SLOVENSKI STANDARD
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Kakovost zunanjega zraka - Vodilo za merjenje elementarnega ogljika (EC) in organskega ogljika (OC), zbranega na filtru

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

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

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

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English Version

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

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

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

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

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Foreword

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

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Introduction

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

MEASUREMENTS AT RURAL BACKGROUND LOCATIONS IRRESPECTIVE OF CONCENTRATION

*A. **Objectives***
The main objectives of such measurements are to ensure that adequate information is made available on levels in the background. This information is essential to judge the enhanced levels in more polluted areas (such as urban background, industry related locations, traffic related locations), assess the possible contribution from long-range transport of air pollutants, support source apportionment analysis and for the understanding of specific pollutants such as particulate matter. It is also essential for the increased use of modelling in urban areas.
*B. **Substances***
Measurement of $PM_{2,5}$ shall include at least the total mass concentration and concentrations of appropriate compounds to characterise its chemical composition. At least the list of chemical species given below shall be included. SO_4^{2-}, Na^+,NH_4^+, Ca^{2+}, elemental carbon (EC), NO_3^-, K^+, Cl^-, Mg^{2+}, organic carbon (OC)
*C. **Siting***
Measurements should be taken in particular in rural background areas in accordance with parts A, B and C of Annex III

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

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

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

a) thermal method with optical correction for EC and OC for samples collected on filters,

b) other off-line analysis techniques for EC and OC for samples collected on filters,

c) other on-line analysis techniques for EC and OC for samples collected on filters,

d) other analysis techniques for either EC and/or OC,

e) other analysis techniques measuring surrogates for either EC and/or OC (i.e. light absorption).

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

1) Resolution 35

Given

— *the urgent need for Member States to have a standardised method for EC and OC, as they are due to start sampling from June 2010, and*

— *in the absence of a mandate from the Commission,*

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

2) Resolution 36

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

3) Resolution 37

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

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

— the applicable concentration ranges of the proposed method are limited by the optical correction and thermal protocols applied in the analysis of EC and OC; since the latter is dependent on the instrument as well as the chosen protocols no definitive values can be given;

— temperature measurement in the instrument ovens: location and reproducibility;

— influence of sampling artefacts on the data quality;

— provision and use of reference materials.

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

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

1 Scope

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

The Technical Report describes the analytical procedures for determining EC and OC on quartz fibre filters as µg/cm^2, and the subsequent calculation of concentrations as µg/m³. Sampling onto filters is to be done in accordance with EN 14907 for $PM_{2,5}$. The sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and ab/desorption of volatile organic compounds on the filter at the time of sampling.

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

The measurement procedures are applicable for:

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

The scope includes non rural site measurements, to allow the assessment of additional exposure of people in urban areas as stated in the objectives of the council directive and to achieve coherence in the European approach. Measurements are made over a nominal sampling period of 24 h, and concentrations are expressed as µg/m³, where the volume of air is the volume at ambient conditions near the inlet of the sampler at the time of sampling.

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

2 Terms, definitions and abbreviations

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

2.1 Terms and definitions

2.1.1
total carbon
TC
total quantity of carbon atoms in a PM sample, whatever the constituent it belongs to. This includes EC, OC and IC

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

2.1.2
elemental carbon
EC
fraction of the non-IC total carbon in a PM sample, characterised by its non-volatility according to a specified thermal / optical protocol. EC evolves from the sample by oxidation only

2.1.3
organic carbon
OC
fraction of the non-IC total carbon in a PM sample that is volatilised or pyrolyzed in a specified thermal/optical protocol

2.1.4
inorganic carbon
IC
fraction of carbon belonging to mineral species, including carbonates and other molecules

2.1.5
carbonate carbon
CC
fraction of carbon belonging to a carbonate group

NOTE Carbonate carbon (mainly $CaCO_3$ and $MgCO_3$) is viewed as the only inorganic carbon fraction being released within the temperature range used in the thermal protocols.

2.1.6
sampling artefact
ab(d)sorption of gaseous species in (on) a PM sampling substrate (positive sampling artefact), and volatilization of particulate species from a PM sampling substrate (negative sampling artefact)

2.1.7
PM_x
particulate matter suspended in air which passes through a size-selective inlet with a 50 % efficiency cut-off at x µm aerodynamic diameter

2.2 Abbreviations

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

3 Principle

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

4 Materials and instruments

4.1 Materials

4.1.1 Gases

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

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

— hydrogen at least 99,997 % (% by volume).

4.1.2 Standard solution

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

4.1.3 Other materials

— precision puncher,

— quartz boat for the filter punch,

— stainless steel tweezers for sample handling,

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

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

4.2 Instruments

4.2.1 Sampling instruments

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

4.2.2 Analytical instruments

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

4.2.2.1 Performance requirements of the analytical instrument

Thermo-Optical EC and OC Analyser,

— the instrument detection limit should be 0,2 µg carbon per cm² of filter;

— the stability of repeated TC measurements of an external standard (e.g. sucrose solution) should be ± 10 % or ± 0,5 µg C/cm² (if 10 % would be less than 0,5 µg C/cm^2) over a working day (see 9.1.2.2).

5 Sampling

5.1 Filter material

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

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

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

This assessment should cover:

— average blank concentrations,

— blank concentration variability.

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

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

5.2 Pre-treatment of filter material and handling

Blank values and the corresponding standard deviation need to be low compared to the expected measured values. In general, pre-treatment (firing) is not needed if the average OC content is ≤ 2 µg C/cm² and the standard deviation of the OC content is ≤ 1 µg C/cm².

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

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

5.3 Conditioning and handling before and after sampling

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

5.4 Sampling duration and frequency

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

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

5.5 Field sampling and type of sampler

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

5.6 Site types

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

5.7 Filter environment during sampling

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

6 Transport and storage

6.1 Handling

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

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

6.2 Time and temperature limits

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

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

6.3 Coding

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

7 Analysis

7.1 General

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