SLOVENSKI STANDARD
kSIST-TP FprCEN/TR 17554:2020

01-september-2020

Zunanji zrak - Uporaba standarda EN 16909 za določevanje elementarnega ogljika (EC) in organskega ogljika (OC) v PM10 in grobih frakcijah

Ambient air - Application of EN 16909 for the determination of elemental carbon (EC) and organic carbon (OC) in PM10 and PMcoarse

Außenluft - Anwendung der EN 16909 zur Bestimmung von elementarem Kohlenstoff (EC) und organischem Kohlenstoff (OC) in PM10 und PMcoarse

Air ambiant - Mesurage (ou Détermination) du carbone élémentaire (CE) et du carbone organique (OC) dans les fractions PM10 et grossières

Ta slovenski standard je istoveten z: FprCEN/TR 17554

ICS:

13.040.20 Kakovost okoljskega zraka Ambient atmospheres

kSIST-TP FprCEN/TR 17554:2020 en,fr,de

TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

FINAL DRAFT
FprCEN/TR 17554

July 2020

ICS

English Version

Ambient air - Application of EN 16909 for the determination of elemental carbon (EC) and organic carbon (OC) in PM10 and PMcoarse

Air ambiant - Mesurage (ou Détermination) du carbone élémentaire (CE) et du carbone organique (OC) dans les fractions PM10 et grossières

Außenluft - Anwendung der EN 16909 zur Bestimmung von elementarem Kohlenstoff (EC) und organischem Kohlenstoff (OC) in PM10 und PMcoarse

This draft Technical Report is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 264.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a Technical Report. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a Technical Report.

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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Contents

European foreword

This document (FprCEN/TR 17554:2020) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document is currently submitted to the Vote on TR.

Introduction

The standard method EN 16909 provides guidance for the determination of organic carbon (OC) and elemental carbon (EC) in airborne particulate matter deposited on filters. It has been developed following the requirement for the EU member states to measure OC and EC in the $PM_{2,5}$ size fraction (less than 2,5 µm in aerodynamic diameter) at background sites [1]. EN 16909 standard states: “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.”

1 Scope

This document describes procedures to assess the applicability of the standard method EN 16909 (determination of OC and EC deposited on filters) to particle size fractions up to 10 µm in aerodynamic diameter (50 % cut off).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 16909, *Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 16909 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
PM_x
particulate matter suspended in air which is small enough to pass through a size-selective inlet with a 50 % efficiency cut-off at x µm aerodynamic diameter

[SOURCE: EN 12341:2014 [27], definition 3.1.14]

3.2
PM_{coarse} fraction
the PM_{10} fraction excluding the $PM_{2,5}$ fraction

3.3
OC_x
organic carbon component of PM_x

3.4
EC_x
elemental carbon component of PM_x

3.5
PC_x
pyrolytic carbon component of PM_x

3.6
TC_x
Total carbon component of PM_x

4 Symbols and abbreviations

TC	total carbon
CC	carbonate carbon
EC	elemental carbon
OC	organic carbon
OC_{sp}	organic carbon in spiked samples
OC_{am}	ambient organic carbon
EC_{sp}	elemental carbon in spiked samples
EC_{am}	ambient elemental carbon
OC_{sm}	organic carbon in spiked blank filters
EC_{sm}	elemental carbon in spiked blank filters
PC	pyrolytic carbon as defined by the thermal-optical method
EBC	equivalent black carbon measured by optical absorption at 658 nm within the OC-EC analyser
CPM_{coarse}	calculated PM_{coarse} mass concentration (PM_{coarse} calculated as $PM_{10} – PM_{2,5}$)
COC_{coarse}	calculated OC_{coarse} mass concentration (OC_{coarse} calculated as $OC_{10} – OC_{2,5}$)
CEC_{coarse}	calculated EC_{coarse} mass concentration (EC_{coarse} calculated as $EC_{10} – EC_{2,5}$)
CPC_{coarse}	calculated PC_{coarse} mass concentration (PC_{coarse} calculated as $PC_{10} – PC_{2,5}$)
CTC_{coarse}	calculated TC_{coarse} mass concentration (TC_{coarse} calculated as $TC_{10} – TC_{2,5}$)
EUSAAR2	thermal-optical analytical protocol for determining OC and EC, from EN 16909

5 Principle

The principle of these procedures is to compare the results of the analytical protocol described in EN 16909, for the analysis of OC and EC deposited on filters in particulate matter, on samples containing different amounts of coarse particles (aerodynamic diameter > 2,5 µm) or different amounts of species that are predominantly in the PM_{coarse} fraction (e.g. sea salt, carbonates, silicates, metal oxides, primary biogenic matter). These comparisons aim at determining the range of mass concentrations of possibly interfering material(s) (or the range of PM_{coarse} mass concentration, as an indicator of those) for which EN 16909 is applicable for the determination of OC and EC concentrations in PM_{10} or PM_{coarse} deposited on filters.

Certain procedures in this document make use of ambient aerosol samples of different size fractions that have been collected simultaneously. They are based on the simple principle that for any PM constituent (including OC and EC), its concentration in $PM_{2,5}$ shall be less than or equal to its concentration in PM_{10}, and its concentration in PM_{10} is equal to the sum of its concentrations in $PM_{2,5}$ and PM_{coarse} (within combined uncertainties).

Other procedures involve the spiking of loaded filters with well-characterized synthetic or natural material. OC, EC or OC:EC mixtures can be spiked onto coarse PM filter sample aliquots (punches). The applicability of EN 16909 is assessed on the recovery of OC and/or EC. Alternatively, species known to be major constituents of PM_{coarse} but which contain no OC or EC (e. g. sea salt, carbonates, silicates, metal oxides) can be spiked on $PM_{2,5}$ ambient filter sample aliquots. In this case, the applicability of EN 16909 is assessed on the consistency of OC and EC loadings in the spiked and non-spiked aliquots.

A robust estimation of the measurement uncertainties is needed to make it possible to draw conclusions from these tests.

Considering the diversity of the aerosol particle compositions (both in the coarse and the fine fraction), the procedures listed in this document can rigorously only give “negative” results (i.e. a conclusion that EN 16909 is not applicable above a certain level of interfering material). If none of these tests gave negative results, it could only be stated that there is no evidence that EN 16909 cannot be applied for the cases that have been tested.

6 Previous studies on interferences from inorganic components

6.1 General

The optically-determined split point between OC and EC in the analysis could be shifted by the presence of coarse material. This will affect the determination of EC and OC only if the assumptions on PC and EC absorption cross-sections become invalid, so that the optical correction for charring is inconsistent with the EC and OC analysis in $PM_{2,5}$. Certain inorganic compounds might interfere with OC and EC determination in this way. These include carbonate carbon, mineral oxides and salts [2]. Carbonates can evolve during thermal-optical analysis and be detected as either OC or EC. Metal oxides and inorganic salts can oxidise EC or catalyse EC oxidation in an inert atmosphere [3]. Carbonate carbon, CC is of primary origin, making usually only a minor contribution to the total carbonaceous matter in the fine fraction. It has been shown to represent less than 5 % of TC in $PM_{2,5}$ mass concentration [2]. However, CC may be an important constituent of PM coarse fractions; e.g. [26] reported high CC concentrations in PM_{10} due to sandstorms (up to 8 % in PM_{10} mass concentration in extreme events). Thus, CC interferences in thermal-optical analysis are more relevant for PM_{10} and PM_{coarse} than for $PM_{2,5}$. Similarly, interferences from mineral oxides on the OC and EC determination, typically from soil, are expected to be high in coarse aerosol particles. Concerning inorganic salts, their effect is relevant for all size fractions because they have different size distribution patterns. Alkali and alkaline-earth metal salts are mostly found in the coarse size fraction, while transition metal salts can be present in all particle size modes [4].

6.2 Carbonate carbon

The lack of information regarding CC content of PM samples may significantly affect OC and EC determination, especially in certain areas (such as sites affected by construction works or resuspended road dust, or at coastal sites), and/or under specific meteorological conditions, e.g. during desert dust intrusions. The overestimation of OC or EC due to CC interference might be negligible for fine particulate matter, since the contribution of CC in $PM_{2,5}$ is usually below 5 % of TC, but it could be significant for PM_{10} or PM_{coarse} fractions if the CC is measured as EC [2].

The decomposition temperature of carbonate during thermal-optical analysis may vary depending on a number of factors such as: the chemical composition of the carbonate compound (e.g. $CaCO_3$ vs. $CaMg(CO_3)_2$), the presence of other minerals (e.g. hematite), the crystal form (e.g. calcite vs. aragonite), the grain size, and the temperature protocol used [5]. [6] demonstrated that natural calcite decomposes at 650 °C in the helium mode of the EUSAAR2 protocol. However, evolution temperatures may vary substantially depending on the mixture of CC with other materials. For example, the presence of NaCl decreased the decomposition temperature of dolomite from 735 °C to 560 °C when pure dolomite was analysed by thermal analysis [7].

EN 16909 described several methods for the determination of CC in $PM_{2,5}$ samples. Jankowski et al. (2008) recommended a thermal treatment of aerosol-loaded filters at 460 °C for 60 min in an O_2 atmosphere to remove OC and EC, and a subsequent determination of TC. This TC would then be completely attributed to CC. [6] suggested a separate analysis for CC by directly determining the amount of CO_2 produced by acidifying the sample. Some researchers ([8], [9], [10]) used acid pretreatment and infrared spectroscopy measurements to identify CC presence in the sample and fitted a Gaussian function to the FID signal to determine CC, EC, and OC levels. [5] compared the HCl acidification method, the manual integration of the sharp peak appearing in the last step of the inert mode of a NIOSH-like protocol, and the acidification of the sample with phosphoric acid. The peak integration method provided higher CC concentrations than the acidification method [5], and therefore the determination of CC with an independent method (e.g. by acidic decomposition of carbonate and subsequent detection of CO_2) is recommended if other parts of the filter are available.

6.3 Metal oxides

The presence of certain minerals in aerosol samples can complicate the optical correction for pyrolysis. [11] and [12] report that mineral oxides like iron oxide might provide oxygen and oxidize some EC at high temperatures in the helium mode. For samples that contain large fractions of resuspended soil, demolition dust, desert dust, sea salt, or samples from sites close to railways, trams, subways, where a high content of Fe oxides is expected, the split point between OC and EC might be moved relative to the position when the minerals are not present [13], [14], [15].

6.4 Inorganic salts

The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants in the filters, or as part of the deposited material, has been shown to catalyse the oxidation of EC at lower temperatures [16]. Such catalysis would affect the distribution of carbon between the peaks during thermal-optical analysis.

In the study reported in [17], metal salt particles generated in the laboratory, including alkali (NaCl, KCl, Na_2SO_4), alkaline-earth ($MgCl_2$, $CaCl_2$) and transition metal salts ($CuCl_2$, $FeCl_2$, $FeCl_3$, CuCl, $ZnCl_2$, $MnCl_2$, $CuSO_4$, $Fe_2(SO_4)_3$), were deposited on a layer of diesel particles to investigate their effect on EC and OC quantification with thermal-optical analysis using the NIOSH5040 protocol. The measurements showed that metal salts lowered the split time, reduced the oxidation temperature of EC and enhanced charring. The split point was more affected by changes in EC oxidation temperature than it was by charring. The resulting EC/OC ratio was reduced by between 0 % and 80 % in the presence of the salts. Transition metals were more active than alkali and alkaline-earth metals; copper was the most active. Copper and iron chlorides were more active than sulphates. The melting point of the metal salts was strongly correlated with the increase of OC charring, but not with the reduction of EC oxidation temperature. [18] analysed mixtures of industrial carbon black and NaCl by thermal-optical analysis and concluded that Na lowers the combustion temperature of EC from 870 °C to approximately 800 °C. An older study [19] reported that high concentrations of the ions Na^+ and K^+ in biomass burning aerosol samples catalyse the combustion of EC material at lower temperatures.

Inorganic constituents that coexist with carbonaceous materials in ambient aerosol samples such as $(NH_4)_2SO_4$ and NH_4HSO_4 can enhance charring of insoluble OC (Yu et al., 2002). Moreover, the presence of the oxygen in $(NH_4)_2SO_4$ could affect the OC and EC concentrations by releasing oxygen in the helium mode and therefore allowing some of the EC to evolve [18].