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Ambient air — Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters

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National foreword

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Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters

Air ambiant - Mesurage du carbone élémentaire (EC) et du carbone organique (OC) prélevés sur filtre

Außenluft - Messung von auf Filtern abgeschiedenem elementarem Kohlenstoff (EC) und organisch gebundenem Kohlenstoff (OC)

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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European foreword

This document (EN 16909:2017) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2017, and conflicting national standards shall be withdrawn at the latest by September 2017.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

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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 European Standard is to present guidance on the measurement procedures to be followed when monitoring elemental carbon (EC) and organic carbon (OC) collected 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 ($PM_{2,5}$) in ambient air, as described in Annex IV.

The method set out in this European Standard provides operational definitions of the measured quantities. Currently no traceable primary reference materials are available for EC and OC analysis and no absolute scientific distinction between EC and OC is possible.

1 Scope

This European Standard is applicable for the measurement of elemental carbon (EC) and organic carbon (OC) following the requirement for all EU member states 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 [1].

This European Standard describes the analytical procedures for determining EC and OC on quartz fibre filters as µg/cm^2, and the subsequent calculation of concentrations as µg/m^3. Sampling onto filters is to be done in accordance with EN 12341:2014 for $PM_{2,5}$. The sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and uptake/loss of volatile organic compounds on the filter at the time of sampling.

The same analysis method may also be used for smaller size fractions than $PM_{2,5}$. Any possible additional artefacts for larger particles, e.g. pyrolysis or higher concentrations of carbonates, should be assessed.

The scope includes rural background and urban background sites. The measurement method can also be applied to other site types, provided that the measurement range given below is not exceeded. The use of this standard at all site types allows 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.

The applicable concentration range of the proposed method is limited by the optical correction and instrument applied in the analysis of EC and OC. This method was validated from 0,2 µg C_{EC}/cm^2 and 1,8 µg C_{OC}/cm^2 to 38 µg C_{EC}/cm^2 and 49 µg C_{OC}/cm^2 in the laboratory and to 16 µg C_{EC}/cm^2 and 45 µg C_{OC}/cm^2 in the laboratory validation exercise and in the field validation exercise.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12341:2014, *Ambient air - Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of suspended particulate matter*

3 Terms, definitions and abbreviations

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

3.1 Terms and definitions

3.1.1
total carbon
TC
total quantity of carbon in a PM sample, including EC, OC and IC

Note 1 to entry: The amount of TC released from a PM sample in the specified thermal desorption and oxidation process may be different from other analytical methods.

3.1.2
inorganic carbon
IC
fraction of carbon belonging to mineral species, including carbonates and other species

3.1.3
carbonate carbon
CC
fraction of carbon belonging to a carbonate compound

Note 1 to entry: Carbonate carbon (mainly $CaCO_3$ and $MgCO_3$) is viewed as the only inorganic carbon fraction being released within the temperature range used in the thermal protocol.

3.1.4
elemental carbon
EC
fraction of total carbon in a PM sample, characterized by its non-volatility and chemical inertness according to the specified thermal-optical protocol

Note 1 to entry: EC evolves from the sample by oxidation at elevated temperatures.

3.1.5
organic carbon
OC
fraction of total carbon in a PM sample that is volatilized or pyrolyzed in the non-oxidizing part of the specified thermal-optical protocol

3.1.6
pyrolytic carbon
PC
fraction of organic carbon transformed by pyrolysis to elemental carbon, which is subsequently corrected by the specified thermal-optical protocol

3.1.7
sampling artefact
ab(ad)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)

3.1.8
PM_x
particulate matter suspended in air which passes through a size-selective inlet with a 50 % efficiency cut-off at x µm aerodynamic diameter

3.2 Abbreviations and acronyms

PM	Particulate Matter
AQD	Council Directive 2008/50/EC on ambient air quality and cleaner air for Europe [1]
C_{EC}	Carbon determined as elemental carbon (EC)
C_{OC}	Carbon determined as organic carbon (OC)
EUSAAR2	EC/OC thermal optical protocol developed for the European Super-sites for Atmospheric Aerosol Research
NIOSH	US-National Institute for Occupational Safety and Health
IMPROVE	US-Interagency Monitoring of Protected Visual Environments
TOT	Thermal-Optical Transmittance

4 Principle

The method for measuring EC and OC in ambient PM samples collected on filters is based on the volatilization and oxidation of carbon-containing PM components, the quantification of the carbon released, with optical correction for the PC (the thermal-optical method). The general procedure described is a thermal-optical transmittance (TOT) method.

5 Materials and instruments

5.1 Materials

5.1.1 Gases

— helium at least 99,999 % (% by volume),

— helium/oxygen (98:2 split) mixture with a maximum of impurities of 0,001 % (% by volume),

— helium/methane for internal calibration (e.g. 95:5) grade zero.

5.1.2 Standard solution

Carbon-containing standard solutions (typically sucrose), with an accurately determined concentration range, e.g. from 0,4 µg C/µl to 5 µg C/µl. Calibrating standard solutions shall be prepared which cover the concentration range of the samples to be analysed.

5.1.3 Other materials

— precision filter cutter of known area,

— quartz boat for the filter punch,

— stainless steel tweezers for sample handling,

— clean cutting surface (e.g. aluminium foil (uncoated) or quartz fibre filter),

— analytical syringe or pipette for calibration using standard solutions, e.g. 10 µl volume.

5.2 Instruments

5.2.1 Sampling instruments

The performance requirements of the sampling instrument are described in EN 12341:2014.

5.2.2 Analytical instruments

5.2.2.1 General

A thermal-optical analyser that allows EC and OC partitioning based on particulate carbon volatilisation and oxidation, and optical correction of pyrolysis by using the light transmittance of the sample.

5.2.2.2 Performance requirements of the analytical instrument

Thermal-optical EC and OC analyser,

— the instrument lower detection limit shall be better than 0,2 µg C/cm^2 of filter;

— the accuracy of TC measurements of an external standard (e.g. sucrose solution) shall be ± 10 % or ± 0,5 µg C/cm² (whichever is greater) over a working day (see 10.4).

6 Sampling

6.1 Filter material

Quartz fibre filters without binding materials shall be used.

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.

NOTE 1 Any filter impurity may influence the analysis and possibly damage the instrument.

Before field measurements are started, the filter batch(es) shall be assessed for blank levels of EC and OC using the measurement method to be used for the field samples.

NOTE 2 Typically only OC will be present in detectable quantities.

This assessment shall cover:

— average blank concentrations, and

— blank concentration variability.

Average OC content of the laboratory blanks shall not be above 2 µg C/cm² and the standard deviation of the OC content shall not be above 1 µg C/cm². No EC concentrations above the lower detection limit shall be measured for the laboratory blank filters. Causes for high blank concentration should be investigated and an appropriate action to eliminate them shall be taken (see 6.2). Specific causes of blank variability can be expected, e.g. for the top and bottom filters of the manufacturers' plastic containers and they should be discarded.

The details of the assessment of the filter material are not specified further in this European Standard. The procedure used and results shall be recorded. When the assessment gives cause for concern (as discussed further below and in Clause 10), either the filters shall be preheated (see below) or alternative batches of filters shall be obtained. Ongoing requirements for checks on the filter material are given in Clause 10.

6.2 Preheating of filter material and handling

Preheating of the filters to reduce the OC content, e.g. to fulfil the requirements of 6.1, is permitted. If preheating is used the blank value of the filters shall be determined according to 6.1. If filters are preheated they shall be heated at a range of 400 °C to 850 °C for a minimum of 1 h.

NOTE The main reason not to preheat filters is to allow the use of the same filters for other purposes such as $PM_{2,5}$ mass measurement since firing can affect the handling and weighing results.

6.3 Sampling duration and frequency

No specific sampling duration or frequency is needed for this standard. In case of use in conjunction with sampling in accordance with EN 12341:2014 and the AQD the sampling shall be from midnight to midnight [13]. A sequential sampler (usually with 14 filters and one field blank) is allowed. Other sampling durations may be chosen as needed for the measurement task.

In the case of measurements for the determination of annual average EC and OC concentrations, the monitoring frequency set out in the 4th Daughter Directive 2004/107/EC for indicative concentration measurements can be used.

6.4 Field sampling and type of sampler

The sampling device shall be in accordance with EN 12341:2014. It is acknowledged that the sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and adherence of volatile organic compounds to the filter at the time of sampling.

6.5 Site types

In accordance to the 2008/50/EC Directive Annex IV and the requirements for EC and OC measurements set therein, this European Standard is for rural background areas. It is also stated in Annex IV that "this information is essential to judge the enhanced levels in more polluted areas (such as urban back-ground, industry related locations or traffic related locations)". Hence, in view of consistency and comparability of methods, this standard is also for the use at other types of monitoring site, including suburban, urban background, roadside and industrial sites, provided that the measurement range of this method is not exceeded.

6.6 Filter environment during sampling

The sampler can be located either indoors or outdoors. No specific demands on temperature control beyond those in EN 12341:2014 are given.

7 Transport and storage

7.1 Handling

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

Transport of filters shall be performed in a clean container. Storage after sampling shall be performed in individual containers.

7.2 Time and temperature limits

Filters shall not be kept longer than 16 days in the field. Transport and any laboratory storage shall be at temperatures below 23 °C. Within 28 days after sampling, filters shall either be analysed or transferred to storage at temperatures below 5 °C. Filters can be stored at this condition for a longer period.

NOTE OC concentration may change depending on handling. This may lead to different results with $PM_{2,5}$ 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.

8 Analysis

8.1 General

To quantify the content of EC and OC in an aerosol sample collected on a quartz fibre filter, thermal volatilisation and oxidation at defined temperatures are used. Optical transmittance through the sample is used for the correction of pyrolysis of OC occurring during the temperature steps in inert carrier gas. CC may interfere with the determination of EC and OC (see 9.4). This standard uses the EUSAAR2 thermal optical transmittance protocol [6], the basic principles of which are described below.

A general scheme of the thermal optical analyser is given in Figure 1. The filter punch is placed into the instrument's oven, which is purged with helium. In the He mode (inert carrier gas), the oven's temperature is increased stepwise up to a first maximum 650 °C. OC either volatilises from the filter, or chars in/on the filter and forms pyrolytic carbon (PC). In the He/O_2 mode (oxidative carrier gas, 2 % O_2 in He), the instrument's quartz oven is cooled to 500 °C, and a second temperature ramp is initialised.

The final temperature in He/O_2 mode is 850 °C. In the He/O_2 mode, EC and PC oxidize off the filter punch. All gases evolved from the filter punch during He mode and He/O_2 mode are carried into a manganese dioxide oven where organic vapours are oxidized to carbon dioxide (CO_2) gas. CO_2 can be detected directly (NDIR detector), or subsequently mixed with hydrogen gas (H_2) and carried along with the helium through a heated nickel catalyst which reduces the CO_2 to methane (CH_4). The CH_4 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 laser transmittance signal (wavelength between 630 nm to 680 nm) shall be used to correct for pyrolysis of OC to PC, which can take place when OC is heated in the He mode of the analysis. Not correcting for pyrolysis leads to an underestimation of OC and a corresponding overestimation of EC. This correction is made by continuously monitoring of the light transmittance through the filter punch. As pyrolysis takes place (i.e. PC is formed), the transmittance drops, whereas it increases when EC and/or PC oxidize(s). Hence, the correction determines the amount of carbon oxidized in the He/O_2 mode that is necessary to return the transmittance back to the initial value before pyrolysis started. Therefore the split point is defined as the time point when the transmittance returns to the initial value. This approach assumes either that PC oxidises before the EC originally on the filter, or that the light transmission per unit mass of PC and EC is the same. These assumptions are unlikely to be met, therefore causing an inherent uncertainty in the determination of the split point between EC and OC.

NOTE A laser transmittance signal wavelength of approximately 658 nm was used for the validation tests in this standard.

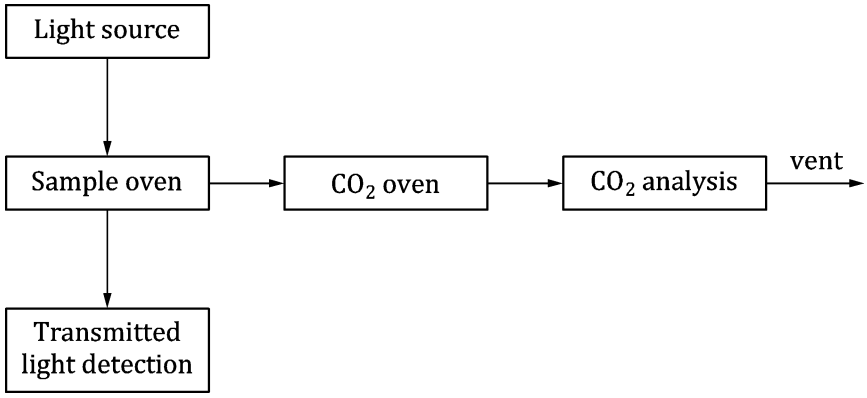


Figure 1 — Simple scheme of a thermal-optical analyser

8.2 Thermal protocol

The thermal protocol of this standard is EUSAAR2 [6] with pyrolysis correction based on transmittance. The temperature profile of the instrument shall be regularly calibrated see 10.6.3.

The analytical parameters for this protocol are listed below (Table 1). Instrumental parameters shall be recorded in a logbook (e.g. as described in Annex A). Detailed exemplary descriptions of the analytical procedures to be implemented are given as an example in Annex B.

Table 1 — Temperature steps and step durations for EUSAAR2

Mode	Step	T in °C, duration in s
He	He 1	200, 120
	He 2	300, 150
	He 3	450, 180
	He 4	650, 180
He/O_2[a]	He	No heating, 30
	He/O_2 1	500, 120
	He/O_2 2	550, 120
	He/O_2 3	700, 70
	He/O_2 4	850, 80
[a] A mixture of 2 % O_2 in He shall be used.		

9 Artefacts and interferences

9.1 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 uptake of OC during sampling,

— chemical reactions leading to losses and/or gains of OC during sampling,

— uptake or losses during transport or storage,

— pyrolysis of OC during analysis,

— carbonates in the sample detected as OC and/or EC,

— 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 shall be seen in this context. Care should be taken to reduce the above artefacts as far as possible and reasonable.

9.2 Sampling

All sampling artefacts are inherent by convention and part of the EC and OC values according to this standard. Sampling artefacts are mainly to be expected for OC and they can be significant (Chow et al. [12]).

9.3 Transport and storage

Some positive (OC uptake by filters during transport and storage) or negative artefacts (OC losses during transport and storage at elevated temperatures) can occur (Karanasiou et al. [15]).

The field and laboratory blank values (covered in Clause 10) generally show that a certain amount of organic substance is bound to the quartz fibre filter and may accumulate on a filter by mechanisms other than the active sampling. To reduce positive artefacts, samples shall be kept and handled away from any contamination sources, e.g. organic liquids or aerosols.

9.4 Analysis

Known factors which influence the analysis are summarized below:

— Carbonate carbon (CC) will interfere with the organic carbon and/or the elemental carbon fraction. If the filter 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 possible.

— 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 shall not be subtracted from the EC and/or OC measurement values but recorded to allow the estimation of possible interferences.

— Light absorbing organic carbon can affect the laser correction as these species are removed from the filter or pyrolyzed during He mode, causing changes in transmittance.

— 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.

— 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 Fe_xO_y as such species.

10 Quality assurance/quality control (QA/QC)

10.1 QA/QC for sampling parameters

QA/QC for parameters such as sampled volume, size fraction, and losses of semi-volatiles shall be performed by following the relevant procedures specified in EN 12341:2014, and other procedures described in Clauses 7 and 8.

10.2 Field blank determination

For every 14 field samples there shall be at least one field blank, a nominally-identical filter to those being sampled, which is prepared, transported to, stored in the sampler and transported back 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 shall be recorded.

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

In general field blank concentrations are not subtracted.

In cases where field blanks are subtracted a detailed justification should be provided.

NOTE Typical field blank values are up to 4 µg OC/cm^2.

10.3 Laboratory blank determination

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 instrument.

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 6.1.

Alongside the filter checks given in 6.1, the laboratory procedures and environment will be checked by analysing laboratory blanks. It is recommended that laboratory blanks are analysed at least once 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 shall be recorded together with the analytical data for the laboratory blanks.

10.4 Calibration for TC

Because there are no traceable primary reference materials available for atmospheric EC and OC, calibration is currently limited to TC.

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. Further information is given in Annex B and in the analytical instrument user's manual. The instrument shall be regularly calibrated for TC at least once every 12 months and after any major maintenance or modification of the system.

The calibration shall be checked at least every measurement day (e.g. by analysis of a control filter – see 10.6.1 and/or sucrose spiked filter) with a quantity of TC relevant to the quantities in the field samples being analysed. The results shall be within ± 10 % or ± 0,5 µg C/cm^2 of the expected value, whichever is greater. If not, the reasons have to be investigated (see Annex B) and the result of the investigation shall be recorded with the other analytical data.

10.5 Long term stability and repeatability

The long term stability of the analytical system shall be determined from control filter measurements (see 10.6.1) and from the spiked filter calibrations. A TC and OC long term stability of 10 % or ± 0,5 µg C/cm^2, whichever is greater, difference from the initial mean of the first ten measurements can be viewed as sufficient. An EC long term stability of 15 % or ± 0,5 µg C/cm^2 difference, whichever is greater, from the initial mean of the first ten measurements can be viewed as sufficient.

The repeatability is calculated as the relative standard deviation of ten measurements of the control filter being conducted during one day. An accepted value for repeatability is 5 % or ± 0,5 µg C/cm^2 difference, whichever is greater. The instrument shall be regularly assessed for repeatability at least once every 12 months and after any major maintenance or modification of the system.

10.6 Other-QA/QC checks

10.6.1 Use of quality control filters

A so-called "control filter" is a filter that has sampled ambient air by a high volume sampler, typically for 24 h. Ten 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 ten filter punches shall also be used to check for homogeneous loading of the filter.

Analyses 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.

10.6.2 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.

10.6.3 Calibration and checks on temperature sensors and optical systems

The temperature sensors including the temperature profile of the instrument shall be regularly calibrated and the optical system checked at least once every 12 months and after any major maintenance or modification of the system.

10.6.4 Stability of the laser signal

An unstable transmittance laser signal affects the determination of the EC/OC split point and potentially alters the EC and OC concentrations (Karanasiou et al. [16]). The stability of the transmittance laser signal shall be monitored during instrument blank analysis. The instrument blank analysis is conducted by repeating the analysis-without opening the oven. When laser instability is identified further actions shall be considered, including:

— check of the laser performance,

— check of the laser signal detectors,

— check of the cooling system and insulation of the optical components.

The laser signal should not deviate more than 3 % from its average value during the instrument blank analysis.

The laser stability shall be regularly checked at least once every 12 months and after any major maintenance or modification of the systems.

An example of a laser signal of the instrument blank analyses is presented in Annex G.

10.7 Applicable concentration range

The applicable concentration range of the proposed method is limited by the optical correction and instrument applied in the analysis of EC and OC. This method was validated from 0,2 µg C_{EC}/cm^2 and 1,8 µg C_{OC}/cm^2 to 38 µg C_{EC}/cm^2 and 49 µg C_{OC}/cm^2 in the laboratory and to 16 µg C_{EC}/cm^2 and 45 µg C_{OC}/cm^2 in the field validation exercise.

The initial transmittance of the filter to be analysed shall not be lower than 6 % of the laser signal of the blank filter of the same analysis day.

The lower detection limit shall be determined by calculating the average laboratory blank filter value plus two times its standard deviation.

One possibility to avoid saturation is to reduce the sampled volume by, e.g. shorter sampling intervals or lower volume flow rates. Appropriate size selective inlets have to be used with lower volume flow rates.

11 Calculation of concentrations of EC and OC

To determine EC and OC mass concentrations in air (in µg C/m³), it is necessary to convert the data from the analyser, which are generally provided as mass loading of carbon per square centimetre of filter (µg C/cm²), using Formula (1):

$$C_{conc} = \frac{m_1 \cdot A}{V} \quad (1)$$

where

C_{conc} is the atmospheric concentration of EC or OC, in micrograms carbon per cubic metre (µg C/m³);

m_1 is the measured loading of EC or OC of the sub-sample (filter punch), in micrograms carbon per square centimetre (µg C/cm²);

A is the loaded filter area, in square centimetre (cm²);

V is the sampled air volume, in cubicmetre (m³), at ambient conditions near the inlet of the sampler at the time of sampling.

It is therefore necessary to know the volume of air sampled, and the loaded area on the filter.

The volume of air that has been sampled is generally recorded by the sampler, following EN 12341:2014.

The loaded filter area shall be measured by the operator. This measurement can be performed in several ways, e.g. by measuring the loaded area on the filter 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.

12 Data recording

The following information shall be recorded:

— concentration data of EC and OC, in micrograms C per cubicmetre (µg C/m³) (referred to the ambient temperature and pressure),

— site type and identification,

— sampling date with start and end time,

— information on any additional treatment, e.g. equilibration for PM mass concentration measurements,

— date of analysis,

— ambient temperature during sampling,

— place, time and conditions of transport and storage,

— corresponding laboratory filter blank concentrations for EC and OC in µg/cm^2,

— corresponding field blank concentrations for EC and OC in µg/cm^2.

Any additional information may be added.

13 Determination of measurement uncertainty

An individual laboratory may produce an assessment of the uncertainty of any individual measurement by performing a full ISO GUM treatment (ISO/IEC Guide 98-3, [14]) on a detailed expression of Formula (1).

The loading of EC or OC of the sub-sample (m_1) is actually calculated by the instrument software as:

$$m_1 = \frac{m}{a} \tag{2}$$

where

m is the mass of EC or OC determined in the sub-sample (filter punch), in micrograms of carbon (µgC);

a is the sub-sample (filter punch) surface area (cm^2).

Combining (1) and (2):

$$C_{con} = m \cdot \frac{A}{a} \cdot \frac{1}{V} \tag{3}$$

A calibration peak is generated for each thermogram by injecting a known volume of gaseous standard (e.g. pure CH_4). The mass of a carbon fraction in the filter sub-sample (filter punch), m, is then calculated as:

$$m = \frac{I_{sam}}{I_{cal}} \cdot m_{cal} \tag{4}$$

where

I_{sam} is the peak area on the thermogram for the EC or OC carbon fraction, assumed dimensionless;

I_{cal} is the calibration peak area on this same thermogram, assumed dimensionless;

m_{cal} is the mass of carbon in the volume of standard injected to produce the calibration peak on this same thermogram.

This is assuming that the response of the instrument during the various phases (He, He/O_2, calibration) of the analysis is constant. If not, introduce a factor k representing the response factor for each analytical phase compared to the “calibration” phase.

The constant volume of gaseous standard injected at ambient pressure P_a and temperature T_a for each thermogram to obtain the calibration peak contains a mass of carbon m_{cal} equal to:

$$m_{cal} = \frac{P_a \cdot v_{inj}}{R \cdot T_a} \cdot M \tag{5}$$

where

P_a is the atmospheric pressure at the time of the analysis (Pa);

v_{inj} is the volume of calibration gas injected to during each thermogram (m^3);

R is the ideal gas constant (8,31 J K^{-1} mol^{-1});

T_a is the ambient temperature (in K);

M is the molar mass of carbon (12,0 g mol^{-1}).

The constant volume of gaseous standard injected for each thermogram is determined using an independent carbon-containing standard. For the analysis of this calibration standard, Formula (4) becomes:

$$m_{std} = \frac{I_{std}}{I^0_{cal}} \cdot m^0_{cal} \tag{6}$$

where variables are the same as in Formula (4), and the superscript ^{0} is relative to the analysis of the external standard.

Substituting m^0_{cal} in Formula (6) using Formula (5):

$$m_{std} = \frac{I_{std}}{I^0_{cal}} \cdot \frac{P^0_a \cdot v_{inj}}{R \cdot T^0_a} \cdot M \tag{7}$$

where variables are the same as in Formula (5), and superscript ^{0} is relative to the analysis of the external standard.

Re-arranging Formula (7) leads to v_{inj} and substituting v_{inj} in Formula (5), then m_{cal} in Formula (4), then m in Formula (3) leads to:

$$C_{conc} = \frac{I_{sam}}{I_{cal}} \cdot \frac{I^0_{cal}}{I_{std}} \cdot \frac{P_a}{P^0_a} \cdot \frac{T^0_a}{T_a} \cdot m_{std} \cdot \frac{A}{a} \cdot \frac{1}{V} \tag{8}$$

An individual laboratory may produce an assessment of the uncertainty of any individual measurement by performing a full ISO GUM treatment (ISO/IEC Guide 98-3, [14]) on Formula (8). The uncertainty due to the instrument blank is viewed as being negligible with respect to the lower detection limit of the instrument. Considering all information given above this yields a combined relative standard uncertainty $\frac{u_c\left(C_{con}\right)}{C_{con}}$ in the measured ambient mass concentration C_{con} of a carbon fraction equal to:

$$\frac{u_c\left(C\right)}{C} = \sqrt{\frac{u^2\left(I_{sam}\right)}{I_{sam}^2} + \frac{u^2\left(I_{cal}\right)}{I_{cal}^2} + \frac{u^2\left(I_{cal}^0\right)}{\left(I_{cal}^0\right)^2} + \frac{u^2\left(I_{std}\right)}{I_{std}^2} + \frac{u^2\left(\frac{P_a}{P_a^0}\right)}{\left(\frac{P_a}{P_a^0}\right)^2} + \frac{u^2\left(\frac{T_a^0}{T_a}\right)}{\left(\frac{T_a^0}{T_a}\right)^2} + \frac{u^2\left(m_{std}\right)}{m_{std}^2} + \frac{u^2\left(A\right)}{A^2} + \frac{u^2\left(a\right)}{a^2} + \frac{u^2\left(V\right)}{V^2}} \quad (9)$$

where

$u(x)$ is the estimated standard uncertainty in x, for $x \in \{ I_{sam}, I_{cal}, I_{cal}^0, I_{std}, P_a / P_a^0, T_a^0 / T_a, m_{std}, A, a, V \}$.

The relative uncertainties of variables I_{sam}, I_{cal}, I_{cal}^0, I_{std}, P_a / P_a^0, T_a^0 / T_a, m_{std}, A and a shall be determined by each laboratory. The repeatability determined according to 10.5 may be used as the relative uncertainty of I_{sam}, I_{cal}, I_{cal}^0, and I_{std}. In case ambient pressure and temperature are not recorded, it may be assumed that $P_a = P_a^0$ and $T_a^0 = T_a$, and the relative uncertainties of P_a / P_a^0 and T_a^0 / T_a may be assessed from their variability. Examples of numerical values are provided in Annex E.

The relative uncertainty of V is set to 3 % (with a rectangular distribution) according to EN 12341:2014.

The relative expanded uncertainty, $U_r\left(C_{conc}\right)$, of the measurement result is then calculated by:

$$U_r\left(C_{conc}\right) = \kappa \frac{u_c\left(C_{conc}\right)}{C_{conc}} \quad (10)$$

where

κ is the coverage factor to provide a 95 % level of confidence, usually assumed to be equal to 2.

No significant between sampler uncertainty was determined for the field measurement campaign. Hence the between sampler uncertainty is seen to be inherently included in the uncertainty budget.

An exemplar uncertainty budget calculation is given in Annex E.

Alternatively, the measurement uncertainty can be determined using the direct approach according to EN ISO 20988 [17] (i.e. based on co-located measurements).

Annex A
(informative)

Example of a logbook information

This annex provides an example of how to write the logbook to document the analysis of the quartz fibre filter punches by the TOT instrument.

Date:

Operator:

Sample:

Flow rates (Air; H_2; He-1; He-2; He-3; He/O_2; CH_4 internal calibration standard):

Thermal Protocol:

Calibration Constant:

Data Output File:

Filter punch area: cm^2

Front oven: °C

Back oven: °C

CH_4-oven: °C

Initial transmittance:

Sample comments:

Analysis comments:

It is recommended to store the complete thermogram information including the temperature and pressure course, as well as the transmittance.

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[1)].

B.2 Start-up

Ensure that the He, He/O_2, Air and Hydrogen gas cylinder pressures are at least 5 bar. Set gas cylinder delivery pressures to 1,5 bar - 2 bar.

Start the instrument operating software or if the software was in standby mode, click the CONTINUE button.

Set gas flow rates according to the user's manual (example: Table B.1) and record flow rates in the logbook.

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

Gas	**Flow rate** $cm^3\ min^{-1}$
Air	280 to 300
H_2	50 to 54
He-1	48 to 52
He-2	12 to 15
He-3	67 to 70
He/O_2	12 to 15[a]
Cal	10 to 15
[a] This flow should be equal to that of He-2 and the end concentration of O_2 should be 2 %.	

In order to ignite the flame in the FID, set the H_2 flow to > 100 $cm^3\ min^{-1}$. 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_2 gas flowing from the FID exhaust outlet. Once the flame has been lit (usually a small pop can be heard), return the H_2 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 shall 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.

1) The Sunset lab instrument is a product of Sunset Laboratory Inc., Oregon, USA, that is identified by its trade marked name. This information is given for the convenience of users of this standard and does not constitute an endorsement by CEN of the product named.

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

In the off-line mode:

a) the back oven temperature shall be approximately 870 °C,

b) the front oven temperature shall be approximately < 75 °C,

c) the CH_4 oven temperature shall be approximately 500 °C,

d) the instrument pressure shall be in the range 0,1 psi to 4 psi (off line pressure: approx. 1 psi)[2)].

e) for a blank filter the transmittance signal should be higher than 6000,

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 shall be in the range indicated by the manufacturer. As this variable varies over a wide range, the range of normal values shall be established for each instrument.

B.3 Cleaning the system

Clean the system running CLEAN OVEN protocol.

B.4 Running the instrument blank

Choose PARAMETER FILE (EUSAAR2). Run it without inserting any new filter or prior opening the oven.

B.5 Running an external calibration standard

If during starting and cleaning procedure there is a filter in the oven then a calibration standard can be spiked on that filter after cleaning the oven and running the instrument blank.

If there is no filter in the oven, punch a 1,5 cm^2 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 filter punch on the 1,5 cm^2 boat.

Slide the boat in gently until it stops by the tip of the thermocouple. 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 0,1 psi to 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 on the filter punch (preferably with a concentration of 2 µg C/µl to 5 µg C/µl). Dry the spiked filter inside the oven without running any protocol for about 10 min or outside of the oven for about 30 min. Analyse the sucrose standard at least twice on every measurement day.

2) 1 psi = 6894,8 Pa.

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/cm² (if 10 % would be less than 0,5 µg C/cm²), consider the following actions:

a) Perform an additional analysis of the external calibration standard.

b) Prepare a new calibration standard or a new stock solution (see Annex D).

c) In case the deviation continues, check for (systematic) error or contact the manufacturer.

B.6 Running an external long term calibration standard

Calibration using external gaseous standards (e.g. CO_2 or CH_4) may be applied. The recommended frequency is three times per year.

Requirements:

a) a cylinder of pure C-containing gas (e.g. CO_2, CH_4) 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 B.1);

Principle:

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

$$m = M \cdot \chi \cdot p \cdot V / \left(R \cdot T\right) \quad \text{(B.1)}$$

where

M is the carbon molar mass ($12*10^{-3}$ kg mol^{-1});

χ 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^{-1} mol^{-1});

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 micrograms (µg).

In standard conditions (p = 1013,25 hPa; T = 25 °C), 10 µl of pure CO_2 or CH_4 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 Formula (B.1).

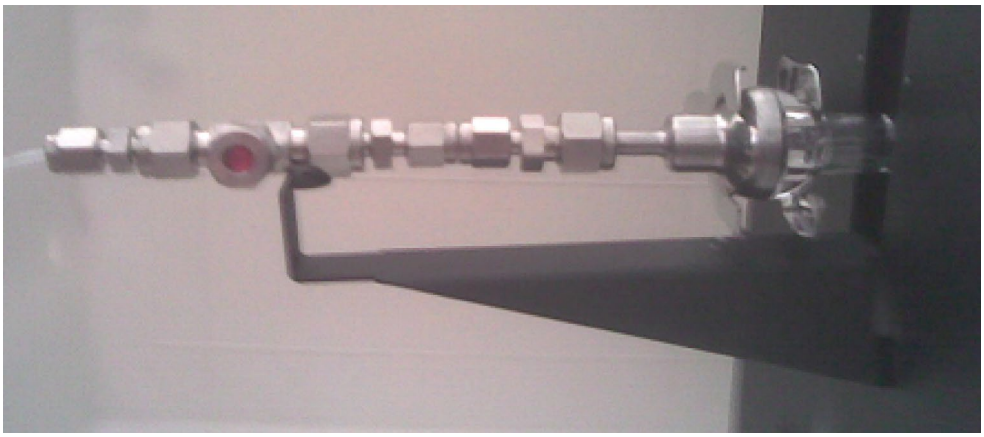
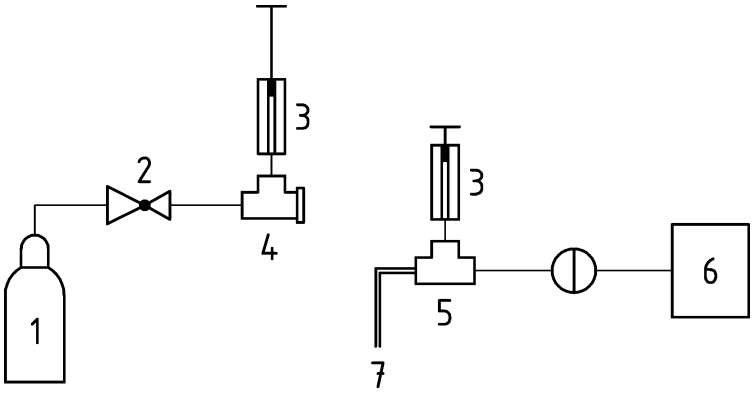


Figure B.1 — Inserting a T with a septum to the carrier gas line of a Sunset lab carbon analyser



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.

The speed of injection of the gas standard shall 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:

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

2) Run the CLEAN OVEN protocol with a punch of blank filter.

3) Start a thermal analytical run.

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

5) Inject the whole volume during the analytical step 1 (e.g. He mode, temp step 200 °C in EUSAAR2).

6) Repeat steps 4 and 5 for each analytical step in the He mode and the O_2 mode.

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

B.7 Running a EC/OC control sample and routine samples

On every measurement day analyse a high volume EC/OC control sample similar to routine samples in order to determine the long term stability of the analytical system (see 10.6.1). A TC and OC long term stability of 10 % or ± 0,5 µg C/cm² (if 10 % would be less than 0,5 µg C/cm²) difference from the initial mean of the first ten measurements can be viewed as sufficient. An EC long term stability of 15 % or ± 0,5 µg C/cm² (if 15 % would be less than 0,5 µg C/cm²) difference from the initial mean of the first ten measurements can be viewed as sufficient.

If the difference of TC concentration exceeds accepted variability consider the following actions:

a) Perform an additional analysis of the control sample.

b) In case the deviation continues, check for systematic error or contact the manufacturer.

If the difference of EC concentration differs more than 15 % form expected value with no change of TC value, check the stability of the laser signal (10.6.4).

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 1,5 cm² from a sample. 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 1,5 cm² filter punch on the boat. Slide the boat in gently until it stops by the tip of the thermocouple. 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 filter punch area. Choose PARAMETER FILE (EUSAAR2). Analyse the sucrose standard always with the same protocol. Click the START ANALYSIS button.

B.8 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 instrument's lower control unit. The back oven will be maintained at a lower than normal temperature, the laser will be shut off and the pressure will be close to zero as the flow of helium will be rather low (Table B.2).

If not intending to use the instrument for the following 10 d, 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 instrument's lower control unit could be tightened gently. The gas supply can now be turned off.

Before turning off the instrument make sure that the ovens are cooled down and the methanator temperature is lower than 100 °C.

Table B.2 — Standard gas flow rates for Sunset instrument in the STANDBY mode

Gas	**Flow rate** $cm^3\ min^{-1}$
Air	off
H_2	off
He-1	6 to 10
He-2	4 to 6
He-3	6 to 10
He/O_2	4 to 6
Cal	off

Annex C
(informative)

Methods for the assessment of carbonate carbon

Across Europe, CC (Carbonate Carbon), estimated from Ca^{2+} and Mg^{2+} measurements) accounts for about 2,5 % of TC in $PM_{2,5}$. CC/TC maxima (over 24 h) range from 0,02 to 0,44 (see Table C.1). CC/EC (maximum ratios) are site dependent and range from 0,05 to 1,1. 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**- Indications of the presence of CC can be derived from the EUSAAR2 thermograms using a method according to Karanasiou et al. [16].

— **C2**- CC can be removed from the sample by sample acidification with HCl fumes (Cachier et al. [8], Jankowski et al. [9].

— **C3**- There is a protocol for direct CC determination, adapted from Pio et al. [11], described below.

— **C4**- A calcium analysis can be performed e.g. using CEN/TR 16269:2011 [3]. The results can then be used to estimate the amount of $CaCO_3$ present in the samples.

— **C5**- CC can be quantified by thermal analysis, following a thermal/oxidative pre-treatment which removes OC and EC from the filter sample (Diapouli et al. [18]).

Regarding C2: It is 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 C3: The determination of carbonate in atmospheric PM samples collected on filters by acidification and quantification of the CO_2 evolved as first described by Cadle et al. [10] and validated by Pio et al. [11] is simple, accurate, and implementable by most laboratories that already perform OC and EC analyses as described in Karanasiou et al. [16].

Table C.1 — CC / EC and CC / TC ratios across Europe, estimated from Calcium and Magnesium measurements, by assuming that calcium comes from $CaCO_3$, and magnesium from $MgCO_3$

Type	Site	Country	$PM_{2,5}$	$EC/PM_{2,5}$	$TC/PM_{2,5}$	$C(CaCO_3)/EC$			$C(CaCO_3)/TC$			$C(MgCO_3)/EC$			$C(MgCO_3)/TC$			$C(CO_3)/EC$	$C(CO_3)/TC$
			average	average	average	average	stdev	max	average	stdev	max	average	stdev	max	average	stdev	max	average	average
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 µg/C µl^{-1}. The stock solution shall be stored in a refrigerator (4 °C), but for not for a period longer than 6 months.

(9,5 g sucrose / 100 ml H_2O) (144 g C/mol / 342 g/mol) (10^{-3} ml / µl) (10^{6} µg/g) = 40 µg/C µl^{-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

	Sucrose stock µg/C µl^{-1}	**Volume of sucrose stock** ml	**Volume final** ml	**Final concentration** µg/C µl^{-1}
Standard 1	40	1	100	0,4
Standard 2	40	5	100	2,0
Standard 3	40	10	100	4,0

Annex E
(informative)

Example for the determination of measurement uncertainty

In case a calibration peak is generated for each thermogram by injecting a known volume of gaseous standard (e.g. pure CH_4), and the external calibration standard consists of a solution with a known concentration of carbon, the formula to calculate the atmospheric concentration C_{conc} of a carbon fraction (e.g. OC or EC) measured using this standard method (Formula (8), Clause 13) can be further detailed as:

$$C_{conc} = \frac{I_{sam}}{I_{cal}} \cdot \frac{I_{cal}^0}{I_{std}} \cdot \frac{P_a}{P_a^0} \cdot \frac{T_a^0}{T_a} \cdot v_{std} \frac{w_{std}}{v_{sol}} \cdot \frac{A}{a} \cdot \frac{1}{V} \quad \text{(E.1)}$$

where variables are specified in Table E.1.

A GUM treatment (ISO/IEC Guide 98-3 [14]) on Formula (E.1) yields a combined relative standard uncertainty $\frac{u_c(C)}{C}$ in the measured ambient mass concentration C of OC or EC equal to:

$$\frac{u_C(C_{conc})}{C_{conc}} = \sqrt{\frac{u^2(I_{sam})}{I_{sam}^2} + \frac{u^2(I_{cal})}{I_{cal}^2} + \frac{u^2(I_{cal}^0)}{(I_{cal}^0)^2} + \frac{u^2(I_{std})}{I_{std}^2} + \frac{u^2(\frac{P_a}{P_a^0})}{(P_a / P_a^0)^2} + \frac{u^2(T_a^0 / T_a)}{(T_a^0 / T_a)^2} + \frac{u^2(v_{std})}{v_{std}^2} + \frac{u^2(W_{std})}{W_{std}^2} + \frac{u^2(v_{sol})}{v_{sol}^2} + \frac{u^2(A)}{A^2} + \frac{u^2(a)}{a^2} + \frac{u^2(V)}{V^2}} \quad \text{(E.2)}$$

Formula (E.2) can be written:

$$\frac{u_c(C_{conc})}{C_{conc}} = \sqrt{\sum_{i=1}^{12} S_i^2 \frac{\sigma^2(x_i)}{D_i^2}} \quad \text{(E.3)}$$

where

x_i are the variables $I_{sam}, I_{cal}, I_{cal}^0, I_{std}, P_a / P_a^0, T_a^0 / T_a, v_{std}, w_{std}, v_{sol}, A, a$ and V (also listed in Table E.1);

$\sigma(x_i)$ are the uncertainties in variables x_i, such that $u(x_i) = \frac{\sigma(x_i)}{D_i}$;

D_i are the divisors which account for the probability distribution in the uncertainty of x_i;

S_i are the sensitivity coefficients

$$\frac{1}{I_{sam}}, \frac{1}{I_{cal}}, \frac{1}{I_{cal}^0}, \frac{1}{I_{std}}, \frac{P_a^0}{P_a}, \frac{T_a}{T_a^0}, \frac{1}{v_{std}}, \frac{1}{w_{std}}, \frac{1}{v_{sol}}, \frac{1}{A}, \frac{1}{a}, and \frac{1}{V}.$$

An example of numerical values for the calculation of u_c (C_{conc}) is shown in Table E.1.

Table E.1 — Exemplar uncertainty budget, calculating the combined standard uncertainty, for a measurement of carbon in ambient air made using this standard method

Symbol	Variable	Unit	Value	Uncertainty	Sensitivity Coefficient[a]	Probability Distribution	Divisor[b]	$\frac{S_i \cdot \sigma(x_i)}{D_i}$ [c]
I_{sam}	Peak area for the relevant carbon fraction (OC or EC) measured on the loaded filter sub-sample thermogram	1	240	9,60	0,02	Normal	1	0,21
I_{cal}	Peak area for the calibration gas measured on the loaded filter sub-sample thermogram	1	250	5,00	−0,02	Normal	1	−0,11
I^{o}_{cal}	Peak area for the calibration gas measured on the external calibration standard thermogram	1	300	6,00	0,02	Normal	1	0,11
I_{std}	Peak area measured on the external calibration standard thermogram	1	275	16,5	−0,02	Normal	1	−0,32
P_a/P^{o}_a	Ratio of atmospheric pressures at the times of the filter sub-sample analysis and of the external calibration standard analysis	1	1,00	0,02	5,26	Normal	1	0,11
T^{o}_a/T_a	Ratio of instrument case temperatures (in K) at the times of the external calibration standard analysis and of the filter sub-sample analysis	1	1,00	0,02	5,26	Normal	1	0,11
v_{std}	Volume of external calibration standard solution analysed	µL	10,0	0,20	0,53	Normal	1	0,11
w_{std}	Mass of carbon contained in the amount of standard material used to make the external calibration standard solution	mg	500	10,0	0,01	Normal	1	0,11
v_{sol}	Volume of ultra-pure water used to make the external calibration standard solution	mL	250	0,25	−0,02	Normal	1	−0,01
A	Loaded filter area	cm^2	13,9	0,26	0,38	Rectangular	√3	0,06
a	Analysed filter sub-sample area	cm^2	1,00	0,02	−5,26	Rectangular	√3	−0,06
V	Sampled air volume at ambient conditions near the inlet of the sampler	m^3	55,2	1,66	−0,10	Rectangular	√3	−0,09
C	Mass concentration of the relevant carbon fraction (OC or EC) in ambient air	$\mu g/m^3$	5,26	0,47				

[a] Sensitivity coefficients' unit are $\mu g\ m^{-3}$ (unit of the corresponding variable)$^{-1}$.

[b] Dimensionless.

[c] Unit = $\mu g / m^3$.

No significant sampler uncertainty was determined for the field measurement campaign. Hence the between sampler uncertainty is seen to be inherently included in the uncertainty budget. Some guidance is given in estimating the standard uncertainties of these components:

$u(I_{sam})$ can be assessed by determining the repeatability of the measurements. It includes uncertainties in the peak area on the thermogram of the relevant carbon fraction measured on the sub-sample (filter punch), and the degree of homogeneity the deposit on the loaded filter.

$u(I_{cal})$ can be assessed by determining the repeatability of the area of the calibration peak by successive injections during a short time (<1 h).

$u(I_{std})$: an upper limit can be assessed by determining the repeatability of the area of the external standard peak. This also includes uncertainties in the spiking of the standard solution to the filter punch to be analysed, which is somewhat already accounted for by $u(v_{std})$.

$u(V)$/V is estimated in EN 12341:2014 to 3 %.

Annex F
(informative)

Statistical analysis of Organic Carbon (OC), Elemental Carbon (EC) and Total Carbon (TC) concentrations collected on filters from field validation exercise

F.1General

Daily $PM_{2.5}$ samples were collected from six monitoring stations over 2013 and 2014 and analysed by four different laboratories. Sub-samples of each daily filter were analysed twice using six thermal-optical protocols (EUSAAR2, NIOSH and IMPROVE) with optical corrections for OC/EC split point performed by using transmittance and reflectance. This resulted in 12 results per laboratory, per sampled filter. NPL performed a statistical analysis to determine the uncertainty of a single measured value based on between-laboratory variability, internal-laboratory variability and between sampler variability. NPL expanded this analysis to rank the different protocol / optical correction methodologies on a site specific and complete data set basis.

F.2Analysis methodology

F.2.1 General

For the purpose of the data analysis described below, the data are divided into three data sets as follows:

a) Data set 1 relates to those sites for which a single sampler is used by all the laboratories. The sampler used at a particular site may be the same as that used at a different site or it may be different from the samplers used at all other sites. The data set is used to investigate between- and within-laboratory effects and to quantify those effects.

b) Data set 2 relates to those sites for which at least two samplers are used by all the laboratories. As for data set 1, a sampler used at a particular site may be the same as that used at a different site, or it may be different from the samplers used at all other sites. The data set is used to investigate a between-sampler effect and to quantify that effect.

c) Data sets 1 and 2 were combined and split into:

    1) Sites to determine specific site classification (rural background, urban background and roadside) uncertainties.

    2) Four concentration ranges to determine uncertainty over the range of concentrations.

The objective of the data analysis is to evaluate the standard uncertainty to be associated with an individual measured value of concentration, which combines the within-laboratory, between-laboratory and between-sampler effects. For data sets 3a and 3b only the within-laboratory and between-laboratory effects were calculated.

F.2.2 Calculating between- and within-laboratory variability

F.2.2.1 Notation

Let there be *S* sites identified by the index $i, i \in \{1,....,S\}$ and *L* laboratories identified by the index $j, j \in \{1,...,L\}$. Suppose measurements are made by all *L* laboratories at site *i* on each of the days identified by the index $k, k \in K_i$. The measured values of concentration are then denoted by:

$$x_{ijk}, \quad k \in K_i, \quad j \in \{1,...,L\}, \quad i \in \{1,...,S.\} \tag{F.1}$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made can be different from one site to another.

F.2.2.2 Data processing

The data processing comprises two stages. In a first stage, the *L* measured values corresponding to each site and each day are processed to remove outlying values, and normalized to remove effects associated with the factors of site, sampler and time. In a second stage, an ANalysis Of VAriance (ANOVA) is applied to the resulting data set corresponding to all sites and all days to decide whether a between-laboratory effect exists. If the effect exists, a calculation of the between- and within-laboratory standard deviations is undertaken. If the effect does not exist, a calculation of the within-laboratory standard deviation only is made. In either case, the within-laboratory standard deviation describes the repeatability standard deviation for the laboratories, which is assumed to be the same for all laboratories.

Each part of the data processing is described below.

F.2.2.3 Outlier rejection

Outlier rejection is applied to the set of measured values $x_{ijk}, j \in \{1,...,L\}$, provided by the *L* laboratories on day *k* at site *i*. Outlier rejection is applied separately for the sets of measured values provided on different days and at different sites.

Outlier rejection involves the following steps:

1) Remove any measured value that is zero, with zero interpreted as denoting a missing value;

2) For the non-zero measured values, evaluate the modified Z-score defined by

$$z_{ijk} = \frac{x_{ijk} - \text{med}\left(\{x_{ijk}\}\right)}{1,483 \times \text{mad}\left(\{x_{ijk}\}\right)},$$

where

$\text{med}\left(\{x_{ijk}\} = \hat{x}_{ik}\right)$ is the median of the non-zero values $\{x_{ijk} : x_{ijk} \neq 0, j = 1,...,L\}$, a robust measure of location, and $\text{mad}\left(\{x_{ijk}\}\right) = \text{med}\left(\{|x_{ijk} - \hat{x}_{ik}|\}\right)$ is the median-absolute deviation of those values, a robust measure of dispersion;

3) Remove any measured value for which $|z_{ijk}| > 3,5$.

The procedure for outlier rejection described in steps 2 and 3 follows the recommendation made in section 1.3.5.17 of the NIST Engineering Statistics Handbook[3)]. Outlier rejection can be problematic for small sample sizes, in this case when the number *L* of laboratories is small. The critical value (of, here, 3,5) for the absolute value of a modified Z-score, which is used to decide whether a measured value is to be considered as an outlier or not, can be adjusted to make outlier rejection easier (using a smaller value of the critical value) or harder (using a larger value). However, such an adjustment leads to a degree of "subjectivity" into the step of outlier rejection, and ought to be justified.

For the majority of the data analysis performed for this standard outlier rejection was not used in order to calculate the uncertainty of a single measured value.

F.2.2.4 Data normalization

Following outlier rejection, the data for site *i* and day *k* is denoted by:

$$x_{ijk}, \quad k \in K_i, \quad j \in J_{ik}, \quad i \in \{1,\ldots,S\} \tag{F.2}$$

where

J_{ik} contains the indices of the laboratories for which measured values are retained.

Data normalization involves the following steps:

1) Evaluate the average

$$\bar{x}_{ik} = \frac{1}{L_{ik}} \sum_{j \in J_{ik}} x_{ijk}$$

where

L_{ik} is the number of indices in J_{ik}.

2) Shift the measured values by the average $\bar{x}_{ik}$, and scale the shifted values by $\bar{x}_{ik}$ to obtain normalized values

$$v_{ijk} = \frac{x_{ijk} - x_{ik}}{\bar{x}_{ik}}, \quad j \in J_{ik}$$

The average value calculated in step 1 is taken as a reference or consensus value for the concentration of OC, EC or TC at the specific site *i* on the specific day *k*. The aim of shifting the measured values is to remove, at least approximately, any dependence of measured concentration on the time of measurement, the site at which the measurement is made, and the sampler that is used to make the measurement. The aim of scaling the shifted values is to remove, at least approximately, any dependence of the variability of measured concentration on the value of concentration. The application of scaling is based on the assumption that the repeatability standard deviation is proportional to the measured concentration, i.e. the relative repeatability standard deviation is approximately constant. The normalized data are reported as a fraction (or percentage) of the reference value.

[3)] www.itl.nist.gov/div898/handbook/

F.2.2.5 Analysis of variance

Following outlier rejection and data normalization, the data are denoted by:

$$v_{ijk}, \quad k \in K_i, \quad j \in J_{ik}, \quad i \in \{1,\ldots,S\} \tag{F.3}$$

Since there is no interest in the factors of site and time, an equivalent representation of the data are as

$$y_{ir}, \quad r \in \{1,\ldots,R_i\}, \quad l \in \{1,\ldots,L\} \tag{F.4}$$

which groups the measured values by laboratory. Here, R_i is the number of retained measured values for laboratory l over all sites and days, and each y_{ir} equates to one of the normalized values v_{ijk}.

An ANOVA is used to test the null hypothesis that the averages for the laboratories are equal, i.e. there is no laboratory effect. The ANOVA calculation shall account for the fact that the data set may be unbalanced, because the numbers of measured values can be different from one laboratory to another. The function "anovan", which is provided in Matlab's Statistics Toolbox[4)], can be used to perform a (multiway) ANOVA and allows for an unbalanced data set. The function returns a p value that is compared with a critical value p_c, usually 0,01 or 0,05, chosen before the analysis. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a 100 p_c % level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

F.2.2.6 Calculation of standard deviations

The within-laboratory variance (squared standard deviation) is calculated as the pooled variance s^2 of the laboratory values, and is given by

$$s^2 = \frac{1}{\left(\sum_{i=1}^{L} R_i\right) - L} \sum_{i=1}^{L} \left(R_i - 1\right) s_i^2 \tag{F.5}$$

where

$$\bar{y}_i = \frac{1}{R_i} \sum_{r=1}^{R_i} y_{ir}, s_i^2 = \frac{1}{R_i - 1} \sum_{r=1}^{R_i} \left(y_{ir} - \bar{y}_i\right)^2 \tag{F.6}$$

If the ANOVA indicates the existence of a between-laboratory effect, then that effect is quantified by the standard deviation s_{lab} of the averages calculated for the laboratories, i.e.

$$s_{lab}^2 = \frac{1}{L-1} \sum_{i=1}^{L} \left(\bar{y}_i - \bar{\bar{y}}\right)^2 \tag{F.7}$$

Where

$$\bar{\bar{y}} = \frac{1}{L} \sum_{i=1}^{L} \bar{y}_i \tag{F.8}$$

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4) Matlab®, The MathWorks Inc.

In the case that the null hypothesis of no laboratory effect is accepted, the between-laboratory standard deviation is taken to be zero.

F.2.3 Calculating between-sampler variability

F.2.3.1 Notation

Let there be S sites identified by the index $i, i \in \{1,\ldots,S\}$ and L laboratories identified by the index $j, j \in \{1,\ldots,L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index $k, k \in K_i$, using samplers identified by index $f, f \in F_i$. The measured values of concentration are then denoted by:

$$x_{ijkf}, \quad f \in F_i, \quad k \in K_i, \quad j \in \{1,\ldots L\}, \quad i \in (1,\ldots,S)$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made, as well as the samplers F_i used, can be different from one site to another.

F.2.3.2 Data processing

In a similar way to that for data set 1, the data processing comprises two stages. In a first stage, considering the data for each sampler separately, the measured values corresponding to each site and each day are processed to remove outlying values. Then, considering the data for the samplers together, the values corresponding to each site and each day are normalized to remove effects associated with the factors of site and time, but preserving any sampler effect. In a second stage, an ANOVA is applied to the resulting data set corresponding to all sites, all days and all laboratories to decide whether a between-sampler effect exists. If the effect exists, a calculation of the between-sampler standard deviations is undertaken.

Following outlier rejection and data normalization, the data are denoted by:

$$v_{ijkf}, \quad f \in F_i, \quad k \in K_i, \quad j \in J_{ikf}, \quad i \in \{1,\ldots,S\} \tag{F.9}$$

where J_{ikf} contains the indices of the laboratories for which measured values are retained for site i, day k and sampler f. Since there is no interest in the factors of site, time and laboratory, an equivalent representation of the data are as:

$$y_{fr}, \quad r \in \{1,\ldots,R_f\}, \quad f \in F_1 \cup \cdots \cup F_S \tag{F.10}$$

which groups the measured values by sampler. Here, R_f is the number of retained measured values for sampler f over all sites, days and laboratories, and each y_{fr} equates to one of the normalized values v_{ijkf}. As for data set 1, the data set is generally unbalanced, because the numbers of measured values can be different from one sampler to another.

If an ANOVA indicates the existence of a between-sampler effect, then that effect is quantified by the standard deviation s_{sam} of the averages calculated for the samplers, i.e.

$$s_{sam}^2 = \frac{1}{F-1}\sum_{f=1}^{F}\left(\bar{y}_f - \bar{\bar{y}}\right)^2 \quad \text{(F.11)}$$

Where

$$\bar{y}_f = \frac{1}{R_f}\sum_{r=1}^{R_f} y_{fr}, \quad \bar{\bar{y}} = \frac{1}{F}\sum_{f=1}^{F}\bar{y}_f \quad \text{(F.12)}$$

and F is the total number of samplers. In the case that the null hypothesis of no sampler effect is accepted, the between-sampler standard deviation is taken to be zero.

F.2.4 Combined standard uncertainty

The relative standard uncertainty u_{rel} associated with an individual measured value of concentration is given:

$$u_{rel}^2 = s^2 + s_{lab}^2 + s_{sam}^2 \quad \text{(F.13)}$$

which combines the standard deviations related to within-laboratory, between-laboratory and between-sampler effects.

The between sampler variability results showed that s_{sam}^2 was insignificant; therefore it was not included in the uncertainty calculation.

F.3Remarks

The data analysis described, including the use of ANOVA and the calculations of the standard deviations to quantify the various effects, depends on assumptions about the homogeneity of these effects for different concentrations, sites, laboratories, samplers and time. Graphical displays of the data, in which the data are plotted against these factors, can be useful to identify obvious departures from these assumptions. In cases that the assumptions do not hold, the results of the data analysis may not be reliable expressions of the various effects considered.

F.4Results

NOTE All results were calculated with the outlier rejection disabled.

F.4.1 Data set 1 – Between laboratory and internal laboratory variability

The following table gives the p values from the analysis of variance for between laboratory effects. If $\geq p_c$, the null hypothesis of no laboratory effect is accepted at a 100 p_c % level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

Table F.1 — *p* value results from between laboratory analysis of variance

Protocol	EC	OC	TC
EUSAAR2 Trans	3,00E-04	0,0006	0,0003
IMPROVE Trans	1,61E-05	1,07E-09	8,80E-17
NIOSH Trans	8,92E-29	0,2399	1,20E-18
EUSAAR2 Refl	0,0003	0,0012	0,0003
IMPROVE Refl	0,0519	3,03E-09	8,65E-17
NIOSH Refl	0,3544	2,35E-38	1,19E-18

It can be seen that only IMPROVE reflectance (EC), NIOSH reflectance (EC) and NIOSH transmittance (OC) show no significant between laboratory effect at the 5 % level of confidence. In all cases the between laboratory variability was calculated and included in the overall uncertainty calculations.

Between laboratory variability and internal laboratory variability were calculated for the 6 thermal / optical protocols and the results shown below.

Table F.2 — Between laboratory variability

Analysis Protocol	Component	Between laboratory variability, %
EUSAAR2 Trans	EC	2,2
IMPROVE Trans	EC	2,9
NIOSH Trans	EC	9,0
EUSAAR2 Refl	EC	12,9
IMPROVE Refl	EC	67,2
NIOSH Refl	EC	488,7
NIOSH Trans	OC	0,6
NIOSH Refl	OC	3,3
IMPROVE Trans	OC	2,1
EUSAAR2 Trans	OC	1,5
EUSAAR2 Refl	OC	1,5
IMPROVE Refl	OC	2,3
NIOSH Refl	TC	1,6
NIOSH Trans	TC	1,6
EUSAAR2 Trans	TC	1,3
EUSAAR2 Refl	TC	1,3
IMPROVE Trans	TC	2,4
IMPROVE Refl	TC	2,4

Table F.3 — Internal laboratory variability

Analysis Protocol	Component	Internal laboratory variability, %
EUSAAR2 Trans	EC	9,4
IMPROVE Trans	EC	11,5
NIOSH Trans	EC	16,1
EUSAAR2 Refl	EC	55,6
IMPROVE Refl	EC	399,2
NIOSH Refl	EC	3922,5
NIOSH Trans	OC	4,3
EUSAAR2 Trans	OC	6,7
EUSAAR2 Refl	OC	7,1
IMPROVE Trans	OC	6,4
IMPROVE Refl	OC	7,0
NIOSH Refl	OC	5,1
EUSAAR2 Trans	TC	5,9
EUSAAR2 Refl	TC	5,9
NIOSH Refl	TC	3,5
NIOSH Trans	TC	3,5
IMPROVE Trans	TC	5,6
IMPROVE Refl	TC	5,6

F.4.2 Data set 2 – Between sampler variability

The following summarizes the results of the between sampler variability:

— No significant between sampler variability was found for TC.

— One protocol gave a possibly significant between sampler variability for OC. IMPROVE Trans gave an ANOVA value of 5,5 % resulting in a between sampler variability of 1,94 % (2σ, 95 %).

— Three protocols showed a significant to very significant between sampler variability for EC. EUSAAR2 Trans gave an ANOVA value of 3,2 %, IMPROVE Trans, gave an ANOVA value of 0,3 % and NIOSH Trans gave an ANOVA value of 0,5 %, resulting in a between sampler variability of 5,8, 6,0 and 8,8 % (2σ, 95 %) respectively. This significant between sampler variability may have only been detected due to the lower repeatability of these 3 protocols, 18 %, 22 % and 32 % (2σ, 95 %)

— The other three protocols, EUSAAR2 Refl, IMPROVE Refl and NIOSH Refl had internal repeatability's of 112 %, 800 % and 7800 % (2σ, 95 %) respectively making the determination of between sampler variability impossible.

— It is safe to suggest that there was no significant between sampler variability detected for most components and most protocols. Where it was detected it was insignificant compared to the protocol repeatability.

Between sampler variability was not included in the overall uncertainty calculations.

F.4.3 Data set 3a – Site specific ranking

Table F.4 — Combined variability calculated from the between laboratory and internal laboratory variability and the results for EC

Analysis Protocol	Component	Site	Combined variability, %
IMPROVE trans	EC	CAB	13,6
EUSAAR2 Trans	EC	CAB	19,0
NIOSH Trans	EC	CAB	23,5
IMPROVE refl	EC	CAB	27,3
EUSAAR2 Refl	EC	CAB	28,7
NIOSH Refl	EC	CAB	34,2
IMPROVE refl	EC	IPR	10,8
IMPROVE trans	EC	IPR	11,0
NIOSH Refl	EC	IPR	11,4
EUSAAR2 Refl	EC	IPR	15,8
EUSAAR2 Trans	EC	IPR	15,9
NIOSH Trans	EC	IPR	16,3
EUSAAR2 Trans	EC	WAL	15,3
IMPROVE trans	EC	WAL	19,7
NIOSH Trans	EC	WAL	30,1
EUSAAR2 Refl	EC	WAL	117,7
IMPROVE refl	EC	WAL	880,0
NIOSH Refl	EC	WAL	8573,5
IMPROVE trans	EC	BCN	4,8
EUSAAR2 Trans	EC	BCN	6,6
NIOSH Trans	EC	BCN	12,3
EUSAAR2 Refl	EC	BCN	16,3
IMPROVE refl	EC	BCN	19,1
NIOSH Refl	EC	BCN	30,1
EUSAAR2 Trans	EC	DUI	5,2
NIOSH Refl	EC	DUI	6,6
IMPROVE trans	EC	DUI	8,9

Analysis Protocol	Component	Site	Combined variability, %
EUSAAR2 Refl	EC	DUI	10,1
IMPROVE refl	EC	DUI	11,3
NIOSH Trans	EC	DUI	15,0
EUSAAR2 Trans	EC	AMS	9,3
IMPROVE trans	EC	AMS	10,1
EUSAAR2 Refl	EC	AMS	11,9
NIOSH Trans	EC	AMS	13,0
NIOSH Refl	EC	AMS	17,1
IMPROVE refl	EC	AMS	17,3

Table F.5 — Combined variability calculated from the between laboratory and internal laboratory variability and the results for OC

Analysis Protocol	Component	Site	Combined variability, %
EUSAAR2 Trans	OC	CAB	7,1
IMPROVE trans	OC	CAB	7,4
NIOSH Trans	OC	CAB	9,2
NIOSH Refl	OC	CAB	11,9
EUSAAR2 Refl	OC	CAB	12,5
IMPROVE refl	OC	CAB	14,3
NIOSH Trans	OC	IPR	5,1
IMPROVE trans	OC	IPR	5,4
NIOSH Refl	OC	IPR	5,7
IMPROVE refl	OC	IPR	7,2
EUSAAR2 Trans	OC	IPR	11,3
EUSAAR2 Refl	OC	IPR	11,5
NIOSH Trans	OC	WAL	5,0
NIOSH Refl	OC	WAL	5,5
EUSAAR2 Refl	OC	WAL	9,1
EUSAAR2 Trans	OC	WAL	9,6
IMPROVE refl	OC	WAL	11,3
IMPROVE trans	OC	WAL	11,6

Analysis Protocol	Component	Site	Combined variability, %
NIOSH Trans	OC	BCN	3,3
IMPROVE trans	OC	BCN	4,0
EUSAAR2 Trans	OC	BCN	5,5
EUSAAR2 Refl	OC	BCN	6,9
IMPROVE refl	OC	BCN	7,1
NIOSH Refl	OC	BCN	9,4
EUSAAR2 Trans	OC	DUI	2,9
NIOSH Trans	OC	DUI	3,5
NIOSH Refl	OC	DUI	3,6
IMPROVE trans	OC	DUI	4,4
EUSAAR2 Refl	OC	DUI	4,7
IMPROVE refl	OC	DUI	5,3
IMPROVE refl	OC	AMS	5,0
IMPROVE trans	OC	AMS	5,0
NIOSH Trans	OC	AMS	5,5
NIOSH Refl	OC	AMS	5,8
Eusaar2 Trans	OC	AMS	8,2
Eusaar2 Refl	OC	AMS	8,3

Table F.6 — Combined variability calculated from the between laboratory and internal laboratory variability and the results for TC

Analysis Protocol	Component	Site	Combined variability, %
EUSAAR2 Refl	TC	CAB	6,0
EUSAAR2 Trans	TC	CAB	6,0
IMPROVE refl	TC	CAB	6,5
IMPROVE trans	TC	CAB	6,5
NIOSH Refl	TC	CAB	8,4
NIOSH Trans	TC	CAB	8,4
IMPROVE trans	TC	IPR	4,3
IMPROVE refl	TC	IPR	4,3

Analysis Protocol	**Component**	**Site**	**Combined variability, %**
NIOSH Refl	TC	IPR	4,6
NIOSH Trans	TC	IPR	4,6
EUSAAR2 Refl	TC	IPR	11,3
EUSAAR2 Trans	TC	IPR	11,3
NIOSH Refl	TC	WAL	5,2
NIOSH Trans	TC	WAL	5,2
EUSAAR2 Refl	TC	WAL	8,9
EUSAAR2 Trans	TC	WAL	8,9
IMPROVE refl	TC	WAL	11,0
IMPROVE trans	TC	WAL	11,0
NIOSH Refl	TC	BCN	3,0
NIOSH Trans	TC	BCN	3,0
IMPROVE refl	TC	BCN	3,3
IMPROVE trans	TC	BCN	3,3
EUSAAR2 Trans	TC	BCN	4,2
EUSAAR2 Refl	TC	BCN	4,2
EUSAAR2 Trans	TC	DUI	2,7
EUSAAR2 Refl	TC	DUI	2,7
NIOSH Refl	TC	DUI	3,2
NIOSH Trans	TC	DUI	3,2
IMPROVE trans	TC	DUI	4,1
IMPROVE refl	TC	DUI	4,1
IMPROVE refl	TC	AMS	3,4
IMPROVE trans	TC	AMS	3,4
NIOSH Refl	TC	AMS	4,2
NIOSH Trans	TC	AMS	4,2
EUSAAR2 Refl	TC	AMS	6,8
EUSAAR2 Trans	TC	AMS	6,8

The results for EC, OC and TC were combined by site classification to give an overall ranking per site classification as shown below:

Table F.7 — Rural Background

EC	OC	TC
IMPROVE Trans	NIOSH Trans	EUSAAR2 Refl
EUSAAR2 Trans	NIOSH Refl	NIOSH Refl
IMPROVE Refl	EUSAAR2 Trans	IMPROVE Refl
NIOSH Trans	IMPROVE Trans	IMPROVE Trans
EUSAAR2 Refl	EUSAAR2 Refl	EUSAAR2 Trans
NIOSH Refl	IMPROVE Refl	NIOSH Trans

Table F.8 — Urban Background

EC	OC	TC
EUSAAR2 Trans	NIOSH Trans	NIOSH Refl
IMPROVE Trans	EUSAAR2 Trans	EUSAAR2 Trans
EUSAAR2 Refl	IMPROVE Trans	NIOSH Trans
NIOSH Refl	EUSAAR2 Refl	EUSAAR2 Refl
NIOSH Trans	NIOSH Refl	IMPROVE Refl
IMPROVE Refl	IMPROVE Refl	IMPROVE Trans

Table F.9 — Roadside

EC	OC	TC
EUSAAR2 Trans	IMPROVE Refl	IMPROVE Refl
IMPROVE Trans	IMPROVE Trans	IMPROVE Trans
EUSAAR2 Refl	NIOSH Trans	NIOSH Refl
NIOSH Trans	NIOSH Refl	NIOSH Trans
NIOSH Refl	EUSAAR2 Trans	EUSAAR2 Refl
IMPROVE Refl	EUSAAR2 Refl	EUSAAR2 Trans

This ranking was repeated just taking internal laboratory variability into account to try and remove any between laboratory dependence. The results are shown below with tables ordered in increasing internal variability:

Table F.10 — Rural Background

EC	OC	TC
IMPROVE Trans	NIOSH Trans	IMPROVE Refl
EUSAAR2 Trans	IMPROVE Trans	NIOSH Refl
IMPROVE Refl	NIOSH Refl	IMPROVE Trans
NIOSH Trans	EUSAAR2 Refl	EUSAAR2 Refl
EUSAAR2 Refl	EUSAAR2 Trans	NIOSH Trans
NIOSH Refl	IMPROVE Refl	EUSAAR2 Trans

Table F.11 — Urban Background

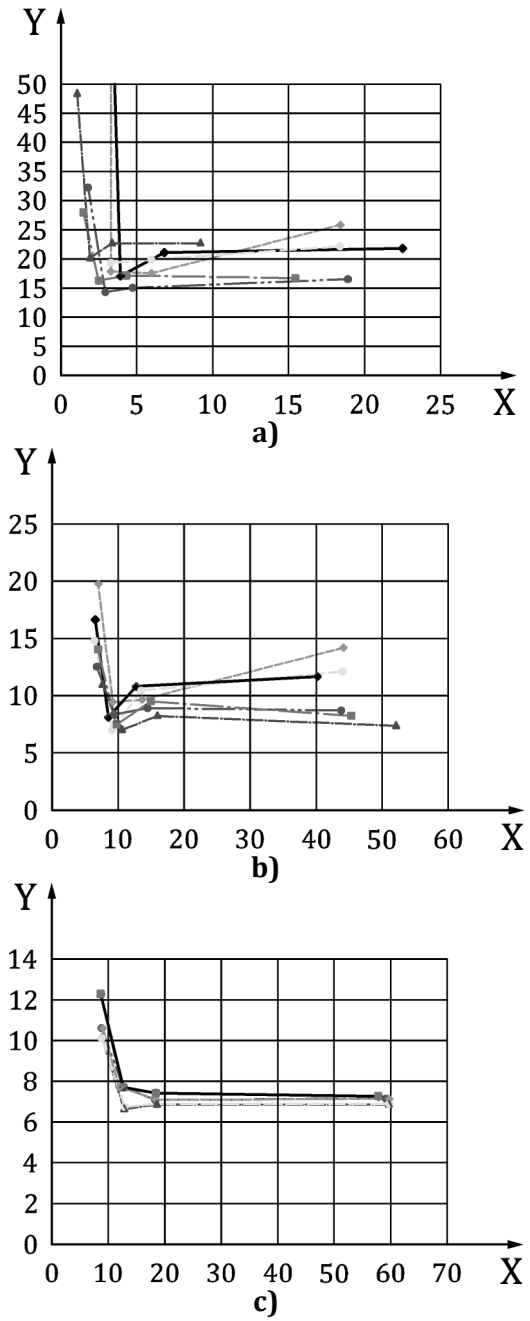
EC	OC	TC
IMPROVE Trans	NIOSH Trans	IMPROVE Refl
EUSAAR2 Trans	IMPROVE Trans	NIOSH Refl
NIOSH Refl	EUSAAR2 Trans	IMPROVE Trans
EUSAAR2 Refl	NIOSH Refl	NIOSH Trans
IMPROVE Refl	IMPROVE Refl	EUSAAR2 Refl
NIOSH Trans	EUSAAR2 Refl	EUSAAR2 Trans

Table F.12 — Roadside

EC	OC	TC
IMPROVE Trans	IMPROVE Trans	IMPROVE Refl
EUSAAR2 Trans	IMPROVE Refl	IMPROVE Trans
NIOSH Trans	NIOSH Trans	NIOSH Refl
EUSAAR2 Refl	NIOSH Refl	NIOSH Trans
NIOSH Refl	EUSAAR2 Trans	EUSAAR2 Refl
IMPROVE Refl	EUSAAR2 Refl	EUSAAR2 Trans

F.4.4 Data set 3B - Uncertainty over the measured concentration range

Results for each thermal / optical protocol from the complete data set were ordered by concentration and then split into 4 concentration bins: 0 % to 25 %, > 25 % to 50 %, > 50 % to 75 % and > 75 % to 100 % with equal number of measurements in each concentration bin. The combined expanded uncertainty (2σ, 95 %) due to between laboratory variability and internal laboratory variability was calculated for each concentration bin, the results of which are shown below:



Key

—◆—	EUSAAR2 reflectance	—▲—	NIOSH transmittance
—●—	NIOSH reflectance	—◆—	IMPROVE transmittance
- -◆- -	IMPROVE reflectance	X	µg.cm^{-2}
—■—	EUSAAR2 transmittance	Y	expanded combined uncertainty, in %

It is noted that the expanded uncertainties stay more or less constant after an initial decrease with increasing carbon concentrations.

Figure F.1 — Expanded combined uncertainties for EC (a)), OC (b)) and TC (c))

The following tables give the full results:

Table F.13 — Full results for EC

Analysis Protocol	Component	Concentration quarter	Between laboratory variability, %	Internal laboratory variability, %	Expanded combined Uncertainty, %	Minimum, µg.cm^{-2}	Maximum, µg.cm^{-2}	Mid-range, µg.cm^{-2}
EUSAAR2 refl	EC	Q1	16,2	86,5	176,0	0,00	2,05	1,03
EUSAAR2 refl	EC	Q2	2,1	8,3	17,1	2,08	3,97	3,03
EUSAAR2 refl	EC	Q3	4,3	9,6	21,1	3,97	6,86	5,42
EUSAAR2 refl	EC	Q4	6,6	8,7	21,8	6,87	22,57	14,72
EUSAAR2 Trans	EC	Q1	2,6	13,7	27,8	0,00	1,54	0,77
EUSAAR2 Trans	EC	Q2	4,5	6,8	16	1,55	2,52	2,04
EUSAAR2 Trans	EC	Q3	4,0	7,6	17,2	2,53	4,38	3,46
EUSAAR2 Trans	EC	Q4	4,2	7,1	16,6	4,39	15,49	9,94
IMPROVE Refl	EC	Q1	98	619	1253	0,00	1,62	0,81
IMPROVE Refl	EC	Q2	4,5	7,8	18,1	1,63	3,37	2,50
IMPROVE Refl	EC	Q3	4,3	7,7	17,6	3,38	5,98	4,68
IMPROVE Refl	EC	Q4	9,2	9,1	25,8	5,98	18,43	12,21
IMPROVE Trans	EC	Q1	1,9	16,0	32,3	0,00	1,82	0,91
IMPROVE Trans	EC	Q2	3,2	6,5	14,5	1,82	2,95	2,39
IMPROVE Trans	EC	Q3	4,0	6,4	15,1	2,95	4,76	3,86
IMPROVE Trans	EC	Q4	3,9	7,3	16,5	4,78	18,96	11,87
NIOSH Refl	EC	Q1	741	6064	12218	0,00	1,62	0,81
NIOSH Refl	EC	Q2	2,7	9,3	19,4	1,63	3,37	2,50
NIOSH Refl	EC	Q3	4,2	9,0	19,9	3,38	5,98	4,68
NIOSH Refl	EC	Q4	5,7	9,5	22,2	5,98	18,43	12,21

NIOSH Trans	EC	Q1	7,2	23,1	48,4	0,00	1,11	0,56
NIOSH Trans	EC	Q2	5,0	8,9	20,4	1,11	1,95	1,53
NIOSH Trans	EC	Q3	5,7	9,8	22,7	1,96	3,38	2,67
NIOSH Trans	EC	Q4	6,6	9,4	22,9	3,38	9,28	6,33

Table F.14 — Full results for OC

Analysis Protocol	Component	Concentration quarter	Between laboratory variability, %	Internal laboratory variability, %	Expanded combined Uncertainty, %	Minimum, $\mu g.cm^{-2}$	Maximum, $\mu g.cm^{-2}$	Mid-range, $\mu g.cm^{-2}$
EUSAAR2 refl	OC	Q1	2,4	7,9	16,6	2,46	6,62	4,54
EUSAAR2 refl	OC	Q2	0,7	4,0	8,1	6,62	8,57	7,60
EUSAAR2 refl	OC	Q3	1,3	5,3	10,8	8,59	12,79	10,69
EUSAAR2 refl	OC	Q4	2,4	5,3	11,6	12,82	40,24	26,53
EUSAAR2 Trans	OC	Q1	1,8	6,8	14,0	2,62	7,03	4,83
EUSAAR2 Trans	OC	Q2	0,9	3,6	7,5	7,04	9,81	8,43
EUSAAR2 Trans	OC	Q3	1,3	4,6	9,5	9,81	15,05	12,43
EUSAAR2 Trans	OC	Q4	0,9	4,0	8,2	15,09	45,33	30,21
IMPROVE Refl	OC	Q1	4,4	8,8	19,7	2,91	7,13	5,02
IMPROVE Refl	OC	Q2	0,9	4,6	9,4	7,47	9,23	8,35
IMPROVE Refl	OC	Q3	1,0	4,7	9,7	9,24	13,63	11,44
IMPROVE Refl	OC	Q4	4,0	5,9	14,2	13,63	44,10	28,87
IMPROVE Trans	OC	Q1	2,6	5,7	12,5	2,46	6,83	4,65
IMPROVE Trans	OC	Q2	1,7	3,8	8,4	6,83	9,51	8,17
IMPROVE Trans	OC	Q3	2,0	4,0	8,9	9,51	14,56	12,04
IMPROVE Trans	OC	Q4	1,1	4,2	8,7	14,57	43,88	29,23

NIOSH Refl	OC	Q1	2,6	6,9	14,7	2,91	6,54	4,73
NIOSH Refl	OC	Q2	0,5	3,4	6,9	7,47	9,23	8,35
NIOSH Refl	OC	Q3	0,7	5,2	10,4	9,24	13,63	11,44
NIOSH Refl	OC	Q4	2,2	5,6	12,0	13,64	44,10	28,87
NIOSH Trans	OC	Q1	1,5	5,3	11,1	2,75	7,74	5,25
NIOSH Trans	OC	Q2	0,7	3,5	7,1	7,75	10,69	9,22
NIOSH Trans	OC	Q3	1,3	3,9	8,3	10,69	15,97	13,33
NIOSH Trans	OC	Q4	1,0	3,6	7,4	15,99	52,09	34,04

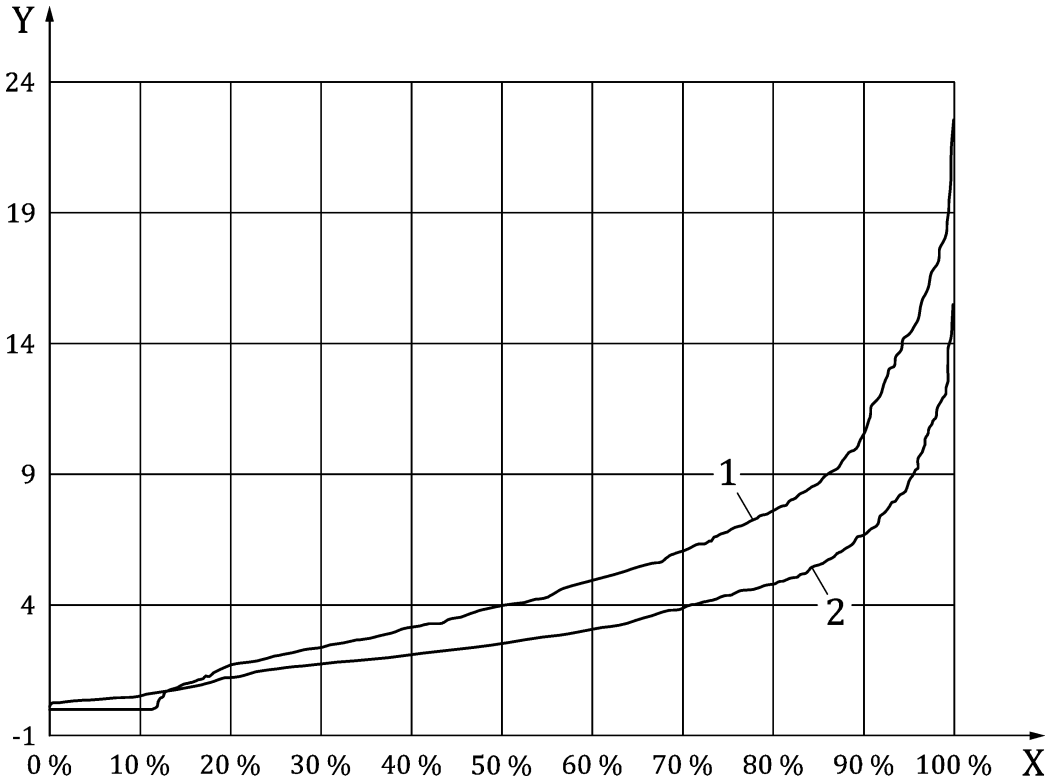
Table F.15 — Full results for TC

Analysis Protocol	Component	Concentration quarter	Between laboratory variability, %	Internal laboratory variability, %	Expanded combined Uncertainty, %	Minimum, µg.cm^{-2}	Maximum, µg.cm^{-2}	Mid-range, µg.cm^{-2}
EUSAAR2 refl	TC	Q1	2,2	5,7	12,2	3,01	8,74	5,88
EUSAAR2 refl	TC	Q2	1,2	3,6	7,7	8,76	12,67	10,72
EUSAAR2 refl	TC	Q3	1,2	3,5	7,4	12,68	18,44	15,56
EUSAAR2 refl	TC	Q4	1,5	3,3	7,2	18,45	57,90	38,18
EUSAAR2 Trans	TC	Q1	2,2	5,7	12,2	3,01	8,74	5,88
EUSAAR2 Trans	TC	Q2	1,2	3,6	7,7	8,76	12,67	10,72
EUSAAR2 Trans	TC	Q3	1,2	3,5	7,4	12,38	18,44	15,41
EUSAAR2 Trans	TC	Q4	1,5	3,3	7,2	18,45	57,90	38,18
IMPROVE Refl	TC	Q1	2,3	4,7	10,6	3,14	9,09	6,12
IMPROVE Refl	TC	Q2	1,9	3,4	7,7	9,10	12,16	10,63
IMPROVE Refl	TC	Q3	1,9	3,0	7,1	12,92	18,80	15,86
IMPROVE Refl	TC	Q4	1,6	3,2	7,1	18,82	59,68	39,25

IMPROVE Trans	TC	Q1	2,4	4,7	10,6	3,10	8,92	6,01
IMPROVE Trans	TC	Q2	1,8	3,4	7,7	8,92	12,81	10,86
IMPROVE Trans	TC	Q3	1,9	3,0	7,1	12,82	18,48	15,65
IMPROVE Trans	TC	Q4	1,6	3,2	7,1	18,51	59,13	38,82
NIOSH Refl	TC	Q1	1,4	4,8	10,0	3,14	9,09	6,12
NIOSH Refl	TC	Q2	1,5	3,0	6,7	9,10	12,91	11,01
NIOSH Refl	TC	Q3	1,4	3,2	6,9	12,92	18,80	15,86
NIOSH Refl	TC	Q4	1,5	3,1	6,8	18,82	59,68	39,25
NIOSH Trans	TC	Q1	1,4	4,8	10,0	3,14	9,09	6,12
NIOSH Trans	TC	Q2	1,5	3,0	6,7	9,10	12,91	11,01
NIOSH Trans	TC	Q3	1,4	3,2	6,9	11,04	18,80	14,92
NIOSH Trans	TC	Q4	1,5	3,1	6,8	18,82	59,68	39,25

As the above uncertainties are calculated on a single measurement result, it shows that repeat analysis is not required to deliver an overall uncertainty of less than 25 % for concentrations above 2 µg.cm^{-2}. For concentrations below this the relative uncertainty is greater than 25 %, but probably limited by the detection limit.

The above results show that the combined uncertainty for the reflectance optical correction increases dramatically at low concentrations due to very large internal variance in repeatabilities. This is due to the reflectance method being unable to detect small EC concentrations. This is highlighted by the chart below which shows the ranked frequency chart for the EUSAAR2 results. All the reflection protocols showed similar behaviour.



Key

X number of measurements

Y µg.cm^{-2}

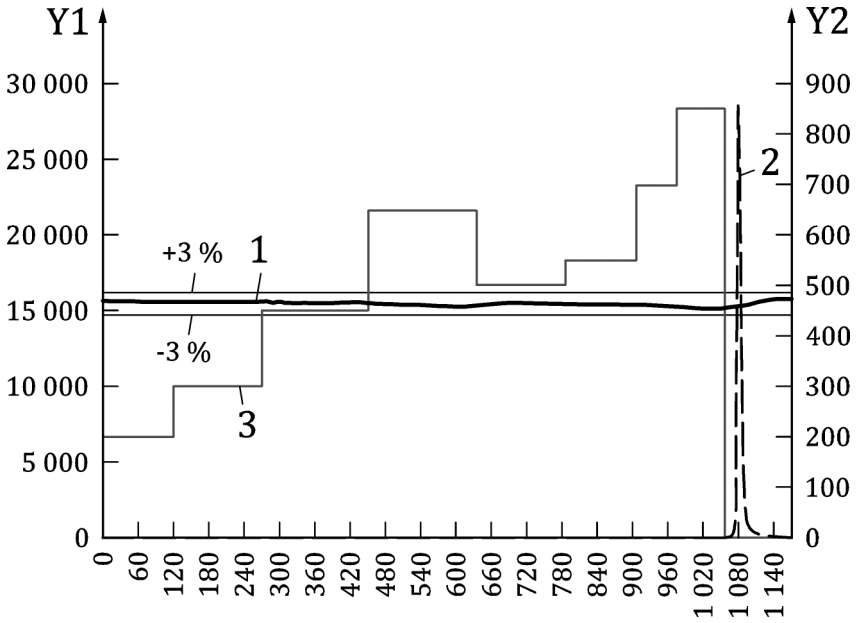
1 reflectance

2 transmission

Figure F.2 — Ranked results of EC measurements indicating lower detection limits for transmission compared to reflection

Annex G
(informative)

Good example for an instrument blank laser signal for EUSAAR2



Key

Y1 laser transmittance, in a.u

Y2 temperature, in °C

1 laser transmittance signal (wavelength approximately 658 nm)

2 FID signal

3 Temperature

Figure G.1 — Good example for an instrument blank laser signal for EUSAAR2 including ± 3 % uncertainty limits

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