Comparison of methods for the quantification of carbonate carbon in atmospheric PM10 aerosol samples

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ABSTRACT

Carbonate carbon (CC) represents an important fraction of atmospheric PM10 along with organic carbon (OC) and elemental carbon (EC), if specific sources (e.g. street abrasion, construction sites, desert dust) contribute to its composition. However, analytical methods for an easy and unambiguous determination of CC in atmospheric aerosols collected on filter matrices are scarce. We propose here a method for the determination of CC based on a heating pretreatment of the sample to remove OC and EC, followed by a total carbon determination to measure CC. This procedure is used for the correction of EC also determined by a heating pretreatment (Cachier, H., Bremond, M.P., Buat-Ménard, P., 1989. Determination of atmospheric soot carbon with a simple thermal method. Tellus 41B, 379–390) but without previous HCl fumigation, as proposed. Comparison of the carbon remaining after the proposed thermal treatment at 460 °C for 60 min in an oxygen stream showed good correlation for the carbonate carbon derived by calculation from the ionic balance for ambient air and street dust samples. Using the “three step” combustion technique it is now possible to determine OC, EC and CC by the use of a TC analyser in the concentration range of 2–200 μg carbon per sample aliquot, with good precision (3–5% RSD for TC and 5–10% for CC) and accuracy. In ambient air samples from a sampling site in Vienna with elevated PM10 levels (“Liesing”) CC values as high as 25% of TC and 27% CO32– of total PM10 mass were observed.

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1. Introduction

Atmospheric particulate aerosol chemistry studies generally comprise the measurement of elemental carbon (EC) and organic carbon (OC). A further constituent of carbonaceous material, carbonate carbon (CC) or alternatively described as inorganic carbon, is often not considered. The reason for this may be found in the fact that in PM2.5 atmospheric aerosol CC levels are generally low (e.g. Ten Brink et al., 2004; Watson et al., 2005; Huang et al., 2006), and hence often negligible. Furthermore, analytical methods for an easy and unambiguous determination of CC in atmospheric aerosols collected on filter matrices are scarce. Some thermal–optical methods (TOM) determine carbonate carbon, along with different organic fractions and EC. The results obtained depend on the operational parameters, in particular on the temperature program; or on the use of a sample pretreatment with acid to eliminate CC prior to thermal analysis (e.g. Chow et al., 1993, 2001; Pio et al., 1994; Birch and Cary, 1996). In some methods CC is possibly not separated from the EC fraction (e.g. VDI 2465, 1999; Castro et al., 1999; Hueglin et al., 2005). The problem of a potential interference of CC with the signal of EC or OC has been mentioned but not assessed in several EC/OC intercomparison studies (e.g. Schmid et al., 2001; Currie et al., 2002; Schauer et al., 2003; Hitzenberger et al., 2006).

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Carbonate-containing mineral dust is often associated with calcium and magnesium, both of which can be found nearly exclusively in the coarse fraction of the aerosol (PM10–PM2.5), as has been demonstrated by size distribution measurements of mineral constituents (e.g. Puxbaum and Woppenka, 1984; Krivácsy and Molnár, 1998; Chow et al., 2004). Thus, the fraction of CC found in PM10 particulate matter may well not be negligible, especially if high concentrations of mineral dust, either natural (natural erosion, sand storms, e.g. Arimoto et al., 2004) or originating from street abrasion or construction sites (e.g. Chow et al., 2003) are present.

In Austria “AQUELLA” – the Austrian Project on Aerosol Source Analysis – has started to derive information about aerosol sources contributing to rural and urban PM10 aerosol. Originally, a combined acid/thermal treatment was used to derive EC and OC concentrations (Cachier et al., 1989). This method involves a pretreatment of the aerosol samples with HCl fumes to eliminate any contribution of CC to the EC signal. It is possible to determine the CO₂ evolved during this acid treatment directly (Chow et al., 2003). Similarly, NIOSH, in method 5040 (NIOSH, 1999), recommends fumigation of the aerosol samples with HCl prior to thermal–optical analysis. The difference in the TC result for an acidified and an untreated sample aliquot should give an estimation of carbonate carbon (\( TC_{\text{acid treat}} - TC_{\text{neutral}} \)). Though there may be changes in the appearance of the carbon profile, the EC peak itself should not be affected significantly. However, preliminary tests in our laboratory showed that prior fumigation with HCl can lead to intense charring phenomena in ambient aerosol samples during TOM in an oxidizing atmosphere. Hence we conclude that there may also be an effect on the EC determination developed by Cachier et al. (1989), when samples are fumigated with HCl prior to the thermal pretreatment.

The \( CO₂ \) which evolves due to the acid treatment is measured directly, salts of volatile organic acids can contribute to the carbonate reading, and will then be missed in the organic fraction when a subsequent quantification by TOM is performed (Chow et al., 1993). Nevertheless many TOM procedures neglect the CC portion, which can then be found in one of the operationally defined OC or EC fractions. Therefore we developed another method of sample pretreatment for the correction of EC, without using HCl. As the TOM-plots for PM10 samples show well defined (though overlapping) peaks for EC and CC, it was felt that a simple oxidation step at a temperature corresponding to the minimum between the two peaks might allow all but the CC to be removed. This pretreatment is followed by a fast high-temperature thermal decomposition of the remaining carbonate in oxygen, making use of quantification by on-line non-dispersive IR (NDIR) measurement of the evolved \( CO₂ \). This idea has been investigated using particulate samples collected on filters, known to contain quite high proportions of carbonate.

2. Experimental

2.1. Samples

PM10 atmospheric aerosol samples from the urban site “Liesing” in Vienna, Austria, were used for the determination of CC. The site is adjacent to a gritted parking lot; furthermore a “do it yourself” store and a “ready-mix” concrete plant are in the vicinity, thus elevated levels of carbonate carbon were expected. The samples were collected on a daily basis (0–24 h) with a DIGITEL DA80H High Volume sampler equipped with a PM10 inlet. The sampling rate was \( 30 \text{ m}^3\text{ h}^{-1} \) (20 °C, 1013 hPa), pumped through quartz fibre filters (Pallflex QAT-UP 2500, 150 mm Ø).

Powdered calcium carbonate (Merck, p.a.) was used as the standard for carbonate carbon, and a finely powdered (<63 μm) dolomite (40% MgCO₃; 55% CaCO₃) from Inn valley near “Ortztal” received from the University of Aberdeen was used as a test material. PM10 fractions of these materials were produced in a home built device, where the standard sample is resuspended in a glass cylinder and the PM10 is collected on filters (Pallflex Tissuequartz, 47 mm Ø) situated under a PM10 sampling head (Digitel DPM10 preseparator). Soot, derived from the combustion of wood, was used to clearly identify the EC peak in the TOM-plot. Different samples of street dust were taken by sweeping parts of a street and pavement. From this material PM10 samples were obtained using a procedure similar to that described above for the standard samples (details are described in Jankowski et al., in preparation).

2.2. Weighing and sample preparation

Gravimetric analysis was performed with a microbalance (Sartorius Micro MC210P, sensitivity 1 μg) after 48 h of equilibration in a room maintained at 20 ± 1 °C and 50 ± 5% r.h. (according to EN12341, 1998). For the analysis of carbonaceous components and extractable ions, discs of 10 mm Ø were punched from the filters with a steel ring punch.

2.3. Fumigation with HCl

Concentrated hydrochloric acid (p.a., Merck, w = 37%, 50 mL) was placed in a glass Petri dish at the bottom of a desiccator. Filter discs (10 mm Ø) were supported on a clean polypropylene tray above the Petri dish and exposed to the vapours for about an hour (according to NIOSH method 5040). After acidification the tray was removed and placed in a clean hood to allow the residual acid to volatilize before the analysis.

2.4. Thermal–optical transmission method with linear temperature program (TTL)

Thermal–optical analysis was performed with a unit originally described by Puxbaum (1979) with the modification of a simultaneous laser transmission measurement (wavelength 632.8 nm) and NDIR detection of the CO₂ (Method # 9b in Schmid et al., 2001). The separation of OC and EC is possible due to the different thermal stabilities of these carbonaceous fractions. A sample disc of the quartz fibre filter (10 mm Ø) was placed in a horizontal furnace FROK 200/50/1000 (AHT Austria) at room temperature in a stream of oxygen and then heated in \( O₂ \) (4.8) to 800 °C with a linear ramp of 20° min⁻¹. A manganese oxide
catalyst heated to 800 °C converts all the carbonaceous gases to CO₂, which is measured continuously using an NDIR analyser (Maihak UNOR 6N). During the heating procedure the transmittance of a laser beam through the filter disc is recorded. The change of the transmittance gives information about charring phenomena which can lead to increased blackness of the filter, and also about the temperature range of the burn-off of the EC, allowing identification of EC in the TLT-plot.

2.5. Determination of total carbon, elemental carbon and carbonate carbon

Total carbon (TC) was determined with a combustion method described by Puxbaum and Rendl (1983), but with NDIR detection instead of a conductometric device for the CO₂ measurement. Filter discs were burned in a vertical oven at 1000 °C in an oxygen stream, and the evolved CO₂ was detected with two NDIR detectors in series (both Maihak SIFOR 200 with two different measurement ranges). Solid tartaric acid standards were used for the calibration, corresponding to 1–200 μg C.

EC was determined with a two-step combustion method based on Cachier et al. (1989). During the first step the samples were kept for 2 h at 340 °C in a muffle oven (AHT Austria, with controller RKC REX-C900) in a flow of pure oxygen (1.3 L min⁻¹, O₂ purity 4.8%) for 2 h. The purpose of this pretreatment is to oxidize organic compounds to CO₂, leaving EC on the substrate. An excess of oxygen should avoid charring phenomena. EC is then quantified in a subsequent combustion at 1000 °C as described above for TC. OC was calculated as the difference between TC and EC. The original method for the EC determination includes fumigation with HCl prior to the thermal pretreatment to exclude a positive artifact of CC in the resulting EC. If no fumigation with HCl is applied, CC is included in the EC signal.

In this work, CC was quantified with the combustion method for TC after the proposed pretreatment step.

2.6. Determination of black carbon

Black carbon (BC) was determined by the “integrating plate” method with a home made photometric device (obtained from Aerosol Research at LBL, designed by Novakov) operating according to the aethalometer principle described by Rosen et al. (1980). Since the specific attenuation cross section was not determined, a default value of 19 m² g⁻¹ was used (Hansen et al., 1984). The linear range of the BC determination is limited at approximately 18 μg BC cm⁻². Filters transported to and from the sampler, but not used for sampling, were available as field blanks. The following equation presents the relationship between black carbon and transmission: BC [μg m⁻²] = - (100/19) × ln (I/I₀).

2.7. Determination of ions

The cations Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ were determined by isocratic cation chromatography. Discs of 10 mm Ø punched from loaded filters were taken as aliquots and extracted ultrasonically in 12 mM methane sulfonic acid (MSA), which was also used as the chromatographic eluent. Filter blanks were treated in the same way as the samples. The determination was performed using a Dionex CS 12A cation-exchange column and a CG 12A guard column. The system is fitted with a CSRS Ultra II 4 mm auto-regenerated suppressor and a Dionex QIC conductivity detector with SRS controller (modified measurement setup as described by Löflund et al., 2001). Quantification was carried out using Chromeleon® 6.6 software. Field blanks were determined from blank filters taken to the sampling site and put into the sampler, but returned to the laboratory unused. The limit of detection (LOD), defined as three-fold standard deviation (3σ) of multiple injections (n = 10) of a standard at concentrations close to the lower limit of determination, are 0.010 μg mL⁻¹ for all analysed cations. Calibration was performed by the

![Fig. 1. TLT-plot of untreated (black line) and HCl fumigated (grey line) ambient PM10 sample (Vienna – Liesing).](image-url)
direct injection of aqueous standard solutions made from 1000 mg L⁻¹ parent solution (Aristar®, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺; Standard, BHD Laboratory Supplies).

The anions Cl⁻, NO₃⁻, SO₄²⁻ and (COO)₂⁻ were determined by isocratic anion chromatography. Filter discs of 10 mm Ø were taken as sample and blank aliquots and extracted ultrasonically in ultra-pure Milli-Q water. The limits of detection were 0.03 µg mL⁻¹ for chloride and oxalate; 0.02 µg mL⁻¹ for all other anions. Calibration was carried out with aqueous standard solutions made from 1000 mg L⁻¹ parent solutions (CertiPUR®, chloride, nitrate, sulfate and oxalate standard, Merck).

2.8. Measurement of pH

The aqueous solutions left after portions had been taken for the determination of anions were used for the measurement of pH-values with a Mettler Toledo MPC 227 pH/Conductivity Meter equipped with a Mettler Toledo InLab® Pure Pro electrode (pH 1–11).

3. Results and discussion

3.1. Acid treatment of PM10 on filters

The combined acid/thermal treatment for the determination of EC and OC recommends a pretreatment with gaseous HCl to remove the CC from the filters (Cachier et al., 1989), followed by a thermal pretreatment at 340 °C for 2 h in an oxygen stream and determination of the remaining carbon defined as EC. However, an investigation in our laboratory of the results for urban PM10 ambient aerosol samples analysed by TLT after fumigation with HCl compared to those for untreated samples showed big differences in the OC and apparent EC contents. A TOM-plot example is shown in Fig. 1. CC (temperature range 500–660 °C) is clearly removed from the samples after the fumigation treatment, but the area of the EC peak (temperature range 400–500 °C) is often seen to increase (up to 25%), showing a more pronounced peak for the fumigated than for the untreated samples.

The lost fraction of OC is from more volatile compounds (desorbed in the temperature range 100–250 °C). Between 250 and 400 °C, where the thermally more stable organic compounds oxidize, peak height and shape both changed. As it is sure that HCl fumigation will not produce EC in the sample, we suggest that the increased EC signal between 400 and 500 °C obtained after fumigation arises from material transformed to more thermally stable substances, may it be polymers or other charred material, which are then broken down only at high temperatures and overlap with the EC peak. Our results lead to the conclusion that the acid fumigation procedure as used in different methods (Cachier et al., 1989; NIOSH, 1999; Chow et al., 1993) leads to under- or over estimation of the OC and positive artefacts in the subsequent determination of EC.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Ambient PM10 samples [µg m⁻³]</th>
<th>Street dust samples [µg m⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n = 17</td>
<td>Range</td>
</tr>
<tr>
<td>PM10</td>
<td>50.87 ± 22.10</td>
<td>14.09–91.26</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.16 ± 0.10</td>
<td>0.05–0.39</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>2.72 ± 1.84</td>
<td>0.42–7.32</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.32 ± 0.20</td>
<td>0.07–0.73</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.76 ± 0.02</td>
<td>0.08–2.34</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4.00 ± 3.26</td>
<td>0.43–12.05</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.06 ± 0.10</td>
<td>0.01–0.41</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.68 ± 4.27</td>
<td>0.30–11.70</td>
</tr>
<tr>
<td>(COO)₂⁻</td>
<td>6.33 ± 3.39</td>
<td>1.71–13.50</td>
</tr>
<tr>
<td>Ox⁻²</td>
<td>0.31 ± 0.14</td>
<td>0.07–0.52</td>
</tr>
<tr>
<td>Ca + Mg</td>
<td>1.57 ± 1.28</td>
<td>0.17–4.76</td>
</tr>
<tr>
<td>IB</td>
<td>1.37 ± 1.18</td>
<td>0.20–4.51</td>
</tr>
</tbody>
</table>

Ca + Mg; CC calculated from Ca and Mg content; IB: CC calculated by ionic balance difference; NA: not analysed.

Table 1

Fig. 2. TLT-plot of dolomite (black line) and CaCO₃ with added soot from wood combustion (grey line).
However, TLT-plots show a relatively well defined minimum between the EC and the CC peak, which led us to experiment with potential temperature ranges where OC and EC are oxidized, while CC has not yet started to decompose. For such an investigation it was necessary to have a second method for the determination of carbonate carbon, so that the results of the thermal method could be validated. An approach based on the calculation of the ionic balance in the samples was considered.

3.2. Thermal decomposition of soot and carbonates in oxygen

Fig. 2 shows TLT-plots for a dolomite powder (Ca and Mg carbonate) and a synthetic mixture of CaCO₃ and soot, the latter obtained from an interior chimney surface. Though the minimum between the EC and CC peaks is in the temperature range of 500–530 °C in the linear temperature mode, the decomposition under static conditions might start below this temperature.

3.3. Deriving carbonate carbon from the ionic balance

The major cations in particulate matter PM10 are Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺, while the major anions are CO₃²⁻, Cl⁻, NO₃⁻, SO₄²⁻ and (COO)₂⁻ (oxalate) (e.g. Puxbaum et al., 2004), with small amounts of other organic acid anions (Limbeck and Puxbaum, 1999) and metal ions. It should be possible to dissolve components from the solid PM10 samples to construct an ionic balance of the species in solution. As all of these species except carbonate can be determined in solution by routine ion chromatography (IC), the carbonate could then be determined by calculating the difference. Acid aerosols were common some decades ago and attracted attention accordingly (e.g. Tanner et al., 1984) and can still be found in areas where ammonia release is small and insufficient to neutralise the acidity (Ziemba et al., 2007). Maritime areas in Europe have also produced PM10 low in ammonia, but Karageorgos and Rapsomanikis (2007) suggest that the free acidity is often neutralised by the calcium and magnesium minerals. In central Europe nowadays the concentration of ammonia is generally at higher levels. In the samples used for these tests free H⁺ should therefore be small as it would have been neutralised by atmospheric ammonia, or have already reacted with the carbonate. Other studies (Ocskay et al., 2006; Kocak et al., 2007) have shown that the fine fraction of the aerosol (<2 μm) is slightly acidic or neutral, while the coarse particles (2–10 μm) are alkaline. Aqueous extracts of the

Fig. 3. Correlation diagrams between CC calculated from Ca and Mg and CC calculated from the ionic balance difference for (a) ambient air samples (n = 17) (b) street dust samples (n = 8).

Fig. 4. Analysis of filter discs carrying airborne PM10, after pretreatment at different temperatures for duration of 60 min. BC was subtracted from the remaining carbon measured by combustion of the filter aliquot.
PM10 samples investigated here were in the range of 5.2 < pH < 7.5. Extracting a PM10 sample with dilute aqueous methane sulfonic acid (MSA) dissolves all of the above combinations of ions (only silicate minerals will remain undissolved), allowing the cations to be determined by ion chromatography. Extraction of another aliquot of the filter for the determination of the soluble anions is carried out using water. Carbonate cannot be determined in the aqueous extracts from the filters by the applied method because the chromatographic eluent used is a carbonate buffer. However, the other major anions can be quantified by ion chromatography and the carbonate can be derived from the ionic balance and compared with the carbonate obtained from the proposed thermal analysis method. The concentrations obtained from the IC analyses are converted to milli-equivalents, and the difference gives the estimate for carbonate in the solid sample: \( \text{CO}_3^{2-} \equiv (\text{Na}^+ + \text{NH}_4^+ + K^+ + \text{Mg}^{2+} + \text{Ca}^{2+}) - (\text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-}) \). Table 1 shows results for the ions determined by IC, as well as the CC calculated from Ca and Mg (assuming, soluble Ca and Mg are present in the form of their carbonates), and from the ionic balance difference for ambient aerosol and street dust samples.

The ratio of Mg/Ca for ambient air samples is 0.19 with a fit of \( R^2 = 0.996 \), and an increasing slope (ratio of 0.26) with a poorer fit for street dusts \( R^2 = 0.965 \). Whether these two mineral constituents exist exclusively in the form of their carbonates on the filter cannot be predicted, as they may already have reacted with ammonium nitrate or sulfate, sulfuric acid or nitric acid. Comparisons between CC calculated from Ca and Mg and the ionic balance difference are shown in Fig. 3.

The correlation between the two calculation methods is excellent for street dust \( (>0.999) \), while ambient air samples show a bigger scatter with a coefficient of determination of about 0.965. The slopes are 0.910 for ambient air samples and 1.034 for street dust samples. This suggests that in street dust samples Mg and Ca are solely in the form of their carbonates, while in ambient air samples they might already have reacted to some extent with acidic components.

### 3.4. Uncertainties in the ionic balance approach

The uncertainty in this procedure derives from other ions which have not been determined, and from measurement errors. Undetermined cations are the "main" trace metals, e.g., Zn, which, in Vienna, is typically present at well below 1% of the total cations. Undetermined anions are mainly organic acids. The main organic acid in atmospheric aerosol is oxalic acid \( (\text{e.g., Limbeck and Puxbaum, 1999}) \), which is considered for ambient air samples in the ionic balance here. Equivalent concentrations of oxalic acid constitute around 1–3% of the anions \( (\text{Puxbaum et al., 2000, 2004}) \). Further, dicarboxylic acids (pyruvic, glutaric, malonic, succinic, adipic) together make up a similar equivalent concentration to the oxalic acid \( (\text{Limbeck and Puxbaum, 1999}) \) and would be expected to be dissociated in neutral aqueous solution if they had dissolved. Similarly, major \( + (\text{COO})_2^2- \) monocarboxylic fatty acids such as palmitic and stearic acid are present in only very small amounts in these samples.

The combined RSD can be calculated as the mean measurement uncertainty according to error propagation, giving a value of 2.3% for the combined RSD for Ca and Mg and a value of 8.8% for the whole ionic balance. These RSDs can be accepted as uncertainties for the CC calculation by these methods.

### Table 2

<table>
<thead>
<tr>
<th>Ionic balance difference from Ca and Mg</th>
<th>Calculated from Ca and Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>( d )</td>
</tr>
<tr>
<td>Ambient air (n = 10)</td>
<td></td>
</tr>
<tr>
<td>450 °C</td>
<td>1.105</td>
</tr>
<tr>
<td>460 °C</td>
<td>0.958</td>
</tr>
<tr>
<td>470 °C</td>
<td>0.762</td>
</tr>
<tr>
<td>490 °C</td>
<td>0.713</td>
</tr>
<tr>
<td>530 °C</td>
<td>0.442</td>
</tr>
<tr>
<td>Street dust (n = 7)</td>
<td></td>
</tr>
<tr>
<td>450 °C</td>
<td>1.006</td>
</tr>
<tr>
<td>460 °C</td>
<td>0.955</td>
</tr>
<tr>
<td>470 °C</td>
<td>0.899</td>
</tr>
<tr>
<td>490 °C</td>
<td>0.830</td>
</tr>
<tr>
<td>530 °C</td>
<td>0.805</td>
</tr>
</tbody>
</table>

\( k \): Slope; \( d \): axis intercept; \( R^2 \): coefficient of determination.

### Fig. 5.

Comparison of measured carbonate carbon with 60 min pretreatment at 460 °C, and that calculated from the ionic balance in (a) ambient air samples \( (n = 10) \), and (b) street dust samples \( (n = 7) \).
Separation conditions between EC and CC might be found by carefully selecting an optimum combination of time and temperature. As decomposition temperatures are lower under static conditions compared to a linear ramped temperature method, the separation temperature should therefore be below 530 °C – which represents the minimum between the EC and CC peaks in the TOM-plots. The separation of EC + OC from CC with a thermal pretreatment in an oxygen stream at a constant temperature was observed in the temperature range 450–530 °C with durations of 30–150 min. The effectiveness of the separation was investigated by measuring the BC remaining on the filters, followed by the determination of the remaining total carbon. BC was subtracted from the remaining total carbon to quantify carbonate carbon. The main part of the OC + EC fraction was lost after 30 min of pretreatment. Durations of 90, 120 and 150 min of pretreatment for the test temperatures gives a maximum RSD of about 10% relative to the value for 60 min of pretreatment, including the measurement uncertainty of TC determination and thermal pretreatment. Therefore a duration of 60 min was adopted as a practical compromise for the burn-off of OC + EC to leave the CC behind on the quartz filters.

Fig. 4 shows the variation in the carbon remaining on the filter after pretreatment at 60 min, in comparison with the BC remaining, measured using the integrating plate method. This photometric method works on the assumption that only black carbon absorbs light. However, comparison of a field blank sample and the filters sampled with CaCO$_3$ or dolomite showed that these single substances, which do not contain soot, do also reduce the optical transmission. Thus we cannot exclude the possibility that alongside the black carbon and the carbonates there are other substances in the aerosol matrix which might also lower the transmission. Variation in the thickness of the carbonate layer also introduces some scatter in the BC values. Nevertheless Fig. 4 shows that black carbon was reduced to a minimum at a temperature between 460 and 490 °C while the CC left on the filter remained consistently high.

### 3.5. Thermal treatment of PM10 on filters

Separation conditions between EC and CC might be found by carefully selecting an optimum combination of time and temperature. As decomposition temperatures are lower under static conditions compared to a linear ramped temperature method, the separation temperature should therefore be below 530 °C – which represents the minimum between the EC and CC peaks in the TOM-plots. The separation of EC + OC from CC with a thermal pretreatment in an oxygen stream at a constant temperature was observed in the temperature range 450–530 °C with durations of 30–150 min. The effectiveness of the separation was investigated by measuring the BC remaining on the filters, followed by the determination of the remaining total carbon. BC was subtracted from the remaining total carbon to quantify carbonate carbon. The main part of the OC + EC fraction was lost after 30 min of pretreatment. Durations of 90, 120 and 150 min of pretreatment for the test temperatures gives a maximum RSD of about 10% relative to the value for 60 min of pretreatment, including the measurement uncertainty of TC determination and thermal pretreatment. Therefore a duration of 60 min was adopted as a practical compromise for the burn-off of OC + EC to leave the CC behind on the quartz filters.

### 3.6. Comparison of results for carbonate in airborne PM10 by thermal method and ionic balance

Table 2 shows the correlations of carbonate determined by the thermal method with different pretreatment temperatures to the values for CC calculated form Ca and Mg and the ionic balance difference. The slopes and the coefficients of determination show the best fit for Mg and the ionic balance difference. Some samples were under the limit of determination; one sample was deleted as an outlier, thus these samples were not included in the correlation.

The correlation for street dust is better, probably because the composition of the street dust is simpler, in particular, being without the large and variable proportion of ammonium nitrate and sulfate (see Fig. 5b).

Table 3 shows the results for CC obtained by the thermal method, and the ratios between the three estimation methods. The ratio of the results from the ionic balance difference and the thermal method (ratio Th/IB) shows good correlation for the majority of the samples, except when the values are under limit of determination (about 0.5 µg m$^{-3}$ for CC determination) or elevated amounts of NO$_3^-$ and SO$_4^{2-}$ are present.

### Table 3

Results for CC obtained by the thermal method, including ratios between the three estimation methods

<table>
<thead>
<tr>
<th></th>
<th>Ambient PM10 samples [µg m$^{-3}$]</th>
<th>Street dust samples [% m$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>CC Th</td>
<td>1.95 ± 1.02 0.80–4.33</td>
<td>2.30 ± 1.83 0.22–5.09</td>
</tr>
<tr>
<td>Ratio IB/Ca + Mg</td>
<td>0.87 ± 0.13 0.63–1.01</td>
<td>1.02 ± 0.02 0.99–1.04</td>
</tr>
<tr>
<td>Ratio Th/Ca + Mg</td>
<td>0.93 ± 0.23 0.47–1.23</td>
<td>1.00 ± 0.07 0.93–1.14</td>
</tr>
<tr>
<td>Ratio Th/IB</td>
<td>1.05 ± 0.15 0.75–1.22</td>
<td>0.98 ± 0.08 0.91–1.14</td>
</tr>
</tbody>
</table>

IB: CC calculated from difference of ionic balance; Ca + Mg: CC calculated from Ca and Mg; Th: CC determined by thermal pretreatment with subsequent flash combustion.

![Fig. 6](image-url) TLT-plots of evolved CO$_2$ for a standard CaCO$_3$ sample with added (a) ammonium sulfate and (b) ammonium nitrate.
3.7. Uncertainties of the thermal pretreatment for the determination of carbonate carbon

In an atmosphere of 100% pure oxygen, carbonates decompose at temperatures much higher than the burn-off of the EC. Qualitative tests, with large excesses of added ammonium nitrate and ammonium sulfate showed CO₂ release peaks in the TLT-plots, which could result from reaction between the ammonium nitrate and sulfate (or nitric or sulfuric acid formed by dissociation of the ammonium salts) and the carbonate. Fig. 6 shows these TLT-plots for ammonium sulfate with its release peaks between 170 and 320 °C, and ammonium nitrate with a release peak between 100 and 220 °C and at about 550 °C.

The extent of such a loss would depend on the amount of nitrate and sulfate in the sample, likely to be in the form of their ammonium salts. This is confirmed by the somewhat poorer agreement between the pairs of carbonate results for samples with high nitrate and sulfate values especially if combined with low Ca and Mg levels. Fig. 7
shows the coherence between the H⁺ concentrations of the extracts used for ion chromatography (calculated from pH-values) and the CC determined thermally for ambient air samples. If the acidity of the extracted samples increases, it is likely that a portion of CC gets lost.

3.8. TLT-plots of pretreated filter samples

TLT-plots of samples pretreated at 460 °C with a duration of 60 min were compared to those of untreated samples. Fig. 8 shows TLT-plots of the original samples compared to the carbon profile after the pretreatment. The EC and the different OC fractions clearly were removed from the filters, and the remaining carbon does correspond to the carbonate carbon in the original sample.

Consequently, variability of results can be attributed to the aliquoting system, the error of integrating the peak areas or to the heterogeneity of the filter sample surfaces. Repeated measurements of TC and CC on six 10 mm Ø filter discs from four different samples give an estimate of the repeatability of the methods as 3.2% and 7.2% average RSD, respectively. CC repeatability is poorer than that for TC, first because of the additional pretreatment step, and second, because of the smaller amounts of CC present on the filters.

4. Conclusions

Here we show that thermal treatment of aerosol loaded filter discs at 460 °C for 60 min in an O₂ atmosphere removes OC and EC, leaving CC as residual carbon on the filter. The CC on the filter disc can then be determined with a TC instrument for solid samples. In combination with TC and the thermal treatment according to Cachier et al. (1989) for EC + CC (without fumigation) a determination of EC, OC and CC is possible. The repeatability of the CC determination by thermal pretreatment followed by a fast high-temperature combustion is between 5 and 10%, compared to the TC measurement (fast high-temperature combustion without pretreatment) with about 3–5%.

In ambient air samples from a sampling site in Vienna with elevated PM10 levels ("Liesing") CC values as high as 3–5% were observed. Also, source samples of PM10 street dust fractions collected on filters were analysed for their carbonate carbon contents. The results show good correlation between CC determined after the thermal treatment and the CC calculated from the ionic balance. The CC content of the street dust samples reached 32% of TC and 25% CO₃²⁻ of total PM10 mass were observed. Also, source samples of PM10 street dust fractions collected on filters were analysed for their carbonate carbon contents. The results show good correlation between CC determined after the thermal treatment and the CC calculated from the ionic balance. The CC content of the street dust samples reached 32% of TC and 25% CO₃²⁻ of total PM10 mass were observed. Also, source samples of PM10 street dust fractions collected on filters were analysed for their carbonate carbon contents. The results show good correlation between CC determined after the thermal treatment and the CC calculated from the ionic balance. The CC content of the street dust samples reached 32% of TC and 25% CO₃²⁻ of total PM10 mass were observed. Also, source samples of PM10 street dust fractions collected on filters were analysed for their carbonate carbon contents. The results show good correlation between CC determined after the thermal treatment and the CC calculated from the ionic balance. The CC content of the street dust samples reached 32% of TC and 25% CO₃²⁻ of total PM10 mass were observed.

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