



BSI Standards Publication

# Ambient air quality — Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters

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**National foreword**

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English Version

## Ambient air quality - Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters

Qualité de l'air ambiant - Guide pour le mesurage du carbone élémentaire (EC) et du carbone organique (OC) déposés sur filtre

Außenluftqualität - Leitfaden zur Messung von auf Filtern abgeschiedenem elementarem Kohlenstoff (EC) und organisch gebundenem Kohlenstoff (OC)

This Technical Report was approved by CEN on 18 June 2011. It has been drawn up by the Technical Committee CEN/TC 264.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

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## **Foreword**

This document (CEN/TR 16243:2011) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

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## Introduction

For air quality across the European Union to be assessed on a consistent basis, Member States need to employ standard measurement techniques and procedures. The aim of this Technical Report is to present guidance on the measurement procedures to be followed when monitoring elemental carbon (EC) and organic carbon (OC) deposited on filters, following Council Directive 2008/50/EC on ambient air quality and cleaner air for Europe [1]. This requires the chemical speciation of the sub-2,5 µm size fraction of suspended particulate matter (PM<sub>2,5</sub>) in ambient air, as described in Annex IV:

### MEASUREMENTS AT RURAL BACKGROUND LOCATIONS IRRESPECTIVE OF CONCENTRATION

#### A. Objectives

*The main objectives of such measurements are to ensure that adequate information is made available on levels in the background. This information is essential to judge the enhanced levels in more polluted areas (such as urban background, industry related locations, traffic related locations), assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter. It is also essential for the increased use of modelling in urban areas.*

#### B. Substances

*Measurement of PM<sub>2,5</sub> shall include at least the total mass concentration and concentrations of appropriate compounds to characterise its chemical composition. At least the list of chemical species given below shall be included. SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, elemental carbon (EC), NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>, organic carbon (OC)*

#### C. Siting

*Measurements should be taken in particular in rural background areas in accordance with parts A, B and C of Annex III*

The method described in this Technical Report is focused primarily on harmonization and improvement of the data quality of thermal-optical measurement method for EC and OC used in monitoring networks, with guidance regarding the different protocols (analytical parameters) used currently within that method. The method is seen to be suitable for practical use in routine monitoring networks.

There are no traceable primary reference materials available for EC and OC analysis and there is no absolute scientific distinction between EC and OC. Therefore, the method set out in this Technical Report provides operational definitions of the measured quantities.

In February 2009, a workshop took place to provide an overview of the measurements made in Europe and worldwide. The workshop was organised by the Joint Research Centre in Ispra, Italy. The report of this workshop is available [2]. Consensus was reached for the following ranking of measurement techniques:

- a) thermal method with optical correction for EC and OC for samples collected on filters,
- b) other off-line analysis techniques for EC and OC for samples collected on filters,
- c) other on-line analysis techniques for EC and OC for samples collected on filters,
- d) other analysis techniques for either EC and/or OC,
- e) other analysis techniques measuring surrogates for either EC and/or OC (i.e. light absorption).

Due to the fact that the networks of the EU member countries have to measure EC and OC starting in June 2010 and CEN/TC 264/WG 35 "EC/OC in PM" has neither a mandate nor other funding available to perform necessary validation trials, WG 35 agreed on the following resolutions:

1) *Resolution 35*

*Given*

- *the urgent need for Member States to have a standardised method for EC and OC, as they are due to start sampling from June 2010, and*
  
- *in the absence of a mandate from the Commission,*

*the WG agrees that they will work on a CEN Technical Report for EC and OC as a priority. The text of the Technical Report will be made available to interested people (e.g. network operators) when it is ready. This TR will describe several protocols for thermal-optical methods that will give different results for EC and OC, because validation data is needed both to specify one standard method and to properly characterise that method. If a mandate is given, the priorities will be reconsidered at the time.*

2) *Resolution 36*

*WG 35 agrees that the Commission shall be formally informed that the Technical Report will be an unsatisfactory substitute for a full standard, as it will delay the start of comparable data across the EU – variations of more than 100 % for EC can be expected. It may also have financial consequences for some Member States who have to change their method when the standard is produced.*

3) *Resolution 37*

*WG 35 agrees that the Technical Report shall include optical charring correction using both transmittance and reflection data, and recording of results using both sets of data shall be encouraged.*

There are some open issues on the measurement procedure that can only be decided after further validation, e.g.:

- the applicable concentration ranges of the proposed method are limited by the optical correction and thermal protocols applied in the analysis of EC and OC; since the latter is dependent on the instrument as well as the chosen protocols no definitive values can be given;
  
- temperature measurement in the instrument ovens: location and reproducibility;
  
- influence of sampling artefacts on the data quality;
  
- provision and use of reference materials.

Attention is given to harmonizing the sampling with that for anions and cations in PM<sub>2,5</sub> as far as possible. The measurements for anions and cations are described in prCEN/TR 264125:2010 [3] and those for PM<sub>2,5</sub> in EN 14907:2005 [4].

NOTE: EN 14907:2005 is under revision and will be incorporated in the revision of EN 12341:1998 *Ambient air quality – Standard gravimetric measurement method for the determination of the PM<sub>10</sub> mass fraction of suspended particulate matter*.

## 1 Scope

This Technical Report gives guidance on the measurement of elemental carbon (EC) and organic carbon (OC) following the requirement for the networks of all EU member countries to measure EC and OC in particulate matter from June 2010 at background sites according to the Council Directive 2008/50/EC on ambient air quality and cleaner air for Europe.

The Technical Report describes the analytical procedures for determining EC and OC on quartz fibre filters as  $\mu\text{g}/\text{cm}^2$ , and the subsequent calculation of concentrations as  $\mu\text{g}/\text{m}^3$ . Sampling onto filters is to be done in accordance with EN 14907 for  $\text{PM}_{2.5}$ . The sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and ab/desorption of volatile organic compounds on the filter at the time of sampling.

The same analysis method may also be used for other size fractions. Any possible additional artefacts e.g. due to charring or higher concentrations of carbonates would need to be assessed in those cases.

The measurement procedures are applicable for:

- rural background,
- urban background,
- road side and
- industrial sites.

The scope includes non rural site measurements, to allow the assessment of additional exposure of people in urban areas as stated in the objectives of the council directive and to achieve coherence in the European approach. Measurements are made over a nominal sampling period of 24 h, and concentrations are expressed as  $\mu\text{g}/\text{m}^3$ , where the volume of air is the volume at ambient conditions near the inlet of the sampler at the time of sampling.

The applicable concentration range of the proposed method is limited by the optical correction, instrument, and thermal protocols applied in the analysis of EC and OC. Therefore no definitive values can be given. The experience from EMEP shows the applicability of the method at regional background sites.

## 2 Terms, definitions and abbreviations

For the purposes of this document, the following terms and definitions apply.

### 2.1 Terms and definitions

#### 2.1.1

##### total carbon

##### TC

total quantity of carbon atoms in a PM sample, whatever the constituent it belongs to. This includes EC, OC and IC

NOTE It is understood that the measure of TC released from a PM sample in a specified thermal desorption and oxidation process may be different for different protocols, and that it will not necessarily be all of the carbon atoms in the sample.

#### 2.1.2

##### elemental carbon

##### EC

fraction of the non-IC total carbon in a PM sample, characterised by its non-volatility according to a specified thermal / optical protocol. EC evolves from the sample by oxidation only



### 2.1.3

#### **organic carbon**

#### **OC**

fraction of the non-IC total carbon in a PM sample that is volatilised or pyrolyzed in a specified thermal/optical protocol

### 2.1.4

#### **inorganic carbon**

#### **IC**

fraction of carbon belonging to mineral species, including carbonates and other molecules

### 2.1.5

#### **carbonate carbon**

#### **CC**

fraction of carbon belonging to a carbonate group

NOTE Carbonate carbon (mainly  $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) is viewed as the only inorganic carbon fraction being released within the temperature range used in the thermal protocols.

### 2.1.6

#### **sampling artefact**

ab(d)sorption of gaseous species in (on) a PM sampling substrate (positive sampling artefact), and volatilization of particulate species from a PM sampling substrate (negative sampling artefact)

### 2.1.7

#### **PM<sub>x</sub>**

particulate matter suspended in air which passes through a size-selective inlet with a 50 % efficiency cut-off at x  $\mu\text{m}$  aerodynamic diameter

## 2.2 Abbreviations

PM	Particulate Matter
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
EUSAAR	European Super-sites for Atmospheric Aerosol Research
NIOSH	National Institute for Occupational Safety and Health
IMPROVE	US-Interagency Monitoring of Protected Visual Environments
TOR	Thermal Optical Reflectance
TOT	Thermal Optical Transmission
SOP	Standard Operating Procedure
PC	Pyrolytic carbon

## 3 Principle

The method for measuring EC and OC in ambient PM samples deposited on filters is based on the volatilisation and oxidation of carbon-containing PM components, the quantification of the carbonaceous gases released, with optical correction for the charring of organic to elemental carbon in the process (the thermal-optical method). The procedure described is a thermal-optical transmittance/reflectance (TOT/TOR) method, which is widely used in networks like EMEP, GAW (Global Atmosphere Watch), STN (US-Speciation Trend Network) and IMPROVE. This method can be implemented with various commercial instruments.

## 4 Materials and instruments

### 4.1 Materials

#### 4.1.1 Gases

The use of high purity gases, with low moisture content, is recommended:

- helium at least 99,999 % (% by volume);
- hydrogen at least 99,997 % (% by volume).

#### 4.1.2 Standard solution

Carbon-containing standard solutions (typically sucrose), with an accurately determined concentration ranging e.g. from  $0,4 \mu\text{g C } \mu\text{l}^{-1}$  to  $4 \mu\text{g C } \mu\text{l}^{-1}$ . Calibrating standard solutions should be prepared which cover the concentration range of the samples to be analysed.

#### 4.1.3 Other materials

- precision puncher,
- quartz boat for the filter punch,
- stainless steel tweezers for sample handling,
- clean cutting surface (e.g. aluminum foil or quartz fibre filter),
- analytical syringe or pipette for calibration using standard solutions, e.g.  $10 \mu\text{l}$  volume.

### 4.2 Instruments

#### 4.2.1 Sampling instruments

The performance requirements of the sampling instrument are given in EN 14907.

#### 4.2.2 Analytical instruments

A Thermo-Optical Analyser that allows EC and OC partitioning based on optical correction of charring by using the light transmission and/or light reflectance of the sample. Preferably, analysers that allow for simultaneous optical correction by both methods (transmission and reflectance) should be used.

##### 4.2.2.1 Performance requirements of the analytical instrument

Thermo-Optical EC and OC Analyser,

- the instrument detection limit should be  $0,2 \mu\text{g carbon per cm}^2$  of filter;
- the stability of repeated TC measurements of an external standard (e.g. sucrose solution) should be  $\pm 10 \%$  or  $\pm 0,5 \mu\text{g C/cm}^2$  (if  $10 \%$  would be less than  $0,5 \mu\text{g C/cm}^2$ ) over a working day (see 9.1.2.2).

## 5 Sampling

### 5.1 Filter material

Quartz fibre filters should be used. It is known that some quartz filters contain binding materials (e.g. silica glass). The use of quartz fibre filters without binding materials is recommended.

Filters should be taken from large batches of nominally identical filters. Filters should be uniquely identified and records kept to allow the identification of each filter with the manufacturer, purchase date, and where possible, manufacturer's batch and pack number.

Before field measurements are started, the filter batch(es) should be assessed for blank levels of EC and OC using the measurement method to be used for the field samples. Typically only OC will be present in significant quantities.

This assessment should cover:

- average blank concentrations,
- blank concentration variability.

Specific causes of blank variability such as higher blank values on filters closest to the top and bottom of the manufacturers' plastic containers should be investigated.

The details of the assessment of the filter material are not specified further in this Technical Report. The procedure used and results should be reported. When the assessment gives cause for concern (as discussed further below and in Clause 9), either the filters should be fired (see below) or alternative batches of filters should be obtained. Ongoing requirements for checks on the filter material are given in Clause 9.

### 5.2 Pre-treatment of filter material and handling

Blank values and the corresponding standard deviation need to be low compared to the expected measured values. In general, pre-treatment (firing) is not needed if the average OC content is  $\leq 2 \mu\text{g C/cm}^2$  and the standard deviation of the OC content is  $\leq 1 \mu\text{g C/cm}^2$ .

It is not unusual to fire filters before use, mainly to minimize OC levels in filters before using the filters. If firing is used, an assessment of blank values in the fired filters, similar to the assessment of unfired filters, should be carried out. If filters are pre-fired they should be heated at a minimum of 500 °C for a minimum of 1 h.

NOTE The main reason not to fire filters is to allow the use of the same filters for other purposes such as PM<sub>2,5</sub> measurement. Since firing can affect the handling and weighing results (due to water absorption and brittle filter material, for example) it is not generally recommended.

### 5.3 Conditioning and handling before and after sampling

The transport and storage details for filters are covered in Clause 7 and Clause 9.

### 5.4 Sampling duration and frequency

For the purposes of this Technical Report, the sampling period should be as required in EN 14907, i.e. close to 24 h. Other sampling durations may be chosen as needed for the measurement task., A sequential sampler (usually with 14 filters and one field blank) is also allowed.

In the absence of specific guidance, the monitoring frequency set out in the 4<sup>th</sup> Daughter Directive 2004/107/EC for indicative measurements can be used to determine the annual average EC and OC concentrations.

## 5.5 Field sampling and type of sampler

Sampling should be carried out in accordance with one of the standard methods of EN 14907, or an equivalent method. It is acknowledged that the sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and ab/desorption of volatile organic compounds on the filter at the time of sampling.

## 5.6 Site types

In the 2008/50/EC Directive the requirement for EC and OC measurements is limited to “rural background areas”. However, the aim of this Technical Report is to provide guidance on standardised methods that can be used at other types of monitoring site, including suburban, urban background, urban roadside and industrial sites.

## 5.7 Filter environment during sampling

The sampler can be located either indoors or outdoors. It is known that in both situations the sampled air temperature can deviate from ambient conditions, and this will have some effect on measured OC concentrations. At this stage, no specific demands on temperature control beyond those given in EN 14907 are given, but the sampling temperature should be kept as close as possible to ambient conditions.

# 6 Transport and storage

## 6.1 Handling

Filters have to be handled with clean tweezers, away from contamination sources (e.g. cigarette smoke and organic solvent vapours – including solvent based pens).

Transport and storage of filters should be performed in a clean container. They should be stored in individual containers, at least after sampling.

## 6.2 Time and temperature limits

Filters should not be kept longer than 16 days in the field. Transport and storage in the laboratory should be at temperatures below 5 °C if practicable. Within 28 days after sampling, filters should either be analysed or transferred to a refrigerator. Filters can be stored below 5 °C for a longer period. No further details can be given at this time.

NOTE OC concentration may change depending on handling. This may lead to different results with PM<sub>2,5</sub> concentrations when these come from 2 filters that have been sampled in the same way but handled differently, as different changes of OC may have occurred.

## 6.3 Coding

Each sample should be identified by an individual code in a way that avoids contamination of the analysed filter punches.

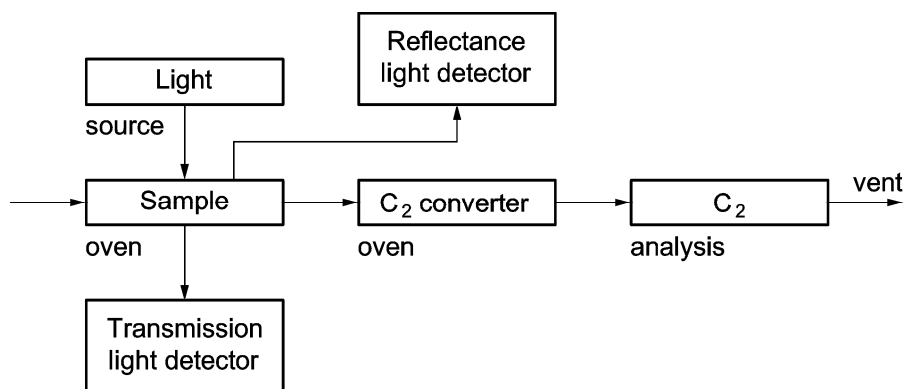
# 7 Analysis

## 7.1 General

To quantify the content of EC and OC in an aerosol sample collected on a quartz fibre filter, thermal desorption and oxidation at defined temperatures are used. Optical transmission through, or reflectance by the sample, is used for the correction of charring of OC occurring during the first temperature steps in inert carrier gas. CC may interfere with the determination of EC and OC (see 8.4).

A precision tool is used to punch a defined area (punch) from the aerosol sample, which is placed into the instrument's oven, which is purged with helium. In mode 1 (inert carrier gas), the oven's temperature is increased up to a first maximum, typically in the range 550 °C to 900 °C, depending on the thermal protocol used. OC either volatilises from the filter, or chars in/on the filter and forms pyrolytic carbon (PC). In mode 2 (oxidative carrier gas, e.g. 10 % O<sub>2</sub> in He), the instrument's quartz oven is cooled to 500 °C to 600 °C (depending on the thermal protocol), and a second temperature ramp is initialised. The final temperature in mode 2 typically in the range 800 °C to 900 °C (depending on the thermal protocol). In mode 2, EC and PC oxidise off the sample punch and form CO<sub>2</sub>. All gases evolved from the filter punch during modes 1 and 2 are carried into a manganese dioxide oven where organic vapours are oxidised to carbon dioxide (CO<sub>2</sub>) gas. CO<sub>2</sub> can be detected directly (NDIR detector), or subsequently mixed with hydrogen gas (H<sub>2</sub>) and carried along with the helium through a heated nickel catalyst which reduces the CO<sub>2</sub> to methane (CH<sub>4</sub>). The CH<sub>4</sub> is then measured using a flame ionization detector (FID). Internal (e.g. methane) and external (e.g. sucrose solution) carbon standards are used for calibration.

The function of the laser transmittance/reflectance is to correct for pyrolysis/charring of OC to PC, which can take place when OC is heated in mode 1 of the analysis. Not correcting for charring leads to an underestimation of OC and a corresponding overestimation of EC. This correction is made by continuously monitoring the reflectance and/or the transmittance of the punch, which is largely dominated by PC and EC. As charring takes place (i.e. PC is formed), the reflectance/transmittance drops, whereas it increases when EC and/or PC oxidised. Hence, the correction is made by determining the amount of carbon oxidised in mode 2 that is necessary to return the reflectance/transmittance back to the initial value before charring started. This approach assumes either that PC oxidises before the original EC in mode 2, or that the light extinction/reflection per unit mass of PC generated during the analysis is the same as the light extinction/reflection per unit mass of the original EC, at least until the reflectance/transmittance regains its initial value. Such assumptions are unlikely to be met. There is therefore an inherent uncertainty in the split point between EC and OC.



**Figure 1 — Simple scheme of a thermal-optical analyser**

The angle for reflectance measurement may vary from one instrument to another.

## 7.2 Charring correction based on optical transmission or optical reflectance measurement

The choice between reflectance and transmission optical charring correction usually gives rise to differences in the split point between EC and OC. Several parameters such as the type of site, the filter loading and PM composition are suspected to affect the difference between reflectance and transmission based determination of EC and OC. As it is currently impossible to advocate one or the other of these techniques based on reliable scientific evidence, it is recommended that both optical parameters should be recorded to allow an evaluation of charring correction a posteriori.

## 7.3 Thermal protocols

One of the widely used analytical protocols such as NIOSH/STN [5], IMPROVE [6] or EUSAAR-2 [7] should be used. When possible, repeated analysis with two or more protocols should be performed.

The analytical parameters for these 4 protocols are listed below (Table 1). Instrumental parameters should be recorded in a logbook as suggested in Annex A. Detailed descriptions of the analytical procedures to be implemented when using a Sunset Laboratory instrument are given in Annex B.

**Table 1 — Temperature set points and plateau durations for various widely used thermal protocols**

	NIOSH-like (quartz)	NIOSH 5040 <sup>b</sup>	IMPROVE <sup>c</sup>	EUSAAR_2
STEP	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s
He1	310, 60-80	250, 60	120, 150-580	200, 120
He2	475, 60	500, 60	250, 150-580	300, 150
He3	615, 60	650, 60	450, 150-580	450, 180
He4	870, 90	850, 90	550, 150-580	650, 180
He	No heating, 50			No heating, 30
He/O <sub>2</sub> 1 <sup>a</sup>	550, 45-60	650, 30	550, 150-580	500, 120
He/O <sub>2</sub> 2	625-650, 45-60	750, 30	700, 150-580	550, 120
He/O <sub>2</sub> 3	700, 45-60	850, 30	800, 150-580	700, 70
He/O <sub>2</sub> 4	770-775, 45-60	940, 120		850, 80
He/O <sub>2</sub> 5	870-890, 110-165			
<p>a A mix of oxygen in helium according to the protocol.</p> <p>b The temperature program for th NIOSH method is reported in [8].</p> <p>c The residence time at each temperature in the IMPROVE protocol is flexible and depends on the flame ionization detector (FID) signal. The residence time at a certain temperature ends when the FID returns to the baseline.</p>				

## 8 Artefacts and interferences

### 8.1 General

Generally, artefacts and interferences can occur during all steps measuring EC and OC. The most important ones are

- loss of semi-volatiles from the sample during sampling,
- additional adsorption of OC during sampling,
- chemical reactions leading to losses and/or gains of OC during sampling,
- adsorption or losses during transport or storage,
- charring of OC during analysis,
- the presence of carbonates in the sample,
- catalytic and other reactions during analysis affecting the OC versus EC split.

The first four of these effects are, to a large extent, common to measurements of PM, and should be seen in this context.

## 8.2 Sampling

Sampling artefacts are mainly to be expected for OC. These can be significant. Currently no recommendations on how to deal with these artefacts can be given.

The issue of OC artefacts should and will be further discussed in a future European Standard dealing with EC and OC, although in CEN/TC 264/WG 15 "PM<sub>10</sub> and PM<sub>2,5</sub>", sampling artefacts are currently considered as part of the "true" PM<sub>10</sub> and PM<sub>2,5</sub>, by definition. Since the relative contribution of artefacts to the mass and to the uncertainty of OC is expected to be much larger than for PM, WG 35 may take a different view on this in the future.

The field and laboratory blank values (covered in Clause 9) generally show that a certain amount of organic substance is bound on to the quartz fibre filter and may accumulate on a filter by mechanisms other than the active sampling. To avoid additional OC artefacts, the use of organic liquids and aerosols in the vicinity of the samples should be avoided, as described in the transport and storage section.

## 8.3 Transport and storage

Some positive (OC adsorption on filters during transport and storage) or negative artefacts (OC losses during transport and storage at elevated temperatures) can occur (see 5.7 and 6.2).

To reduce positive artefacts, samples should be kept and handled away from any contamination sources.

## 8.4 Analysis

- a) Carbonate carbon (CC) will interfere with the organic carbon and/or the elemental carbon fraction in a way that depends on which temperature protocol is used. If the punch subjected to analysis is still coloured after the analysis is finished, a significant inorganic material content (soil/crustal material) can be suspected, and therefore inorganic carbon interference is likely.

Possible methods for assessing carbonate carbon are given in Annex C. No recommendations on how often the CC assessment has to be performed can currently be given. Policies for the frequency and timing of CC assessment are left to the responsible personnel. The results of the analysis should not be subtracted from the EC and/or OC measurement values but recorded to allow the estimation of possible interferences.

- b) Light absorbing organic carbon can affect the laser correction as these species are removed from the filter or pyrolyzed during mode 1, causing changes in transmission/reflectance. No recommendation regarding this can currently be given.
- c) Certain elements (e.g. Na and K), which can be present either as contaminants in the filter or as part of the deposited material, have been shown to catalyse the removal of EC at lower temperatures, thus affecting the thermal evolution of EC. This interference may be reduced by choosing filters with low alkali metal contents. No further recommendation can currently be given.
- d) Oxygen donating species in the samples may interfere with the EC and OC analysis. Filters that remain coloured after the analysis may be an indication of the presence of such species. No further recommendation can currently be given.
- e) Samples that are heavily loaded with EC will lead to difficulties in determining the split point between EC and OC, as the transmittance and/or the reflectance signal will be saturated. Also, depending on the analytical protocol, oxidation of EC may not be finalised within the analytical run.

The applicable concentration range of the proposed method is limited by the optical correction, instrument, and thermal protocols applied in the analysis of EC and OC. Therefore, no definitive upper concentration limits can be given to the method. One possibility to avoid saturation is to reduce the sampled volume by e.g. shorter sampling intervals or lower volume flow rates.

NOTE Appropriate size selective inlets have to be used with lower volume flow rates. Different flow rates or changes of filter sizes lead to varying face velocities which may influence the size of sampling artefacts

## 9 Quality assurance/quality control (QA/QC)

### 9.1 QA/QC for sampling parameters

QA/QC for parameters such as sampled volume, size fraction, and losses of semi-volatiles should be performed by following the relevant procedures specified in EN 14907, and other procedures described in Clauses 5 and 6.

#### 9.1.1 QA/QC for field artefacts

##### 9.1.1.1 Field blanks

For every 14 field samples there should be at least one field blank, a nominally-identical filter to those being sampled, which is prepared and transported to and from the monitoring site in the same way as the sampled filters. The full details of how the blank filters are transported and kept at the monitoring site should be recorded.

The field blanks should be analysed for EC and OC in the same way as the field samples. The results should be reported together with the field sample results.

The detailed use of the field blank results is left to the responsible personnel. They may be used, for example, to help estimate the measurement uncertainty of results, to identify contaminated sets of samples, or to help improve field and laboratory procedures. The current practice within EMEP and European standards (ENs) related to the 4<sup>th</sup> Daughter Directive is that the field blank concentrations are not subtracted from sampled concentrations.

NOTE Typical field blank values are up to 4 µg OC/cm<sup>2</sup>.

#### 9.1.2 QA/QC for laboratory analysis

##### 9.1.2.1 Laboratory blanks

The analysis of laboratory blanks serves two purposes:

- to check that the batches of filters used have low EC and OC content when they are purchased; and
- to check that the laboratory environment and laboratory procedures in use do not introduce significant OC and/or EC contamination, either from material collected onto the blank filters or from contamination within the instruments.

These purposes will generally be addressed in parallel.

The requirement for initially assessing whether a specific filter type is suitable for EC and OC monitoring is described in 5.1 and 5.2.

Alongside the filter checks given in 5.1 and 5.2, the laboratory procedures and environment will be checked by analyzing laboratory blanks. It is recommended that laboratory blanks are analysed at least each working week, or when very high field blank concentrations are found.



Details of the laboratory blank procedures are left to the responsible personnel. These procedures should be recorded, together with the analytical data for the laboratory blanks.

#### **9.1.2.2 Calibration for TC**

Because there are no traceable primary reference materials available for atmospheric EC and OC, calibration is currently limited to that of the TC and to the response of the carbon detector.

The principal calibration of the analytical system can be conducted via TC values provided by blank filter samples spiked with calibration solutions of pure organic compounds such as sucrose or oxalic acid. Further information is given in Annex B and in the analytical instrument user's manual. The instrument should be regularly calibrated (e.g. every four months) and after a major modification of the system.

The calibration should be checked at least every measurement day (e.g. by analysis of a control filter – see 9.1.3.1) with a quantity of TC relevant to the quantities in the field samples being analysed. The results should be within  $\pm 10\%$  or  $\pm 0,5 \mu\text{g C/cm}^2$  (if  $10\%$  would be less than  $0,5 \mu\text{g C/cm}^2$ ) of the expected value. If not, the reasons have to be investigated (see Annex B) and the result should be recorded with the other analytical data.

#### **9.1.2.3 Repeatability**

The repeatability of the analytical system should be determined from either the spiked filter calibrations or from "control filter" measurements (see 9.1.3.1). A repeatability of  $5\%$  (one standard deviation) can be viewed as sufficient. The data of the calibration check may be used for the repeatability data

### **9.1.3 Other recommended QA/QC checks**

#### **9.1.3.1 Use of quality control filters**

A so-called "control filter" is a large filter that has sampled ambient air through a high volume sampler, typically for 24 h. 5 punches of this filter are analysed so that a mean TC value and a mean EC/TC ratio are determined as local reference values. These five punches should also be used to check for homogeneous loading of the filter.

Analysis of new punches from the control filter, for example on each measurement day, give valuable information about both the TC calibration and the consistent operation of the temperature profiles and optical correction, and hence the EC versus OC split. Typically, TC values should not differ by more than  $5\%$ , and the EC/TC ratio should be used for quality check, although no specific value on the repeatability of the latter ratio can currently be given.

#### **9.1.3.2 Calibration gas injections**

Some analytical instruments incorporate an injection of calibration gas (e.g. such as  $5\%$  methane in helium) after each analytical run for internal calibration (to correct for any drift in the response of the carbon detector). This provides a calibration of the flame ionization detector.

Other uses of calibration gases can be:

- calibration of the carbon detector,
- check of the efficiency of the catalyst and/or converter.

Action criteria are left to the user.

### 9.1.3.3 Checks on thermometers and optical systems

Direct checks on the accuracy of the temperature profile used for the desorption, and of the optical system used for the charring correction, are encouraged. No practicable direct methods are available currently. The use of a quality control filter provides a practical indirect check.

## 10 Calculation of concentrations of EC and OC

To determine the EC and OC concentration it is necessary to convert the results from the analyser, which are in  $\mu\text{g C/cm}^2$ , to  $\mu\text{g C/m}^3$ .

It is therefore necessary to know the volume of air sampled, and the sampled area on the filter. This is of course smaller than the area of the filter itself.

The volume of air that has been sampled is generally recorded by the sampler, following EN 14907.

The sampled area has to be measured by the operator. This measurement can be done in several ways. It can be done by measuring the sampled diameter once, or occasionally, and using this as a fixed parameter. The sampled diameter can alternatively be measured on each filter, for example using an automated optical instrument.

To calculate the concentration of  $\mu\text{g C/m}^3$  Equations (1) and (2) can be used.

Calculating the loaded surface area

$$a = \pi \cdot (d / 2)^2 \quad (1)$$

where

$\pi$  is 3,142

$a$  is the sampled area of the filter, in  $\text{cm}^2$

$d$  is the diameter of the sampled area of the filter, in  $\text{cm}$

For the calculation of the concentration of C, use Equation (2)

$$c_1 = B \cdot \frac{a}{V} \quad (2)$$

where

$c_1$  is the concentration of C, in microgram C per cubic metre ( $\mu\text{g/m}^3$ )

$B$  is the measured value of C of the filter punch, in microgram C per square centimetre ( $\mu\text{g C/cm}^2$ )

$a$  is the loaded filter area, in square centimetre ( $\text{cm}^2$ )

$V$  is the sampled volume, in cubic metre ( $\text{m}^3$ ) (the volume at ambient conditions near the inlet of the sampler at the time of sampling)

## 11 Data reporting

### 11.1 General

Two levels of EC and OC data reporting can be differentiated: full reporting with all auxiliary data for future multipurpose use such as uncertainty assessment, and a minimum requirement reporting to fulfil the preliminary foreseen needs for the reporting for the European Commission.

### 11.2 For the European Commission

The following data is recommended for reporting to the European Commission:

- concentration data of EC and OC, in microgram C per cubicmetre ( $\mu\text{g C/m}^3$ ) (referred to the ambient temperature and pressure),
- thermal protocol, see Table 1 in 7.3,
- optical correction method (TOT or TOR ),
- site type and identification,
- sampling date,
- information about whether the filter has also been used for PM mass concentration measurements.

### 11.3 Auxiliary data

In addition to the data reported to the European Commission, data on each filter has to be recorded and stored with regard to

- date of analysis,
- sampling start and end time,
- ambient temperature during sampling,
- place, time and conditions of transport and storage,
- laboratory filter blank concentrations for EC and OC in  $\mu\text{g/cm}^2$ ,
- field blank concentrations for EC and OC in  $\mu\text{g/cm}^2$ ,
- time spent by filters in the field,
- conditions during equilibration (humidity, temperature and time period) if mass concentration is also determined.

These data is needed to assess uncertainties. The filter blanks are also used for the calculation of the lower detection limit.

Institutes conducting EC and OC measurement are encouraged to measure the concentrations if possible with two different protocols. This may lead to four different values for both EC and OC since each protocol may use reflectance or transmission optical measurements for the correction. Data collected in this way will lead to an extended database which will facilitate the development of the European standard method.

## Annex A (informative)

### Example of a logbook

This annex provides an example of how to write the logbook, which should be completed to document the analysis of the quartz fibre filter punches by TOT/TOR instrument.

Date (dd/mm/yy)

Operator:

Samples:

	Cylinder Pressure (bar)	Flow Rate (cc/min)
Air		
H <sub>2</sub>		
He-1		
He-2		
He-3		
He / O <sub>2</sub>		
CH <sub>4</sub> std		

Thermal Protocol:

Output Data File:

Calibration constant or file

Punch Area

1,5 cm<sup>2</sup>

1,0 cm<sup>2</sup>

other cm<sup>2</sup>

Front Oven Temp.	°C	FID (nA)	Pressure (psi)	Blank Filter T Laser      R Laser	
Back Oven Temp.	°C				Dark Signal
CH <sub>4</sub> Oven Temp.	°C				PD2Lo

Specific Comments:

Sample	Comment

**NOTE** It is recommended to store the complete thermogram including the temperature and pressure course, as well as the transmission and/or reflection signal.

## Annex B (informative)

### An example of a standard operating procedure for analysing EC and OC

#### B.1 General

This annex gives specific information about a commonly used commercial instrument<sup>1)</sup>.

#### B.2 Start-up

Ensure that the He, He/Ox, Air and Hydrogen gas cylinder pressures are at least 5 bar. Set gas cylinder delivery pressures to 1,5 bar - 2 bar.

If the program has been turned off, restart it by double-clicking on the OCECINST icon on your desktop. If the program is in standby mode, click the CONTINUE button.

Set gas flow rates using the gas valves on the instruments lower control unit according to the user's manual (example: Table B.1) and record flow rate in the logbook that stated in Table B.1, and record flow rates in the log book manual.

**Table B.1 — Standard procedure to run the Sunset lab instrument**

Gas	Flow rate cm <sup>3</sup> min <sup>-1</sup>
Air	290
H <sub>2</sub>	50
He-1	50
He-2	12 to 15
He-3	67 to 70
He/O <sub>2</sub>	12 to 15 <sup>a</sup>
Cal	- 15
<sup>a</sup> The flow should be equal to that of He-2.	

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1) The Sunset lab instrument is a product of Sunset Laboratory Inc., Oregon, USA, that is identified by its trade market name. It is unique and has a sole manufacturer. This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by CEN of the product named.

In order to ignite the flame in the FID set the H<sub>2</sub> flow to > 100 cc min<sup>-1</sup>. For recent models of the instrument, ignite the FID by pressing the red button on the upper part of the instrument control unit. For old models, the FID is lit by igniting the H<sub>2</sub> gas flowing from the FID exhaust outlet. Once the flame has been lit (usually a small pop can be heard), return the H<sub>2</sub> flow rate to its operating level. Check that the flame is alight by bringing a cold metallic surface towards the FID exhaust outlet: Condensation of water vapour should be observed when the flame is on.

Select the proper PARAMETER FILE to be used and either select the RAWDATA FILE or enter a new file name into the RAWDATA TEXT BOX.

Fill in the following variables in the instrument logbook: Date; operator; sample name; gas cylinder pressures; flow rates; parameter file; output data file; punch area; calibration constant; temperature of the front oven, of the back oven and of the methanator; instrument pressure; transmittance and reflectance signal with a clean quartz fibre filter punch; transmittance and reflectance dark signal.

In the off-line mode:

- a) the back oven temperature should be approximately 870 °C,
- b) the front oven temperature should be approximately < 50 °C,
- c) the CH<sub>4</sub> oven temperature should be approximately 500 °C,
- d) the instrument pressure should be in the range 0,5 psi to 4 psi (off line pressure: approx. 1 psi)<sup>2)</sup>,
- e) for a blank filter the transmittance signal should be in the range indicated by the manufacturer,
- f) the FID can only be checked for a signal or a numerical readout when the cycle commences; the peak area for the calibration peak should be in the range indicated by the manufacturer. As this variable varies over a wide range, the range of normal values should be established for each instrument.

### B.3 Running an external calibration standard

Punch a 1,0 or 1,5 cm<sup>2</sup> from a clean quartz fibre filter.

Open the door to the oven and place it safely on a flat surface.

Pull the quartz boat partially out from the oven using the stainless steel tweezers and place it on the support arm. Place the punched filter piece on the 1,0 cm<sup>2</sup> or the 1,5 cm<sup>2</sup> boat.

Slide the boat in gently until it stops by the tip of the thermocouple, and then pull it backwards by one (1) mm.

Close the oven door ensuring that the O-ring seals tightly into the front of the oven and close the door by a clamp. Check that the oven pressure is in the range of 0,25 psi - 4 psi.

Select CLEAN OVEN from the options menu to clean the filter punch.

After the CLEAN OVEN CYCLE, open the oven door, pull the quartz boat partially out from the oven using the stainless steel tweezers and place it on the support arm.

Use a pipette to spike 10 µl of the sucrose calibration standard (4 µg C to 40 µg C) to the filter punch on the boat (see Annex D). Slide the boat gently in until it stops by the tip of the thermocouple and then pull it backwards by 1 mm. Close the oven door, ensuring that the O-ring seals tightly into the front of the oven and close the door by a clamp, and allow the filter punch to dry for 8 min to 20 min inside the oven. Check that the oven pressure is in the range of 0,5 psi to 4 psi.

---

2) 1 psi = 6894,8 Pa

Analyse the sample as described under point f and g in B.5.

Compare the amount of carbon determined for the external calibration standard with the expected value; if the difference exceeds 10 % or 0,5 µg C/cm<sup>2</sup> (if 10 % would be less than 0,5 µg C/cm<sup>2</sup>), consider the following actions:

- a) Perform an additional analysis of the external calibration standard.
- b) Make a new calibration standard or a new stock solution.
- c) Change the calibration constant set in the instrument in calcpar.txt (see Annex D).

#### **B.4 Running an external long term calibration standard**

Three times a year run calibration using external gaseous standards (e.g. CO<sub>2</sub> or CH<sub>4</sub>).

What is necessary:

- a) a cylinder of pure C-containing gas (e.g. CO<sub>2</sub>, CH<sub>4</sub>) or with a certified concentration of C-containing gas in He, equipped with a pressure reducer set to close-to-normal pressure (1,5 bar recommended), and connected to a septum holder;
- b) a gas micro-syringe that allows you to inject 1 µg C to 5 µg C per injection. The volume of the syringe depends on the concentration of your gaseous standard;
- c) a T with a septum, and connections to the usual analytical line (see Figure 1);
- d) the carbon thermal analyser calibrated according to the standard procedure.

Principle:

The amount  $m$  of C contained in a volume  $V$  in the micro-syringe is equal to:

$$m = M \cdot \chi \cdot p \cdot V / (R \cdot T) \tag{B.1}$$

where:

$M$  is the carbon molar mass (12 10<sup>-3</sup> kg mol<sup>-1</sup>)

$\chi$  is the content of the standard gas in the cylinder (if pure gas,  $\chi = 1$ )

$p$  is the room pressure, in Pascal (normally 101325 Pa)

$V$  is the standard gas volume taken with the syringe, in microlitre (µl)

$R$  is the gas constant ( $R = 8,314$  J K<sup>-1</sup> mol<sup>-1</sup>)

$T$  is the room temperature, in Kelvin (normally  $T = 298$  K)

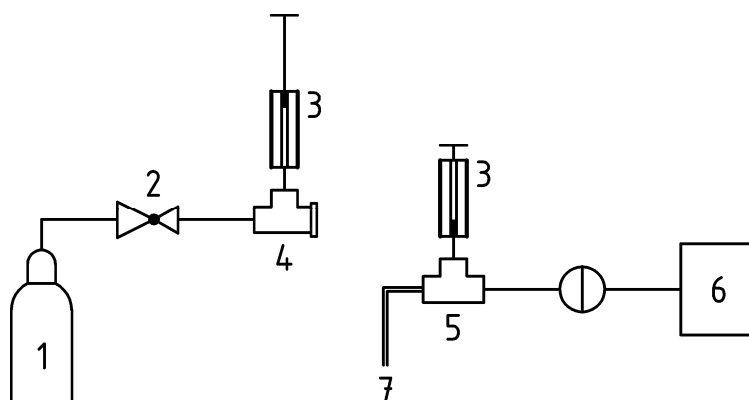
$m$  is the mass of carbon contained in volume  $V$  into the syringe, in microgram (µg)

In standard conditions ( $p = 1013,25$  hPa;  $T = 25$  °C), 10 µl of pure CO<sub>2</sub> or CH<sub>4</sub> contain 4,9 µg C.

A known volume of standard gas is injected during each step of the analysis. The amount of carbon detected by the instrument is compared to the amount of C calculated from Equation (B.1).



Figure B.1 — Inserting a T with a septum to the carrier gas line of a Sunset lab carbon analyser



**Key**

- |   |                       |   |                         |
|---|-----------------------|---|-------------------------|
| 1 | standard gas cylinder | 5 | T with septum           |
| 2 | pressure reducer      | 6 | carbon thermal analyser |
| 3 | gas syringe           | 7 | carrier gas             |
| 4 | septum holder         |   |                         |

Figure B.2 — Schematic of procedure points 4 and 5

Look at the amount of C determined by the instrument for each injection and compare to the expected value calculated.

NOTE The speed of injection of the gas standard should be as constant as possible, in order to obtain comparable peak shapes or use an electrical driven gas injection valve with a fixed loop.

**PROCEDURE:**

Insert the T with the septum just upstream the point where the sample is usually loaded (see Figure B.2).

Run the analysis protocol with a punch of blank filter 2 to 3 times, until no more C is detected by the instrument.

Start a thermal analytical run.



Take a precisely known volume of standard gas from the cylinder through the septum. The volume of gas in the syringe should be equilibrated to room temperature and pressure. Log the volume injected, and the room pressure and temperature.

Inject the whole volume during the analytical step 1 (e.g. He mode, temp step 200 °C in EUSAAR\_2).

Repeat steps 4 and 5 for each analytical step in the He mode and the Ox mode.

Steps 3 to 6 can be repeated e.g. injecting different volumes of standard gas.

## **B.5 Running a routine sample**

A new sample should only be placed into the oven when the computer displays

"SAFE TO PUT IN A NEW SAMPLE" in the green message bar.

Punch a 1,0 cm<sup>2</sup> or 1,5 cm<sup>2</sup> from a clean quartz fibre filter.

Open the door to the oven and place it safely on a flat surface.

Pull the quartz boat partially out from the oven using the stainless steel tweezers and place it on the support arm. Place the punched filter piece on the 1,0 cm<sup>2</sup> or the 1,5 cm<sup>2</sup> boat.

Slide the boat in gently until it stops by the tip of the thermocouple, and then pull it backwards by one 1 mm.

Close the oven door ensuring that the O-ring seals tightly into the front of the oven and close the door by a clamp. Check that the oven pressure is in the range given by the manufacturer.

Type in the sample identification name and select with respect to actual punch size.

Click the START ANALYSIS button on the computer.

## **B.6 Shutdown of instrument**

If intending to return to the analyser the day after and in the following days, click on the STANDBY BOX, and close the gas valves on the instruments lower control unit. The back oven will be maintained at a lower than normal temperature, the laser will be shut off and the pressure is close to zero as the flow of helium is kept rather low.

If not intending to use the instrument for the following 10 days, choose EXIT from the file menu. This will turn off the power to the instrument, and allowing the ovens to cool off. The gas valves on the instruments lower control unit could be tightened gently. The gas supply can now be turned off.

## Annex C (informative)

### Methods for the assessment of carbonate carbon

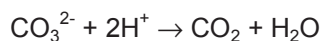
Across Europe, CC (estimated from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  measurements) accounts for about 2,5 % of TC in  $\text{PM}_{2,5}$ . Maximum CC/TC values (over 24 h averages) range from <0,03 to >0,35 (see Table C.1). CC/EC maximum ratios are site dependent and range from 0,05 to > 1,0. A protocol in which CC evolves together with EC can therefore lead to significant errors in EC determination. There are several methods to assess or to eliminate the interference from CC in the measurement of OC or EC, i.e.

- **C1**- CC can be removed from the sample by sample acidification with HCl fumes [9].
- **C2**- There is a protocol for direct CC determination, adapted from Pio et al [12], described below.
- **C3**- Jankowski et al., described a “three step” combustion method to measure CC [10].
- **C4**- A calcium analysis can be performed by ion chromatography analysis of the samples following a protocol such as prCEN/TR 264125:2010 [3]. The results can then be used to estimate the maximum amount of  $\text{CaCO}_3$  present in the samples.
- **C5**- CC can be estimated using software within the analytical instrument, such as the Sunset Laboratory instrument.

No conclusions or recommendations can be made regarding CC measurement at this time. Comments on some of the methods are given below.

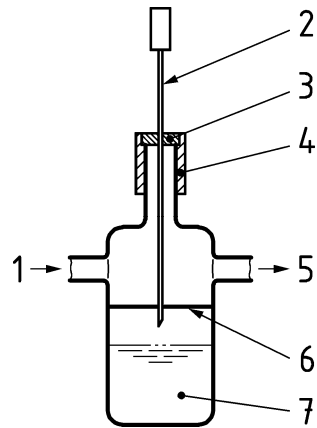
**Regarding C1:** It should be noted that the use of this method can lead to irreversible damage to some of the most widely used OC and EC thermal-optical analysers.

**Regarding C2:** The determination of carbonate in atmospheric PM samples deposited on filters by acidification and quantification of the  $\text{CO}_2$  evolved as first described by Cadle [11] and validated by Pio [12] looks simple, accurate, and implementable by most laboratories that already perform OC and EC analyses. Indeed, suitable glassware is the only equipment needed (Figure C.1) if use is made of the  $\text{CO}_2$  detection chain of the OC/EC instrument. After the filter punch is placed at the tip of a needle in the enclosure, the glass enclosure has to be fully flushed by the carrier gas (so that the  $\text{CO}_2$  signal at the detector reaches the baseline). Then the filter punch is dropped into the concentrated phosphoric acid concentration ( $\text{H}_3\text{PO}_4$ ), and  $\text{CO}_2$  evolves.



The  $\text{CO}_2$  signal should be integrated and compared to standards.

The volume of the reactor should be as small as possible and the carrier gas flow rate chosen to ensure an optimised response of the detector. When using a NDIR  $\text{CO}_2$  detector,  $\text{H}_2\text{O}$  interferences should be eliminated by stripping out water (e.g. with Silicagel). Using the detection chain of commercial OC/EC analysers (methaniser + FID) has not been tested yet, but is very likely to be feasible.

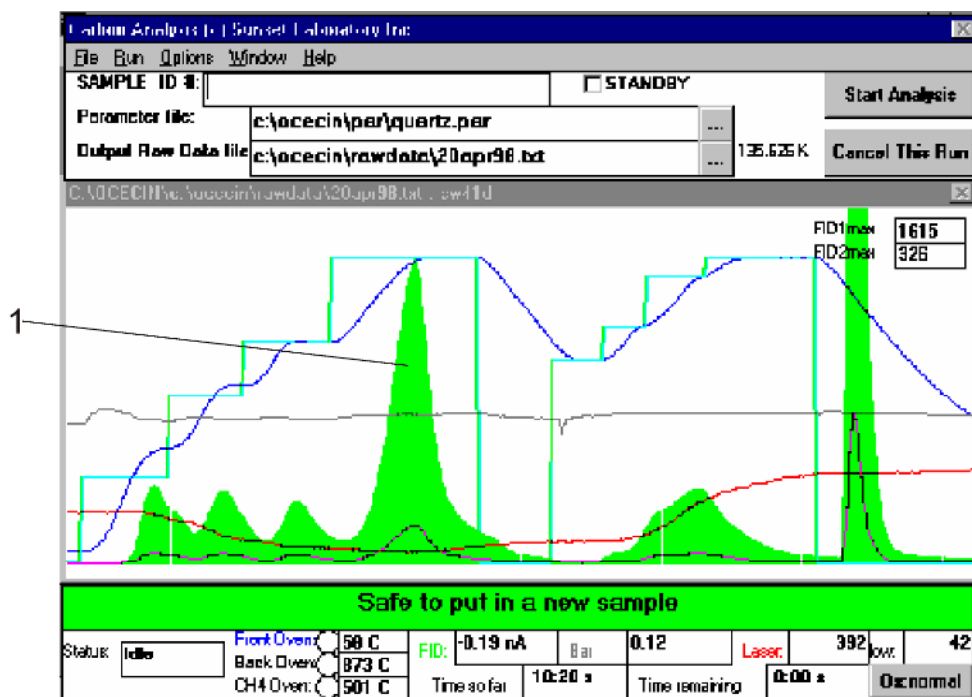


**Key**

- |   |                                  |   |   |
|---|----------------------------------|---|---|
| 1 | He or N <sub>2</sub> carrier gas | 5 | to CO <sub>2</sub> detection            |
| 2 | needle                           | 6 | filter punch                            |
| 3 | septum                           | 7 | H <sub>3</sub> PO <sub>4</sub> solution |
| 4 | cap                              |   |   |

**Figure C.1 — Apparatus for determining the amount of carbonate deposited on a filter punch**

**Regarding C5:** When there is a substantial amount of CaCO<sub>3</sub> present in the sample, it will show up as a distinct peak (normally at a temperature above 800 °C) in the EC and OC analysis thermogram. Figure C.2 shows a thermogram obtained for a Total Suspended Particulate sample, which was collected in the Negev desert, Israel, during a dust storm and analysed with the “quartz” (NIOSH-like) temperature protocol. The last peak in mode 1 is essentially due to CaCO<sub>3</sub>.



**Key**

- 1 peak with mainly CaCO<sub>3</sub>

**Figure C.2 — EC and OC analysis thermogram for a TSP sample with a large amount of CaCO<sub>3</sub>**

The left part of Figure C.3 shows the results which are obtained when the calculations for EC and OC are done with the software of Sunset Lab in the standard way. The CC is counted as OC and is included in the OC result. However, the software offers the possibility to set lower and upper (start and end) limits for the CC peak and to estimate OC and CC separately. The results of this (when using lower and upper limits of 190 s and 296 s, resp.) are shown in the right part of Figure C.3. The yellow area is counted as CC, but what is below it is counted as part of the OC.

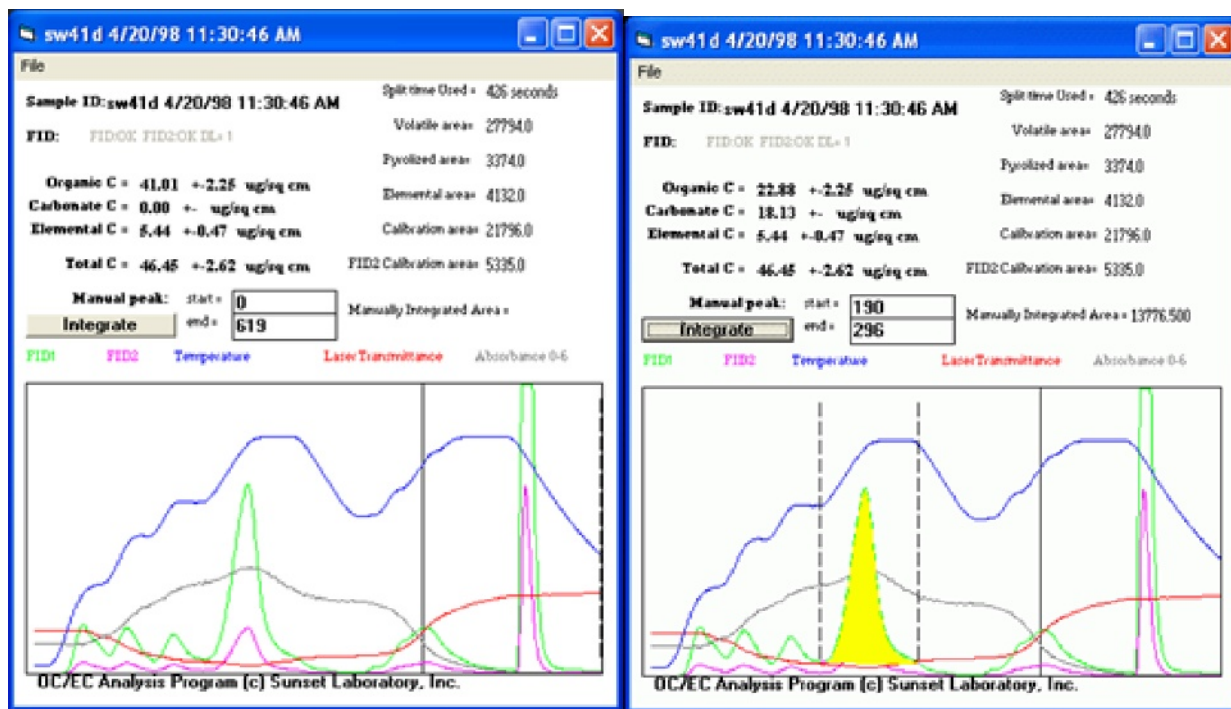


Figure C.3 — Results from the Sunset Lab calculation program for the thermogram of Figure C.2.

NOTE The left part shows the results when the calculation is done in the standard way; the right part gives the results when lower and upper bounds are manually set for the CC peak.

Table C.1 — CC / EC and CC / TC ratios across Europe, estimated from Calcium and Magnesium measurements, by assuming that calcium comes from CaCO<sub>3</sub>, and magnesium from MgCO<sub>3</sub>

Type	Site	Country	PM2,5 average	EC/PM2,5 average	TC/PM2,5 average	C(CaCO <sub>3</sub> )/EC			C(CaCO <sub>3</sub> )/TC			C/MgCO <sub>3</sub> /EC			C(MgCO <sub>3</sub> )/TC			C(CO <sub>3</sub> )/EC	C(CO <sub>3</sub> )/TC
						average	stdev	max	average	stdev	max	average	stdev	max	average	stdev	max	average	stdev
urban	Duisburg	(DE)	25,4	0,10	0,23	0,02	0,01	0,11	0,01	0,00	0,03	0,01	0,01	0,06	0,00	0,00	0,02	0,02	0,01
near-city	Ispra	(IT)	32,2	0,06	0,34	0,02	0,08	1,08	0,00	0,01	0,07	0,00	0,01	0,06	0,00	0,00	0,01	0,02	0,00
urban	Las Palmas	(ES)	20,8	ND	0,39				0,01	0,00	0,02				0,02	0,04	0,24		0,03
urban	Llodio	(ES)	25,5	ND	0,31				0,01	0,01	0,05				0,01	0,01	0,03		0,02
urban	Tarragona	(ES)	23,1	ND	0,33				0,02	0,01	0,05				0,01	0,00	0,03		0,02
urban	Huelva	(ES)	20,8	ND	0,27				0,02	0,01	0,06				0,02	0,02	0,13		0,04
urban	Algeriras	(ES)	25,3	ND	0,19				0,01	0,01	0,07				0,01	0,01	0,03		0,02
urban	Barcelona S	(ES)	28,3	ND	0,39				0,01	0,01	0,05				0,01	0,01	0,03		0,02
urban	Bologna	(IT)	35,8	0,08	0,25	0,08	0,06	0,28	0,03	0,02	0,10							0,08	0,03
kerbside	Madrid	(ES)	39,4	ND	0,42				0,03	0,06	0,35				0,01	0,02	0,09		0,03
kerbside	Barcelona H	(ES)	33,3	ND	0,34				0,02	0,02	0,15				0,00	0,00	0,02		0,02
rural	Chaumont	(CH)	8,1	0,05	0,20	0,06	0,04	0,13	0,01	0,01	0,04	0,03	0,03	0,13	0,01	0,01	0,04	0,09	0,02
rural	Streithofen	(AT)	17,5	0,11	0,30	0,01	0,01	0,06	0,00	0,00	0,02	0,00	0,00	0,03	0,00	0,00	0,02	0,01	0,00
rural	Illmitz	(AT)	19,9	0,08	0,28	0,01	0,02	0,09	0,01	0,01	0,03	0,01	0,00	0,02	0,00	0,00	0,01	0,02	0,01
urban	Zuerich	(CH)	19,0	0,09	0,25	0,02	0,02	0,14	0,01	0,01	0,03	0,01	0,01	0,06	0,00	0,00	0,03	0,03	0,01
urban	Basel	(CH)	17,95	0,09	0,25	0,03	0,02	0,14	0,01	0,01	0,04	0,01	0,02	0,13	0,00	0,04	0,04	0,04	0,01
urban	Linz	(AT)	21,9	0,18	0,30	0,01	0,01	0,04	0,01	0,00	0,03	0,00	0,01	0,06	0,00	0,00	0,03	0,01	0,01
urban	Wien W	(AT)	21,8	0,17	0,36	0,01	0,01	0,08	0,00	0,00	0,03	0,00	0,00	0,03	0,00	0,00	0,01	0,01	0,01
urban	Praha	(CZ)	19,8	0,07	0,33	0,02	0,05	0,30	0,00	0,01	0,05	0,01	0,04	0,25	0,00	0,01	0,04	0,03	0,01
kerbside	Bern	(CH)	22,75	0,17	0,31	0,01	0,01	0,04	0,01	0,00	0,02	0,00	0,00	0,01	0,00	0,00	0,00	0,01	0,01
kerbside	Wien S	(AT)	38,5	0,24	0,40	0,02	0,02	0,10	0,01	0,01	0,04	0,01	0,00	0,03	0,00	0,00	0,01	0,03	0,02

## Annex D (informative)

### Preparation of stock sucrose solutions and calibration standards

This annex gives guidance on how to prepare stock sucrose solutions and calibration standards.

Preparation of stock sucrose ( $C_{12}H_{22}O_{11}$ ) solutions:

Dissolve sucrose (9,5 g) in reagent grade water and dilute to 100 ml. This solution has a concentration of  $40 \mu\text{g C } \mu\text{l}^{-1}$ . The stock solution should be stored in a refrigerator ( $4 \text{ }^\circ\text{C}$ ), but for not for a period longer than 6 months.

$$(9,5 \text{ g sucrose} / 100 \text{ ml H}_2\text{O}) (144 \text{ g C/mol} / 342 \text{ g/mol}) (10^{-3} \text{ ml} / \mu\text{l}) (10^6 \mu\text{g/g}) = 40 \mu\text{g C } \mu\text{l}^{-1}$$

Calibration standards are prepared which span the measurement range of the samples to be analysed by diluting the stock solution with reagent or Milli-Q water (for example, see Table D.1).

**Table D.1 — Preparation of stock sucrose solutions and calibration standards**

	<b>Sucrose stock</b> $\mu\text{g C } \mu\text{l}^{-1}$	<b>Volume of sucrose stock</b> ml	<b>Volume final</b> ml	<b>Final concentration</b> $\mu\text{g C } \mu\text{l}^{-1}$
Standard 1	40	1	100	0,4
Standard 2	40	5	100	2,0
Standard 3	40	10	100	4,0

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