**Atmospheric
Measurement
Techniques**

On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols

A. Karanasiou[1], **E. Diapouli**[2], **F. Cavalli**[3], **K. Eleftheriadis**[2], **M. Viana**[1], **A. Alastuey**[1], **X. Querol**[1], and **C. Reche**[1]

[1]Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain
[2]Institute of Nuclear Technology and Radiation Protection, Environmental Radioactivity Laboratory, National Centre of Scientific Research "Demokritos", 15310 Ag. Paraskevi, Attiki, Greece
[3]European Commission, Joint Research Centre, Institute of Environment and Sustainability, via E. Fermi, 2749, 21027 Ispra, Italy

Abstract. The objective of this work was to study the possibility of identifying and quantifying atmospheric carbonate carbon (CC) by thermal-optical analysis. Three different temperature protocols, two modified NIOSH-like protocols (RT-QUARTZ-840 and RT-QUARTZ-700), and the EUSAAR_2 protocol were tested on filter samples containing known amounts of CC with the semi-continuous Sunset analyzer. Carbonate was quantified by the manual integration of the sharp peak appeared at the maximum temperature step of the inert mode. High recoveries of CC were achieved by all the thermal protocols. Using the EUSAAR_2 thermal protocol, more than 95 % of CC evolved as OC during the maximum temperature step in inert atmosphere for CC amounts up to 56 µg. Using the RT-QUARTZ-840 protocol specifically developed for on-line analyses, CC completely evolves as OC during the maximum temperature step in the inert node, regardless of the CC concentration. However, the quantification of CC by the RT-QUARTZ-840 protocol suitable for the semi-continuous analyzer implies a high level of uncertainty (manual integration, residual contribution of organic carbon). Therefore, it is advisable to determine CC with an independent method (e.g. by acidic decomposition of CO_3^{2-} and subsequent detection of CO_2) when other sample aliquots are available. The comparison of the peak integration method with the direct determination of the CC sample content by acidic CO_2 release showed that the peak integration method provides always higher CC concentrations of about 33 %. Nevertheless, the determination of CC with the RT-QUARTZ-840 protocol may be considered in cases where on line monitoring instruments are used and for areas where CC concentrations are expected to be significant e.g. Southern European countries. This case study suggests that users of the semi continuous Sunset analyzer can manually integrate the sharp peak (if present) at the maximum temperature step of the He mode (between 128–130 and 160–165 s when using the RT-QUARTZ-840 protocol) and calculate the CC concentration though with a rather high error.

1 Introduction

Carbonaceous particulate matter, usually classified into two categories, organic carbon (OC) and elemental carbon (EC), constitutes an important component of the atmospheric aerosol forming typically 10 to 50 % of the total particulate matter (PM_{10}) mass concentration (Putaud et al., 2004, 2010; Yttri et al., 2007; Pio et al., 2001). OC can be of both primary and secondary origin, i.e. emitted directly into the atmosphere or formed by the condensation of compounds produced in the atmosphere by photo-oxidation of volatile organic precursors (Fuzzi et al., 2006). In contrast, EC is exclusively of primary origin (incomplete combustion of carbon-containing fuels).

Thermal-optical analysis has been widely used for the determination of OC and EC (Phuah et al., 2009) in atmospheric aerosol samples. According to this method, the carbonaceous species are thermally desorbed firstly in an inert atmosphere (He) and then in an oxidizing atmosphere (mixture of He and O_2). Ideally, OC desorbs in the inert atmosphere while EC combusts in the oxidizing atmosphere at high temperature. However, some OC is pyrolytically converted to EC (char) when heated up in inert atmosphere. This process that darkens the filter, is used to correct for charring, by continuously monitoring the transmittance (or

reflectance) of the filter during the analysis (Bae et al., 2004; Birch and Cary, 1996). The most commonly employed thermal protocols for the analysis of OC and EC in atmospheric aerosols are the IMPROVE (Chow et al., 1993), the NIOSH (Birch and Cary, 1996), and the EUSAAR_2 (Cavalli et al., 2010) protocols. Although these protocols show good agreement for total carbon (TC) determination, they yield different OC and EC concentrations (Chow et al., 2001; Schmid et al., 2001). Furthermore, they are not all well characterized with respect to interferences by carbonate.

Carbonate carbon (CC), another primary carbonaceous species present in natural ground and building/demolition dust, is generally not considered in many atmospheric chemistry studies. The reason for this may be its low contribution to the atmospheric fine particle mass concentration in most studied areas (Sillanpää et al., 2005), along with the lack of a robust and popular technique to determine CC concentration in atmospheric aerosols (Jankowski et al., 2008).

However, CC concentrations may be significant in certain areas and/or under specific meteorological conditions. For instance, soil dust outbreaks may greatly increase the ambient PM air levels especially in Southern Europe and across the Mediterranean basin. Sillanpää et al. (2005) measured carbonaceous aerosol in six European cities (i.e. Duisburg, Prague, Amsterdam, Helsinki, Barcelona and Athens) and detected carbonate carbon (by thermal-optical analysis) in the aerosol coarse fraction (PM_{10}–$PM_{2.5}$) of Athens and Barcelona. In that study, CC was mainly present as $CaCO_3$ with an average coarse fraction concentration of $15.9\,\mu g\,m^{-3}$ (9.8–$29.2\,\mu g\,m^{-3}$) in Athens and $2.6\,\mu g\,m^{-3}$ (0.3–$6.3\,\mu g\,m^{-3}$) in Barcelona (over 7 weeks in spring-summer 2003), accounting, for 55 % and 11 % of the coarse aerosol mass concentration in Athens and Barcelona, respectively. In Athens, a daily average PM_{10} concentration of $441\,\mu g\,m^{-3}$ was also reported during an intense dust event by the Greek Ministry of the Environment with an hourly PM_{10} mass concentration reaching at $2384\,\mu g\,m^{-3}$ (Athanassiadou et al., 2006). In Eastern Mediterranean, severe dust events have been reported, where PM_{10} daily (24 h average) concentrations exceeded $200\,\mu g\,m^{-3}$ in Crete (Gerasopoulos et al., 2006) and reached a maximum of $326\,\mu g\,m^{-3}$ along Mediterranean Tunisian coasts over year 2002–2003 (Koçak et al., 2007). Recently, Querol et al. (2009) quantified the African dust contribution to PM_{10} concentration at 21 regional background sites across the Mediterranean basin. The highest mean annual net African dust contribution to PM_{10} was observed in the Eastern part of the Mediterranean Basin and specifically, at Finokalia (Crete, over year 2004–2006), and at Ayia Marina (Cyprus, over year 2003–2006) reaching values of $10\,\mu g\,m^{-3}$ and $9\,\mu g\,m^{-3}$, respectively. At these sites during African dust outbreaks, daily PM_{10} levels were frequently above $100\,\mu g\,m^{-3}$ and the characterization of individual particles revealed that $CaCO_3$ formed up 30–40 % of the PM_{10} particle number. Dust storms are also frequent in Eastern Asia. For example, at Xi'an located at the margin

of a dust source region (Loess Plateau, China), the average level of CC measured (by acidification) in $PM_{2.5}$ during five dust storms in spring 2002 was $7.2\,\mu g\,m^{-3}$ (Cao et al., 2005).

The decomposition temperature of carbonate may vary depending on a number of factors (Chow et al., 2001 and references therein), including the mixture of calcium carbonate with other materials, the chemical composition of the carbonate compound (e.g. $CaCO_3$ vs. $CaMg(CO_3)_2$), and the crystal form of the carbonate compound (e.g. calcite vs. aragonite vs. amorphous $CaCO_3$). Carbonate thermal decomposition is also expected to depend on the material grain size (Chow et al., 2001). Furthermore, as various protocols have different temperature set points and plateau duration, CC can be detected at different temperatures. Indeed, CC was reported to evolve during the maximum temperature step in He, i.e. between $700\,°C$ and $850\,°C$ (Miyazaki et al., 2007; Birch and Cary, 1996) for a NIOSH-type protocol (i.e. reaching $>700\,°C$ in the inert atmosphere mode during the last temperature step only). In contrast, CO_2 was observed to evolve from laboratory-grade calcium carbonate at the $550\,°C$ set point with the IMPROVE protocol (Chow et al., 2001). However, Cavalli et al. (2010) demonstrated recently that natural calcite decomposes at $650\,°C$ but not at $550\,°C$ in the inert mode of the analysis performed with a Sunset OCEC laboratory analyzer. Actually, CC could well interfere with the determination of OC or EC, depending on carbonate characteristics, and on the thermal protocol employed (Sillanpää et al., 2005; Sciare et al., 2003; Schmid et al., 2001). If not accounted for, the interference of CC with the OC or EC signal can lead to an overestimation of the OC or EC concentration. This overestimation might be negligible for fine mode OC and EC concentrations, as the contribution of CC to $PM_{2.5}$ is generally very low (Querol et al., 2004). But it can be significant for PM_{10} or coarse OC or EC concentration. Indeed, Koulouri et al. (2008) showed that without the subtraction of CC, thermal-optical analysis of coarse aerosol samples from Finokalia in Crete (Greece) would overestimate organic carbon content by 20 % when using a NIOSH-like protocol.

In previous works CC was determined by integrating the peak appeared during the transition to the maximum temperature step of the inert mode of a NIOSH-like protocol (Miyazaki et al., 2007; Xu et al., 2004; Schauer et al., 2003; Birch and Cary, 1996). Alternative methods were described by Jankowski et al. (2008) and Cavalli et al. (2010), which require a separate analysis for CC determination.

The objective of this study is to determine how well atmospheric carbonate can be identified and quantified using only the thermal optical analysis. Three different temperature protocols (namely EUSAAR_2 and two modified versions of the NIOSH protocol, RT-QUARTZ-840 and RT-QUARTZ-700) were tested against standard samples containing known amounts of CC. The RT-QUARTZ-840 protocol was applied to ambient samples from sites characterised by frequent African dust intrusions: Barcelona (Spain) and Athens (Greece). Off-line thermal-optical measurements of CC in

samples from Barcelona were confronted to other methods (fumigation, acidification). The precision of on-line CC measurements performed in Athens with the RT-QUARTZ-840 protocol was also investigated.

2 Methodology

2.1 Instrumentation

In this study two OCEC Sunset analyzers were used: a semi-continuous OCEC field instrument (Sunset Laboratory Inc.) installed at the N.C.S.R. "Demokritos" Athens urban background site (GAW-DEM, http://gaw.empa.ch/gawsis/reports.asp?StationID=2076202728) and a laboratory OCEC analyzer installed at Barcelona (IDAEA, http://www.idaea.csic.es/). This latter is primarily used for the analysis of PM_{10}, $PM_{2.5}$ and PM_1 samples collected at a Barcelona urban site, belonging to the local air quality monitoring network and for samples collected at the EUSAAR regional background site, Montseny (MSY, http://www.eusaar.net/files/overview/infrastructures-descript.cfm). For the determination of OC and EC on a routine basis the EUSAAR_2 thermal protocol is used.

The semi-continuous instrument is equipped with an in-line parallel carbon denuder, so that the sample is denuded of volatile gases during sampling. A cyclone was used upstream of the instrument to pass particles smaller than 2.5 μm. Aerosol particles are collected at a sampling flow rate of 8 l min^{-1} on a round 16-mm quartz fibre filter which is mounted inside the instrument. The quartz fibre filter is always installed with a second backup filter, mostly to serve as support for the front filter. After collection, the oven of the instrument is purged with helium and the temperature is increased in multiple programmed steps based on the selected thermal protocol. The evolved organic carbon flows through a manganese dioxide (MnO_2) oxidizing oven and all carbon is transformed into carbon dioxide (CO_2). The CO_2 is then quantified by a non-dispersive infrared (NDIR) detector. The oven is cooled prior to the second part of the analysis, where the oven is purged with a mixture of 2 % oxygen in helium and the sample is again heated in steps. During this stage, all remaining carbon on the filter, including elemental carbon, is oxidized, the oxidation products are carried through the MnO_2 oven, and carbon is detected by the NDIR detector as CO_2. For charring correction a He-Ne laser beam monitors the sample transmittance throughout the heating process. At the time where the laser signal returns to its initial value, the split point between OC and EC is set (Birch and Cary, 1996).

The operating principle of the laboratory OCEC analyzer is similar to the semi-continuous analyzer with the difference that the CO_2 produced is converted into CH_4 and detected by a Flame Ionization Detector (FID), which improves the limit of detection.

2.2 Standard samples

The studied CC concentration range covers extreme dust events reported in the literature, in particular by Koçak et al. (2007), by Gerasopoulos et al. (2006) and by Sillanpää et al. (2005). The chemical characterization of airborne African dust plumes suggests that it is mainly composed of silicate (i.e. of Al-felsic silicates and of Si-felsic silicates roughly in equal proportions) with $CaCO_3$ representing at a very maximum 40 % of the PM_{10} aerosol particle number (Querol et al., 2009; Kandler et al., 2007). This composition has been applied to estimate the maximum mass concentration of $CaCO_3$ expected during the episodes mentioned above. The corresponding CC concentrations (in μg CC cm^{-2}) have been calculated for three cases differing for sampling conditions and analyzer configuration (Table 1). Case 1 represents a 24 h sampling with a flow rate of 1 m^3 h^{-1} on a 47 mm diam filter; Case 2 corresponds to a 3 h sampling with a flow rate 0.48 m^3 h^{-1} on a 16 mm diam filter and on-line analysis using the semi-continuous OCEC analyzer (i.e. conditions employed in Athens field study, Sect. 3.3); and finally Case 3 represents a 24 h sampling with a flow rate of 30 m^3 h^{-1} on a 150 mm dia filter (i.e. conditions adopted by the field study in Barcelona, Sect. 3.3).

Thirty-two standard samples of CC were prepared in the laboratory by depositing known amounts of powdered calcium carbonate (Merck, $CaCO_3$) on pre-weighted quartz fibre filter punches (PALLFLEX, Tissuquartz). Although commercial precipitated $CaCO_3$ may differ from atmospheric carbonate, was previously used to prepare carbonate carbon standards (e.g. Jankowski et al., 2008; Chow et al., 2001). Weighing was conducted with a Sartorius microbalance after 48h of equilibration in a room maintained at $20 \pm 1\,°C$ and $50 \pm 5\,\%$ RH (according to EN12341, 1998). The filter punch (16 mm diam) loaded with $CaCO_3$ was covered by a second blank filter punch to avoid any loss (in the semi-continuous instrument two filter punches are always used during the analysis). Standard samples containing 25–220 μg CC/punch were prepared. This is much larger than the CC amounts expected to be collected during dust events (Table 1), but an accurate reference value for lower concentrations could not be obtained by gravimetric analysis. In order to better simulate "airborne $CaCO_3$", additional three test samples were prepared by collecting commercial precipitated $CaCO_3$ suspended in a clean chamber on quartz fibre filters. A TOPAS 210 polydisperse aerosol atomizer was used for this purpose while the $CaCO_3$ mass deposited on the quartz fibre filter was calculated by weighing on a 5 digit balance (Sartorius, BP211D). The CC concentration on the filter samples prepared with this method was in the range 10–56 μg(C). All samples were subsequently analyzed off-line, using the semi-continuous OCEC field instrument (Sunset Laboratory Inc.).

Table 1. Expected atmospheric CC concentrations during dust events based on previous published studies.

	Gerasopoulos et al. (2006)	Koçak et al. (2007)	Sillanpää et al. (2005)
PM_{10} ($\mu g\,m^{-3}$)	200	326	
Mineral dust ($\mu g\,m^{-3}$)	130	222	
$CaCO_3$ ($\mu g\,m^{-3}$)	26	44	29
CC $\mu g\,cm^{-2}$ (CASE 1)	5	9	3
CC $\mu g\,cm^{-2}$ (CASE 2)	2	4	3
CC $\mu g\,cm^{-2}$ (CASE 3)	13	22	15

2.3 Thermal protocols

In this work, three different thermal protocols were applied: (1) RT-QUARTZ-840, a NIOSH-like protocol with a maximum temperature of 840 °C in the He-mode which is the default thermal protocol in the Sunset semi-continuous analyzer, (2) RT-QUARTZ-700, a modified NIOSH protocol with a maximum temperature of 700 °C in the He-mode and (3) EUSAAR_2 protocol with a maximum temperature of 650 °C in the He-mode. A detailed description of each protocol is given in Table 2.

Briefly, a NIOSH-like protocol (NIOSH, 1999) with a maximum temperature in the He-mode around 840 °C has been extensively used for urban aerosol samples. When applying this protocol, Subramanian et al. (2006) have observed loss of light-absorbing carbon in the He-mode. Thus, they suggested lowering the maximum temperature to 700 °C, in order to limit premature evolution of EC. Chow et al. (2001) also suggested that the fraction of carbon evolving at around 850 °C in inert-mode may be EC, which is oxidized by oxygen supplied by mineral oxides in the particle mixture on the filter. Nevertheless, the increase in light transmittance and reflectance observed at 850 °C in the He stage could be also attributed to the evolution of light-absorbing OC products or of pyrolytic carbon (Yu et al., 2002). Birch and Cary (1996) found that in a NIOSH-like protocol CC evolves during the maximum temperature step of the inert mode of the analysis between 700–850 °C. Thus, in a NIOSH-like protocol, this carbon peak, when present in ambient aerosol samples, could be attributed to CC so its concentration is determined by the manual integration of this peak.

EUSAAR_2 has been recently developed for regional background sites in order to improve the accuracy of the discrimination between OC and EC. The use of lower temperature steps and of longer residence times aims at the reduction of pyrolysis and at a more complete evolution of OC (by favouring its volatilization), while early evolution of light absorbing carbon species is prevented by lowering the maximum temperature in the He-mode. The analysis of natu-

ral calcite sample with this protocol showed that CC decomposes in the inert mode around 650 °C (Cavalli et al., 2010).

2.4 Fumigation with HCl

For comparison with the determination of CC by the RT-QUARTZ-840 protocol, two high-loaded urban aerosol samples from Barcelona, as well as a standard carbonate sample, were fumigated with HCl prior to thermal-optical analysis, for the removal of their CC content (Cachier et al., 1989). During the fumigation procedure, the filter punches were placed on a perforated tray and set above a glass beaker containing concentrated hydrochloric acid (Merck, 37 %). They were exposed to the acid vapors for about one hour and then were placed in a clean hood for one hour again, in order to allow the residual acid to volatilize. It must be noted however that this procedure has been known to cause damage in the combustion oven of the OCEC analyzer due to the possible incomplete volatilization of the residual acid (Cavalli et al., 2010).

2.5 Direct determination of CC by acidification and subsequent CO_2 detection

Specific techniques for determining carbonate concentrations in various matrices have been known for more than 15 yr (Pio et al., 1994 and references therein). The determination of CC in atmospheric PM samples deposited on filters by acidification and determination of the CO_2 evolved as first described by Cadle et al. (1980) and validated by Pio et al. (1994) is simple, accurate, and easily implementable by laboratories that already perform OC and EC analyses. Indeed, suitable glassware that contains the concentrated phosphoric acid (H_3PO_4) is the only equipment needed if use is made of the CO_2 detection chain of the OCEC instrument. The glass enclosure has to be fully flushed by a carrier gas (He). The filter punch is dropped into the concentrated phosphoric acid (H_3PO_4), and CO_2 that evolves (Eq. 1), is carried to the detector of a commercial OCEC analyzer by the carrier gas.

$$O_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O \tag{1}$$

Spiking quartz fibre filter punches with known amounts of CC contained in 10 μl of Na_2CO_3 solutions, we checked that the CC recovery of this technique is 99 % over the range 1.8–12 μg CC.

3 Results

3.1 Detection and recovery of carbonate

We firstly tested the recovery of CC by the three different protocols, namely RT-QUARTZ-840, RT-QUARTZ-700 (version for semi-continuous analyzer) and EUSAAR_2. Standard samples containing 25–220 μg CC/sample were

**Table 2.** Thermal protocols used: Temperature (°C), Duration (s).

		RT-QUARTZ-840	RT-QUARTZ-700	EUSAAR_2
Step	Carbon peak	Temperature, Duration	Temperature, Duration	Temperature, Duration
He 1	OC1	600, 95	600, 95	200, 120
He 2	OC2	840, 90	700, 90	300, 150
He 3	OC3	0, 33	0, 33	450, 180
He 4	OC4	550, 2	550, 2	650, 180
He 5				0, 33
He/O$_2$ 1	EC1	550, 30	550, 30	500, 120
He/O$_2$ 2	EC2	550, 25	550, 25	550, 120
He/O$_2$ 3	EC3	650, 45	650, 45	700, 70
He/O$_2$ 4	EC4	870, 80	870, 80	850, 80

analysed. The three thermal protocols tested, provided a rather accurate estimate of the CC content (Figs. 1, 2 and 3). The regression slope was about 0.90, with an R^2 value close to 1. The intercepts of the regressions in Figs. 1, 2, 3 were negligible equal to -0.003, -0.002 and $+0.004$ and respectively. This recovery test demonstrates that CC decomposes almost completely during thermal optical analysis regardless of the protocol implemented. Since a recovery of 90 % was found for these high CC content levels, it can be assumed that at least similar recovery rates can be obtained with lower CC amounts corresponding to atmospheric dust concentrations.

In order to better characterise the behaviour of CC in relation to each temperature protocol, we conducted further experiments using the test samples which were prepared from precipitated CaCO$_3$ suspended in a clean chamber and sampled on a quartz fibre filter as aerosol particles. The CC content of the filter samples prepared with this method was in the range 10–56 µg(CC). These filter samples were analysed using the RT-QUARTZ-840 and the EUSAAR_2 protocols, which are the most widely used at European monitoring sites with both the semi-continuous and the laboratory OCEC analyzers.

The thermograms obtained with the EUSAAR_2 protocol from the analysis of 10, 15 and 56 µg of CC indicated that 100, 96 % and 95 % of CC respectively evolved in the OC4 step of the analysis at 650 °C, and the remaining in the EC3 step at 700 °C. In Figs. 4 and 5 the thermograms of the analysis of 10 and 56 µg CC by EUSAAR_2 protocol are given. The thermograms obtained with the RT-QUARTZ-840 protocol showed one single sharp peak at the maximum temperature step (840 °C) of the He mode regardless of the deposited amount of CC up to 56 µg (Fig. 6).

In general, for the amount of CC collected even during extreme dust events as reported in Table 1, CC will completely evolve in the inert mode of the analysis with all three thermal protocols (at $T \leq 650$, 700, and 840 °C for EUSAAR_2, RT-QUARTZ-700 and RT-QUARTZ-840, respectively), and
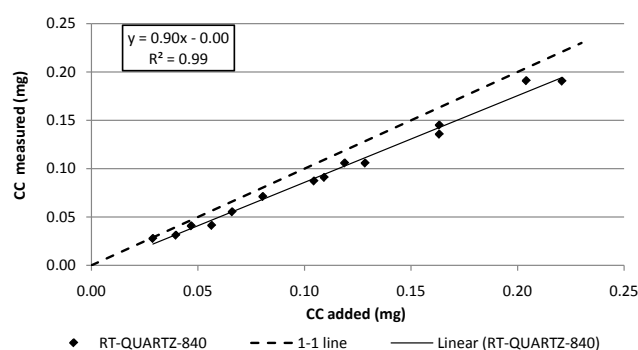
Fig. 1. Regression between CC quantities measured by the RT-QUARTZ-840 thermal protocol and CC quantities initially added on filter blanks.
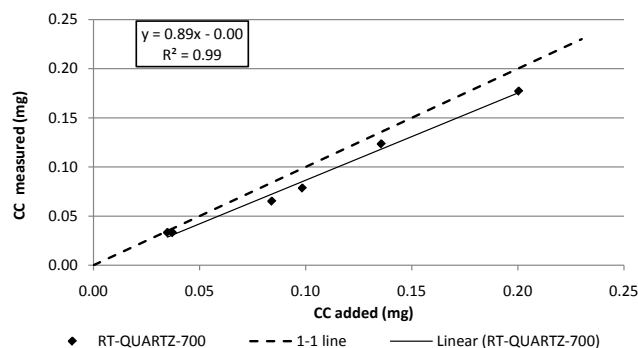
Fig. 2. Regression between CC quantities measured by the RT-QUARTZ-700 thermal protocol and CC quantities initially added on filter blanks.

will therefore interfere only with the determination of OC. The concentration of CC might be determined by integrating the CO$_2$ peak that could be specifically attributed to the decomposition of CC.
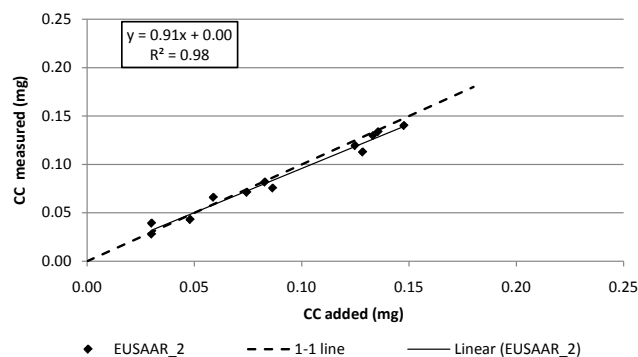
Fig. 3. Regression between CC quantities measured by the EU-SAAR_2 thermal protocol and CC quantities initially added on filter blanks.
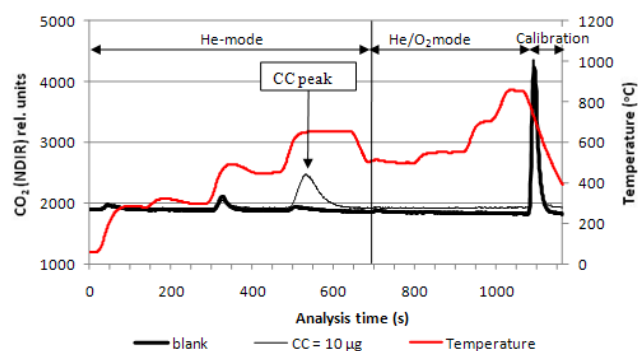

Fig. 4. EUSAAR_2 thermogram for a blank and a CC-loaded filter ($10 \mu g$) (He-mode: 1–230 s, He/O_2-mode: 231–410 s and Calibration-mode: 410–510 s). The vertical line represents the splint point between OC and EC. The response of the NDIR detector is given in relative units.

Fig. 5. EUSAAR_2 thermogram for a blank and a CC-loaded filter ($56 \mu g$) (He-mode: 1–230 s, He/O_2-mode: 231–410 s and Calibration-mode: 410–510 s). The vertical lines represents the splint point between OC and EC. The response of the NDIR detector is given in relative units.

Fig. 6. RT -QUARTZ-840 thermogram for a blank and a CC-loaded filter ($56 \mu g$) (He-mode: 1–673 s, He/O_2-mode: 674–1063 s and Calibration-mode: 1064–1163 s). The vertical line represents the splint point between OC and EC. The response of the NDIR detector is given in relative units.

3.2 CC peak integration and comparison with fumigation by HCl

In this study we applied the RT-QUARTZ-840 protocol to determine CC in real atmospheric samples by manually integrating the sharp "OC2" peak occurring during the transition to the maximum temperature plateau in the inert mode of the analysis. It should be noted that CC is not automatically determined by the OCEC Sunset analyzers: the analyst has to calculate the CC amount (if detected) by using the manual integration option available in the calculation program. Based on the feature of the CC peak observed on CC standard thermograms, CC was estimated by integrating the OC2 peak of the RT-QUARTZ-840 protocol between 128–130 and 160–165 s. The uncertainty of the manual integration due to the definition of the time integral of the CC peak was calculated. The definition of the time integral influences the CC concentration by 3–12 % with the highest uncertainty associated to the lowest concentrations.
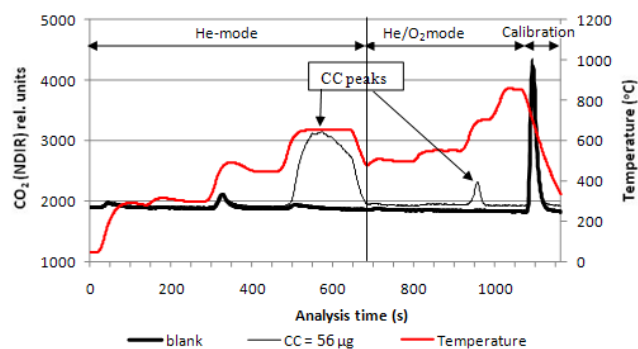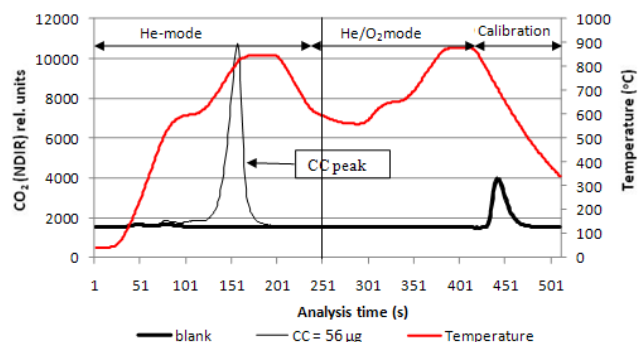
This methodology was tested versus the HCl fumigation procedure for the removal of CC (NIOSH, 1999). One standard CC filter sample, as well as two urban aerosol filters collected in Barcelona site (with high CC content), were fumigated with HCl, prior to being analyzed by the RT-QUARTZ-840 protocol. The fumigation treatment almost entirely removed CC (by approximately 99 % according to the initial quantity added) from the standard CC sample. The thermograms obtained from one of the urban aerosol samples, prior and after HCl fumigation, are presented in Fig. 7. Fumigation led to a large decrease of the peak attributed to carbonate carbon (by approximately 86 %, in both of the ambient filter samples). However, we noticed changes in the organic carbon volatility properties after the fumigation. The area of OC1 peak was larger after the fumigation. This indicates that a fraction of OC, which was evolving as OC2 (840 °C) from the untreated sample, evolves at lower temperature (i.e. 600 °C) after the treatment with HCl. Moreover, fumigation with HCl has been shown to cause loss of volatile organic
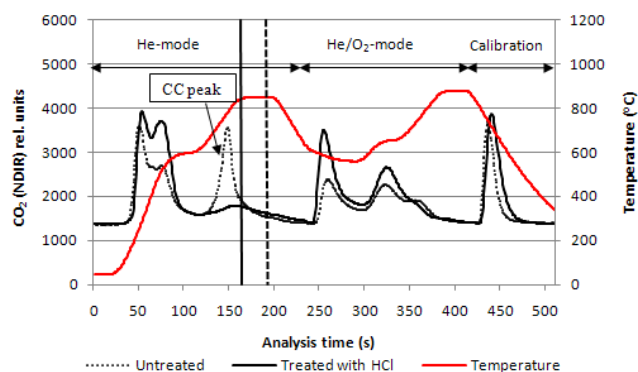
Fig. 7. RT-QUARTZ-840 thermogram for an ambient aerosol sample filter treated with HCl and untreated (He-mode: 1–230 s, He/O₂-mode: 231–410 s and Calibration-mode: 410–510 s). The vertical lines represent the splint point between OC and EC. The response of the NDIR detector is given in relative units.

compounds. Salts of volatile organic acids, if present, will react with HCl and will be correspondingly missing from the OC fraction if fumigation is used (Chow et al., 1993). Consequently the decrease of OC2 peak area cannot be solely attributed to CC loss. Furthermore, a small wide peak (about 14 % of the OC2 peak area) remains after the treatment with HCl, suggesting the presence of organic compounds that co-evolve with CC in the OC2 peak during the highest temperature step in the He mode. The estimation of CC should therefore be based on the loss of TC in the sample aliquot after fumigation. However, the CC concentration in the sample prior to the fumigation (as determined by the integration of the OC2 peak in the untreated sample) corresponds to the TC loss after fumigation in one of the two ambient samples only: in the second sample, the TC loss after the fumigation was twice as high as the CC concentration determined by the integration of the OC2 peak in the untreated sample. This suggests that fumigation is able not only to eliminate CC, but also to cause losses of organic compounds like organic acids. In conclusion, it was not possible to validate the determination of CC in ambient samples by integration of the OC2 peak through a comparison with the fumigation method.

3.3 Urban aerosol measurements

CC was determined by integrating the sharp peak at the maximum temperature step of the He mode of the RT-QUARTZ-840 protocol (see Sect. 3.2) for two sets of ambient samples representative of Mediterranean urban/urban background aerosols collected in Barcelona and Athens during different periods. At the urban monitoring site in Barcelona (IDAEA-CSIC), CC was determined off-line in PM_{10}, $PM_{2.5}$ and PM_1 in 24 h – integrated samples collected during February–August 2008 using a MCV high volume sampler set at $30\,m^3\,h^{-1}$ (MCV S.A, www.mcvsa.com). At the urban background site in Athens (GAW-DEM), CC was

determined on-line from 3 hr - integrated samples by the semi-continuous Sunset instrument during November 2009–February 2010. A $PM_{2.5}$ cut-off cyclone was employed along with the semi-continuous OCEC analyzer.

OC, EC and CC concentrations recorded at the sampling sites in Athens and Barcelona are presented in Table 3. CC was not detected in PM_1 ambient samples collected in Barcelona. The lowest CC concentration that could be detected in PM_{10} and $PM_{2.5}$ was $0.04\,\mu g\,m^{-3}$. As expected, CC concentrations in PM_{10} and $PM_{2.5}$ were generally low with respect to OC but CC concentration in PM_{10} reached half of the EC ambient concentration at Barcelona on 19 June 2008. This fact points out the importance to ensure that CC evolves together with OC rather than with EC during the thermal-optical analysis. On average, the concentration of CC in PM_{10} was $0.59\,\mu g\,m^{-3}$ at the Barcelona site, accounting for about 10 % of the total carbon concentration.

For the maximum concentrations of CC observed at both Athens and Barcelona sites, back-trajectories analysis (Draxler and Rolph, 2010) revealed African dust intrusions (Fig. 8). For the Athens site, these events were detected on 18–19 November 2009 and 18–20 February 2010 while for Barcelona occurred on 25–26 June 2008.

For the 24 h samples collected in Barcelona, a complete chemical characterisation was available. The measured CC concentrations were compared to the maximum CC concentrations calculated as 0.3 (12/40) times the corresponding total calcium concentration determined by Inductively coupled plasma atomic emission spectroscopy, ICP-AES (as if all Ca^{2+} were in the form of $CaCO_3$). The results of Ca^{2+}, maximum expected CC and measured CC concentrations are presented in Table 4. Almost for all samples (except for the samples on 27 August 2008 and 21 July 2008) the measured CC concentration was lower than the upper limit indicating that CC was not overestimated by integrating the OC2 peak of the RT-QUARTZ-840 protocol. Generally, Ca and CC correlated well ($R^2 = 0.85$), and measured CC concentration was 55 ± 11 % (99 % confidence level) of the maximum CC calculated from Ca^{2+} measurements.

Furthermore, for a set of samples, i.e. 14, from Barcelona urban site and EUSAAR regional background site, Montseny, Spain (MSY, http://www.eusaar.net/files/overview/infrastructures-descript.cfm) the CC concentrations measured by peak integration were compared to those directly measured by acidification and subsequent CO_2 detection. CC determined by the two different methods correlated well ($R^2 = 0.98$) and the CC concentration determined by peak integration was $1.33(\pm 0.06)$ times plus $0.19(\pm 0.12)$ $\mu g\,m^{-3}$ the concentration determined by acidification, Fig. 9. For the studied sites the slope of the relationship indicates systematic differences between the two methods. It seems that the peak integration method gives constantly higher CC concentrations than the acidification method, probably due to the contribution of some OC fraction. The presence of an intercept indicates that the peak integration can provide
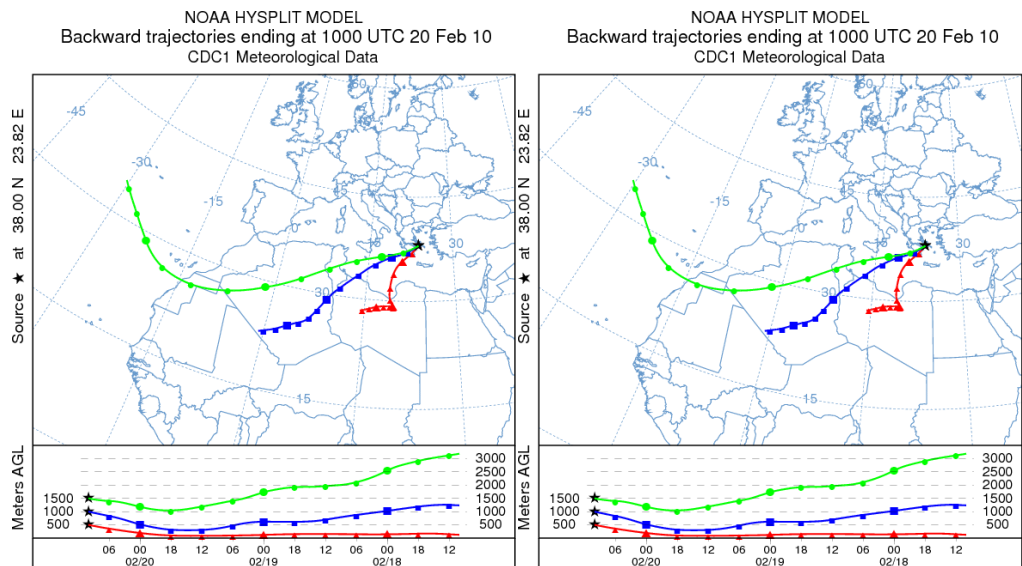
Fig. 8. HYSPLIT back-trajectory analysis at different vertical levels (red: 500 m, blue: 1000 m, green: 1500 m) ending over Barcelona (26 June 2008) and Athens (20 February 2010) showing dust episodes.

Table 3. OC, EC and CC mean daily concentrations [µg m^{-3}], measured at Barcelona site during February–August 2008 and at Athens site during October 2009–February 2010 (semi-continuous measurements 3 h).

µg m^{-3}	PM$_{10}$ Barcelona, (6/2008–11/2008) $N = 10$ days		PM$_{2.5}$ Barcelona, (6/2008–11/2008) $N = 8$ days		PM$_{2.5}$ Athens, (11/2009–2/2010) $N = 72$ days	
	Mean	Min.–Max.	Mean	Min.–Max.	Mean	Min.–Max.
EC	1.74	1.01–3.10	1.08	0.27–2.64	0.61	0.22–1.61
OC	4.01	3.00–4.92	3.12	1.42–4.88	2.10	0.86–6.40
CC*	0.59	0.04–1.27	0.22	0.04–0.51	0.07	0.00–0.40

*CC determined by integrating the OC2 peak of the RT-QUARTZ-840 protocol

Fig. 9. Regression between CC concentrations determined by the RT-QUARTZ-840 thermal protocol using the manual integration and by direct determination by acidification with phosphoric acid.

a non-zero CC concentration also for samples not containing any CC. During the temperature step that carbonate decomposes other organic compounds (like organic acids) might also decompose resulting in an artificial CC concentration. CC concentrations determined by acidification resulted $46 \pm 2\%$ ($R^2 = 0.98$) of the maximum CC concentrations calculated from Ca^{2+} concentrations. In the studied areas, roughly half of the calcium appears to be associated to carbonate. The remaining calcium can be present in other forms such as CaO, CaSO$_4$ and Ca^{2+} from sea salt (i.e. the portion which is not balanced by CO$_3$, 75 % in mass) (Kandler et al., 2007; Hoornaert et al., 1996).

The analysis of aerosol samples from Barcelona urban site, EUSAAR regional background site (MSY) and Athens urban background site evidences that in Southern European countries CC may constitute a significant fraction of the atmospheric carbonaceous matter, and therefore contribute to the
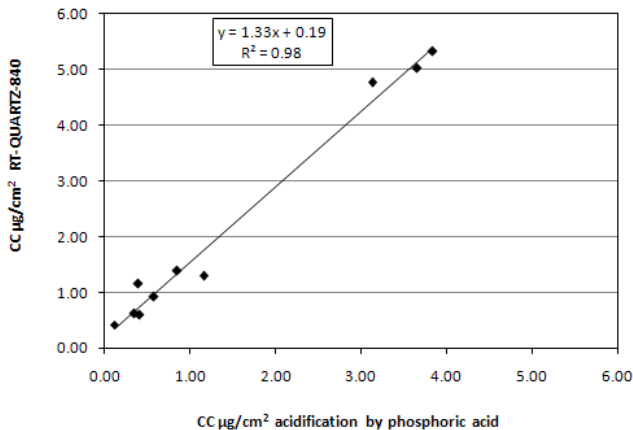
exceedances of daily and annual PM$_{10}$ limit values (Escudero et al., 2007). In these cases, it is essential that CC is quantified along with the other carbonaceous constituents since, if not considered, it would interfere with the OC (or even EC) signal, leading to artifacts in OC, EC determination. Especially under certain meteorological conditions, it can be demonstrated that high CC result from long range transport of natural Saharan desert dust.

Table 4. Comparison of the maximum CC concentrations (determined as 0.3 times the calcium concentration) with the measured CC concentrations for PM_{10} and $PM_{2.5}$ samples

Date	Ca measured by ICP-AES	maximum CC	measured CC
PM_{10}	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$
18/06/2008	6.19	1.86	1.20
19/06/2008	7.33	2.20	1.27
26/06/2008	7.42	2.23	1.09
01/07/2008	6.29	1.89	1.14
15/07/2008	1.72	0.52	0.42
29/07/2008	1.37	0.41	0.40
26/08/2008	1.22	0.37	0.32
27/08/2008	1.25	0.37	0.41
22/10/2008	0.13	0.04	0.04
23/10/2008	0.20	0.06	0.05
$PM_{2.5}$	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$	$\mu g\,m^{-3}$
18/06/2008	2.30	0.69	0.33
26/06/2008	4.44	1.33	0.62
01/07/2008	3.27	0.98	0.05
15/07/2008	0.38	0.12	0.10
21/07/2008	0.44	0.13	0.22
12/08/2008	2.06	0.62	0.37
23/10/2008	0.13	0.04	0.04
04/11/2008	0.08	0.02	N.D

4 Conclusions

The objective of this work was to study the possibility of identifying and quantifying atmospheric carbonate by thermal-optical analysis. Three different temperature protocols, two modified NIOSH-like protocols (RT-QUARTZ-840 and RT-QUARTZ-700), and the EUSAAR_2 protocol were tested on filter samples containing known amounts of CC. High recoveries of CC were achieved by all the thermal protocols tested for CC amounts up to 220 μg (CC). Using the EUSAAR_2 thermal protocol, more than 95 % of CC evolved as OC during the maximum temperature step in inert atmosphere for CC amounts up to 56 μg (C), corresponding to the mass of CC that would be collected during extreme desert dust events (i.e. with PM_{10} concentration above 200 μg m^{-3}). Using the RT-QUARTZ-840 protocol specifically developed for on-line analyses, CC completely evolves as OC, regardless of the CC amount.

The quantification of CC with RT-QUARTZ-840 protocol (a NIOSH- like protocol) suitable for the semi-continuous analyzer implies a high level of uncertainty (manual integration, residual contribution of organic carbon). Therefore, it is advisable to determine CC with an independent method (e.g. by acidic decomposition of CO_3^{2-} and subsequent detection of CO_2) when other sample aliquots are available. The comparison of the peak integration method with the direct determination of the CC sample content by acidic CO_2 release showed that the peak integration method provides always higher CC concentrations than the acidification method (slope of the regression equal to 1.33). Nevertheless, the de-

termination of CC with the RT-QUARTZ-840 protocol may be considered in cases where on line monitoring instruments are used and for areas where CC concentrations are expected to be significant e.g. Southern European countries. The results of this case study suggest that users of the semi continuous analyzers could manually integrate the sharp OC2 peak (if present) at the maximum temperature step of the He mode (between 128–130 and 160–165 s when using the RT-QUARTZ-840 protocol) and thus calculate the CC concentration though with a rather high error.

The RT-QUARTZ-840 protocol was used to determine CC in real atmospheric samples. Over a set of samples, CC represented 2.5 % of TC in $PM_{2.5}$ in Athens, and 5.0 and 9.3 % of $PM_{2.5}$ and PM_{10}, respectively, in Barcelona. The amount of CC measured in the filters collected in Barcelona correlated quite well with the amounts of Ca^{2+} as determined by ICP-AES, and suggest that about half of the calcium atoms were associated with carbonate at Barcelona urban site.

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References

Athanassiadou, M., Flocas, H., Harrison, M. R. J., Hort, M. C., Witham, C. S., and Millington, S.: The dust event of 17 April 2005 over Athens, Greece, Weather, 61, 125–131, 2006.

Bae, M. S., Schauer, J. J., DeMinter, J. T., Turner, J. R., Smith, D., and Cary, R. A.: Validation of a Semi-Continuous Instrument for Elemental Carbon and Organic Carbon Using a Thermal-Optical Method, Atmos. Environ. 38, 2885–2893, 2004.

Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, Aerosol Sci. Tech., 25, 221–241, 1996.

Cachier, H., Bremond, M. P., and Buat-Menard, P.: Determination of atmospheric soot carbon with a simple thermal method, Tellus, 41B, 379–390, 1989.

Cadle, S. H., Groblicki, P. J., and Stroup, D. P.: Automated carbon analyzer for particulate samples, Anal. Chem., 52, 2201–2206, 1980.

Cao, J. J., Lee, S. C., Zhang, X. Y., Chow, J. C., An, Z. S., Ho, K. F., Watson, J. G., Fung, K., Wang, Y. Q., and Shen, Z. X.: Characterization of airborne carbonate over a site on Asian dust source regions during spring 2002 and its climatic and environmental significance, J. Geophys. Res., 110, D03203, doi:10.1029/2004JD005244, 2005.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring

atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.

Chow, J. C., Watson, J. G., Prithett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation, and Applications in U.S. Air Quality Studies, Atmos. Environ., 27A, 1185–1201, 1993.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., Merrifield, T.: Comparison of IMPROVE and NIOSH Carbon Measurements, Aerosol Sci. Tech., 34, 23–34, 2001.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website http://ready.arl.noaa.gov/HYSPLIT.php, NOAA Air Resources Laboratory, Silver Spring, MD, 2010.

EN12341: Air quality – determination of the PM_{10} fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods, 1998.

Escudero, M., Querol, X., Pey, J., Alastuey, A., Pérez, N., Ferreira, F., Alonso, S., Rodríguez, S., and Cuevas, E.: A methodology for the quantification of the net African dust load in air quality monitoring networks, Atmos. Environ., 41, 5516–5524, 2007.

Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Russell, L. M., and Pöschl, U.: Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, Atmos. Chem. Phys., 6, 2017–2038, doi:10.5194/acp-6-2017-2006, 2006.

Gerasopoulos, E., Kouvarakis, G., Babasakalis, P., Vrekoussis, M., Putaud, J.-P., and Mihalopoulos, N.: Origin and variability of particulate matter (PM) mass concentrations over the eastern Mediterranean, Atmos. Environ., 40, 4679–4690, 2006.

Hoornaert, S., Van Malderen, H., and Van Grieken, R.: Gypsum and other Calcium-Rich Aerosol particles above the North sea, Environ. Sci. Technol., 30, 1515–1520, 1996.

Jankowski, N., Schmidl C., Marr, I.L., Bauer, H., and Puxbaum, H.: Comparison of Methods for the Quantification of Carbonate Carbon in Atmospheric PM_{10} Aerosol Samples, Atmos. Environ., 42, 8055–8064, 2008.

Kandler, K., Benker, N., Bundke, U., Cuevas, E., Ebert, M., Knippertz, P., Rodriguez, S., Schutz, L., and Weinbruch, S.: Chemical composition and complex refractive index of Saharan Mineral Dust at Izana, Tenerife (Spain) derived by electron microscopy, Atmos. Environ., 41, 8058–8074, 2007.

Koçak, M., Mihalopoulos, N., and Kubilay, N.: Contributions of natural sources to high PM_{10} and $PM_{2.5}$ events in the eastern Mediterranean, Atmos. Environ., 41, 3806–3818, 2007.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., and Mihalopoulos, N.: Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean, Atmos. Environ., 42, 6542–6550, 2008.

Miyazaki, Y., Kondo, Y., Han, S., Koike, M., Kodama, D., Komazaki, Y., Tanimoto, H., and Matsueda, H.: Chemical characteristics of water-soluble organic carbon in the Asian Outflow, J. Geophys. Res., 112, D22S30, doi:10.1029/2007JD009116,

2007.

NIOSH: Method 5040 (Issue 3): Elemental Carbon (Diesel Particulate), NIOSH Manual of Analytical Methods, 4rth Edition, 1999.

Phuah, C. H., Peterson, M. R., Richards, M. H., Turner, J. H., and Dillner, A. M.: A Temperature Calibration Procedure for the Sunset Laboratory Carbon Aerosol Analysis Lab Instrument, Aerosol Sci. Tech., 43, 1013–1021, 2009.

Pio, C. A., Castro, L. M., and Ramos, M. O.: Differentiated determination of organic and elemental carbon in atmospheric aerosol particles by a thermal-optical method, in: Proceedings of the Sixth European Symposium: Physico-Chemical Behaviour of Atmospheric Pollutants, edited by: Angeletti, G. and Restelli, G., Report EUR 15609/2 EN, European Commission, 706–711, 1994.

Pio, C., Alves, C., and Duarte, A.: Identification, abundance and origin of atmospheric particulate matter in a Portuguese rural area, Atmos. Environ., 35, 1365–1375, 2001.

Putaud, J.-P., Raes, F., Van Dingenen, R., Brueggemann, E., Facchini, M. C., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Jones, A., Laj, P., Maenhaut, W., Mihalopoulos, N., Müller, K., Palmgren, F., Querol, X., Rodriguez, S., Spindler, G., Brink, H., Tunved, P., Dingenen, R., Wehner, B., Weingartner, E., Wiedensohler, A., Wåhlin, P., and Raes, F.: European aerosol phenomenology – 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, Atmos. Environ., 38, 2579–2595, 2004.

Putaud, J.-P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H. C., Harrison, R. M., Herrmann, H., Hitzenberger, R., Huglin, C., Jones, A. M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T. A. J., Loschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F.: A European aerosol phenomenology – 3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe, Atmos. Environ., 44, 1308–1320, 2010.

Querol, X., Alastuey, A., Ruiz, C. R., Artiñano, B., Hansson, H. C., Harrison, R. M., Buringh, E., ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P., and Schneider, J.: Speciation and origin of PM_{10} and $PM_{2.5}$ in selected European cities, Atmos. Environ., 38, 6547–6555, 2004.

Querol, X., Pey, J., Pandolfi, M., Alastuey, A., Cusack, M., Pérez, N., Moreno, T., Viana, M., Mihalopoulos, N., Kallos, G., and Kleanthous, S.: African dust contributions to mean ambient PM_{10} mass-levels across the Mediterranean Basin, Atmos. Environ., 43, 4266–4277, 2009.

Schauer, J. J., Mader, B. T., DeMinter, J. T., Heidemann, G., Bae, M. S., Seinfeld, J. H., Flagan, R. C., Cary, R. A., Smith, D., Huebert, B. J., Bertram, T., Howell, S., Quinn, P., Bates, T., Turpin, B., Limp, H. J., Yu, J., Yang, C. H., and Keywood, M. D.: ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon, Environ. Sci. Tech., 37, 993–1001, 2003.

Schmid, H., Laskus, L., Abraham, H. J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., Ten Brink, H. M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A.,

Putaud, J.-P., Toom-Sauntry, D., and Puxbaum, H.: Results of the "carbon conference" international aerosol carbon round robin test stage I, Atmos. Environ., 35, 2111–2121, 2001.

Sciare, J., Cachier, H., Oikonomou, K., Ausset, P., Sarda-Estève, R., and Mihalopoulos, N.: Characterization of carbonaceous aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach, Atmos. Chem. Phys., 3, 1743–1757, doi:10.5194/acp-3-1743-2003, 2003.

Sillanpää, M., Frey, A., Hillamo, R., Pennanen, A. S., and Salonen, R. O.: Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe, Atmos. Chem. Phys., 5, 2869–2879, 2005,
http://www.atmos-chem-phys.net/5/2869/2005/.

Subramanian, R., Khlystov, A. Y., and Robinson, A. L.: Effect of Peak Inert-Mode Temperature on Elemental Carbon Measured Using Thermal-Optical Analysis, Aerosol Sci. Tech., 40, 763–780, 2006.

Xu, J., Bergin, M. H., Greenwald, R., Schauer, J. J., Shafer, M. M., Jaffrezo, J. L., and Aymoz, G.: Aerosol chemical, physical, and radiative characteristics near a desert source region of northwest China during ACE-Asia, J. Geophys. Res., 109, D19S03, doi:10.1029/2003JD004239, 2004.

Yttri, K. E., Aas, W., Bjerke, A., Cape, J. N., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M. C., Forster, C., Hanssen, J. E., Hansson, H. C., Jennings, S. G., Maenhaut, W., Putaud, J. P., and Tørseth, K.: Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP, Atmos. Chem. Phys., 7, 5711–5725, doi:10.5194/acp-7-5711-2007, 2007.

Yu, J. Z., Xu, J., and Yang, H.: Charring Characteristics of Atmospheric Organic Particulate Matter in Thermal Analysis, Environ. Sci. Tech., 36, 754–761, 2002.