SLOVENSKI STANDARD
SIST EN 16909:2017

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Zunanji zrak - Merjenje elementarnega ogljika (EC) in organskega ogljika (OC), zbranega na filtru

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

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

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

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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 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of an identical text or by endorsement, at the latest by September 2017, and conflicting national standards shall be withdrawn at the latest by September 2017.

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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/cm², and the subsequent calculation of concentrations as µg/m³. 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}/cm² and 1,8 µg C_{OC}/cm² to 38 µg C_{EC}/cm² and 49 µg C_{OC}/cm² in the laboratory and to 16 µg C_{EC}/cm² and 45 µg C_{OC}/cm² 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.

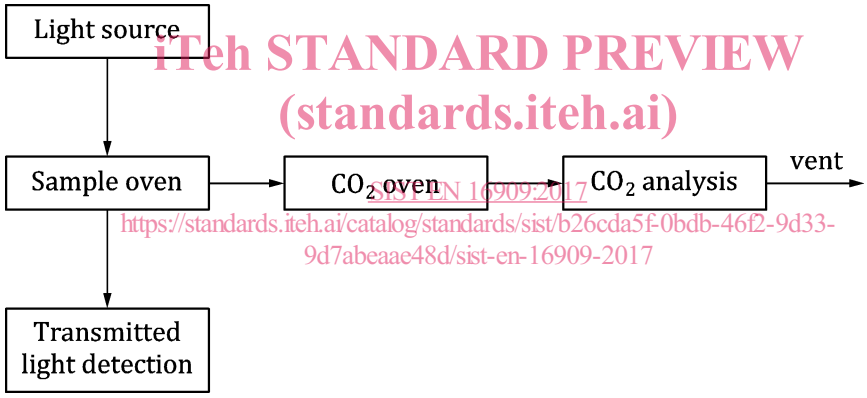

Figure 1 — Simple scheme of a thermal-optical analyser

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]).