_{\text{fumaric acid}}/c_{\text{maleic acid}} = 1.5\)) in the aged air mass. Much more laboratory and field research is needed to understand the atmospheric chemistry which leads to the C\(_4\) diacids.

**Acknowledgements**

We thank Christine Stahlschmidt for help during the analyses. This research received financial support from BMBF in the frame of the German Aerosol Research Focus, AFS.

**References**


