SLOVENSKI STANDARD
SIST-TP CEN/TR 16269:2011

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Kakovost zunanjega zraka - Vodilo za merjenje anionov in kationov v frakciji PM2,5

Ambient air quality - Guide for the measurement of anions and cations in PM2,5

Außenluftqualität - Leitfaden zur Messung von Anionen und Cationen in PM2,5

Qualité de l'air ambiant - Guide pour le mesurage des anions et des cations dans la fraction PM2,5

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13.040.20	Kakovost okoljskega zraka	Ambient atmospheres

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TECHNICAL REPORT
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English Version

Ambient air - Guide for the measurement of anions and cations in PM2,5

Air ambiant - Guide pour le mesurage des anions et des cations dans la fraction PM2,5

Außenluft - Leitfaden zur Messung von Anionen und Kationen in PM2,5

This Technical Report was approved by CEN on 8 August 2011. It has been drawn up by the Technical Committee CEN/TC 264.

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

Management Centre: Avenue Marnix 17, B-1000 Brussels

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Contents

Page

Foreword

This document (CEN/TR 16269:2011) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

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Introduction

This CEN Technical Report describes how to measure a specified range of anions and cations in $PM_{2,5}$.

The new EU Air Quality Directive 2008/50/EC on ambient air quality and cleaner air for Europe requests the measurements of concentrations of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in $PM_{2,5}$ at rural background locations. In Annex IV of the Directive, guidance for these measurements is given (see Annex D).

Until now measurements of anions and cations in PM have been performed by the EMEP programme, mainly by using a filterpack with limited size selectivity. The Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe (EMEP) was launched in 1977 as a response to the growing concern over the effects on the environment caused by acid deposition. EMEP was organized under the auspices of the United Nations Economic Commission for Europe (UNECE). Today EMEP is an integral component of the cooperation under the Convention on Long-range Transboundary Air Pollution.

Directive 2008/50/EC requires that measurements at rural sites, where appropriate, shall be coordinated with the monitoring strategy and measurement programme of EMEP. Although, there are different sampling procedures involved, a common approach is used for the analytical procedure.

In order to keep the agreement between existing EMEP data and data to be produced using this CEN technical report as close as possible, the EMEP protocol has been taken as starting point for this CEN technical report. This CEN technical report differs from the EMEP protocol in the sense that measurement of anions and cations are done in $PM_{2,5}$, and that a number of critical parameters (e.g. choice of filter materials) are fixed.

Additional attention is given to harmonizing these critical parameters with elemental carbon/organic carbon (EC/OC) measurements and with $PM_{2,5}$ measurements as well, as the sampling usually is done simultaneously.

Finally, it should be noted that this CEN Technical Report has been produced in order to give assistance to those making measurements in accordance with Directive 2008/50/EC as rapidly as possible. However, there are still some open issues, including the influence of various sampling artefacts on the data quality, which can only be answered via validation work. This CEN Technical Report is not intended to supersede existing (inter)national standards or harmonized methods.

1 Scope

This CEN Technical Report specifies a method for the determination of the mass of water soluble NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in $PM_{2,5}$ samples which can be used to comply with Directive 2008/50/EC.

This CEN Technical Report describes a measurement method which comprises sampling of anions and cations as part of the $PM_{2,5}$ particulate phase, sample extraction and analysis of anions and cations by ion chromatography. Alternately, cations, excluding ammonium can be analysed by inductively coupled plasma optical emission spectrometry (ICP-OES).

This CEN Technical Report may be used at rural background monitoring sites that are in accordance with the requirements of Directive 2008/50/EC. However, since this CEN Technical Report has not been validated in the field for these, or any other, monitoring site types, it may be considered equally applicable to all site types.

NOTE The detection limits described in this CEN technical report method will be limited by the noise level of the detector and the variability of the mass in laboratory blank filters rather than by the concentrations of anions and cations in ambient air.

2 Terms and definitions

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

2.1
ambient air
outdoor air in the troposphere excluding workplace air

[EN 14907]

2.2
high volume sampling method
HVS
method for sampling particulate matter with a flow rate of 30 m^3/h

[EN 14907]

2.3
low volume sampling method
LVS
method for sampling particulate matter with a flow rate of 2,3 m^3/h

[EN 14907]

2.4
$PM_{2,5}$
fraction of suspended particulate matter which passes through a size-selective inlet with a 50 % cut-off efficiency at 2,5 µm aerodynamic diameter

[EN 14907]

2.5
PM_{10}
fraction of suspended particulate matter which passes through a size-selective inlet with a 50 % cut-off efficiency at 10 µm aerodynamic diameter

2.6

suspended particulate matter

SPM

notion of all particles surrounded by air in a given, undisturbed volume of air

[EN 14907]

2.7

measurement uncertainty

non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

[JGCM 200:2008 (VIM)]

3 Symbols and abbreviations

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

3.1 Symbols

γ_{amb}	mass concentration of anions or cations in ambient air, in µg/m^3
δ_i	deviation of the i th calibration point from the best-fit calibration relationship
I_i	peak area on the ion chromatogram for the relevant ion generated from measurement i
I_{sam}	peak area on the ion chromatogram for the relevant ion measured on the sampled filter
$\overline{I}$	average of n measurements of I_i
$\overline{I}_{\mathrm{blk}}$	average peak area on the ion chromatogram for the relevant ion measured on a given number of blank filters
k	coverage factor to provide a 95 % level of confidence, usually assumed to be equal to 2
$m_{\mathrm{blk},i}$	mass of anions or cations measured on the i th blank filter in a set of n, in µg
$\overline{m}_{\mathrm{blk}}$	average of n measurements of m_{blk}
$m_{\mathrm{ext\ t}}$	mass of extraction solution, in g
m_{ion}	filter blank corrected mass of anions or cations measured in the PM on the sampled filter, in µg
m_{MDL}	method detection limit, expressed in µg
r	ratio of sub-sampled filter area to the total filter area, in m^2/m^2
R	peak resolution

σ_{R}	relative standard deviation of a set of n measurements
s	relative standard deviation of the measured analytical response in the centre of the application range based on 10 repeat measurements
s_{D}	relative standard deviation of the measurements of multiple extractions of sub-samples from the same filter
s_i	standard deviation of the measured analytical response for the i^{th} calibration point
t_1	retention time, in seconds, of the first peak
t_2	retention time, in seconds, of the second peak
$u(x)$	estimated standard uncertainty in x
U_{r}	relative expanded uncertainty of the measurement result
V_{amb}	volume of ambient air sampled, in m^3
$\dot{V}_{\mathrm{cal}}$	gradient of calibration curve (sensitivity) produced by the ion chromatograph, in g/µg
$\dot{V}_{\mathrm{cal},\,t=0}$	measured sensitivity of the instrument at time $t = 0$
$\dot{V}_{\mathrm{cal},\,t=t}$	measured sensitivity of the instrument at time t
$\Delta\dot{V}_{\mathrm{cal}}$	drift in the sensitivity of the ion chromatograph over a time, t
w_1	peak width on the time axis, in seconds, of the first peak
w_2	peak width on the time axis, in seconds, of the second peak
w_i	peak width of peak i
x_{ext}	filter blank corrected mass fraction of anions or cations in the PM extract, in µg/g

3.2 Abbreviations

CD	conductivity detector
EA	European cooperation for accreditation
FEP	hexafluoroethene propene
HDPE	high density polyethene
HPLC	high performance liquid chromatography
HVS	high volume sampler

ICP-MS	inductively coupled plasma atomic mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
LVS	low volume sampler
MLA	multi-lateral agreement
NIST	national institute for standards and technology
PE	polyethene
PFA	perfluoroalkoxy
PM	particulate matter
PP	polypropylene
PTFE	polytetrafluoroethene
SPM	suspended particulate matter
UV	ultraviolet

4 Principle

This method allows the determination of anions (chloride, nitrate and sulfate) and cations (sodium, ammonium, potassium, magnesium and calcium) in $PM_{2,5}$ collected on filters used for sampling ambient air. The method is divided into two main parts: the sampling in the field and the analytical procedure in the laboratory.

During the sampling, particles containing anions and cations are collected by drawing a measured volume of air through a filter mounted in a sampler designed to collect the $PM_{2,5}$ fraction of suspended particulate matter. The sampled filter is transported to the laboratory, where the anions and cations are taken into solution by ultrasonic extraction with deionised water. The resultant extract is analysed separately for anions and cations by ion chromatography (for all ions), or ICP-OES (for cations, except ammonium).

5 Apparatus

5.1 Sampling equipment

5.1.1 $PM_{2,5}$ samplers, in conformity with EN 14907.

High volume samplers (HVS) or low volume samplers (LVS) may be used and the samplers may be single-filter devices or sequential samplers.

NOTE To minimise contamination of the sample, all components of the filter holder in contact with the filter should be made of a suitable material with as low a metal and salt content as possible, such as polytetrafluoroethene (PTFE), glass, quartz etc.

5.1.2 Greasing agent, if required, suitable for greasing the sampler impaction plate.

5.1.3 Filters, of a diameter suitable for use with the samplers (5.1.1), with a separation efficiency of at least 99,5 % at an aerodynamic diameter of 0,3 µm.

Any filter type in accordance with EN 14907 may be used (i.e. glass fibre, quartz fibre, PTFE or PTFE coated glass fibre filters), provided that the requirements for the method detection limit (9.7) are met. Also, each new batch of filters should be tested to confirm that the filter blank variability is sufficiently low that the method detection requirements are met.

NOTE 1 It is recommended that filters used should be sourced from a manufacturer who has determined the separation efficiency of the filter material according to standard methods such as EN 13274-7 or EN 1822-1.

NOTE 2 The anion and cation content of the filter should be as low as possible because it is usually the case that higher filter blank values lead to higher variability of the blank values.

NOTE 3 In choosing a filter, the user should consider the initial pressure drop across the filter and the increase in this that occurs due to the collection of the dust and ensure that there is no possibility of an excessive pressure drop developing during sampling. This depends on the type of filter (i.e. membranes), unusual high concentrations of $PM_{2,5}$, the use of longer sampling time than 24h and the capability of the sampling device to handle the resulting pressure drop. Quartz fibre filters are proven to be efficient in most cases although they may have weak mechanical properties.

NOTE 4 Glass and/or quartz fibre filters may be washed with deionised water before sampling in order to lower blank values

5.1.4 Flowmeter, with a measurement uncertainty that is sufficient to enable the volumetric flow rate of the samplers (5.1.1) to be measured to within ±5 %.

The calibration of the flowmeter should be traceable to (inter)national standards.

The expanded uncertainty (at 95 % confidence) of the transfer standard flow meter measurements should be better than 2 % at laboratory conditions. If the flow rate determined using the transfer standard deviates more than 2 % from the value required for correct operation of the inlet, the flow controller should be adjusted according to the manufacturer's instructions.

5.2 Laboratory apparatus

5.2.1 General requirements

All surfaces in contact with the sample, measuring and calibration solutions should be made of inert material with respect to the analytes measured. In the working range of this method high density polyethylene (HDPE) is normally a suitable material. However, always check the material with respect to the specific purpose, e. g. for the storage of standard solutions as well as for the determination of elements at an ultra-trace level, fluorocarbon polymer materials such as perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP) may be advantageous. If cations are to be analysed, do not use glass surfaces.

Wash all labware thoroughly with water (E.2.1) before use. Labware dedicated to the use for analysis of cations should additionally be washed thoroughly with diluted nitric acid (e.g., mass content $w(HNO_3) = 1\ \%$) in prior to use. Do not use nitric acid for cleaning labware used for analysing anions.

NOTE Contaminated labware can be cleaned with hot tap water and alkaline detergent before being taken through the normal cleaning procedure.

5.2.2 General labware

In addition to ordinary laboratory apparatus (e. g. a range of volumetric flasks, Erlenmeyer flasks and pipettes) the equipment as given under 5.2.3 to 5.2.6 is needed. If ICP-OES is chosen for analysis of cations (except ammonium) the equipment given under 5.2.7 is additionally required.

5.2.3 Storage bottles, for the stock, standard, calibration and sample solutions

5.2.4 Dispensers, variable volume

NOTE The use of piston pipettes is allowed. It enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed. Test each batch of pipette tips and disposable plastics vessels for impurities.

5.2.5 Filtration equipment

Membrane filtration equipment and membrane filters of a medium pore size 0,45 µm reserved for trace element determination. PE, PP and PTFE filtering apparatus are recommended to avoid possible contamination with, or adsorption by, metal elements. Test each batch of membrane filters for impurities.

Alternatively, single use syringe filters (e.g. cellulose acetate or nylon; pore size 0,45 µm) together with single use medical syringes can be used.

5.2.6 Ion chromatography system

In general, it consists of the following components:

5.2.6.1 Eluent reservoir, and a degassing unit

5.2.6.2 Metal-free high performance liquid chromatography (HPLC) pump

5.2.6.3 Sample injection system, incorporating a sample loop of appropriate volume (e.g. 0,02 ml) or autosampler device

5.2.6.4 Separator column, with the specified separating performance

5.2.6.5 Conductivity detector (CD)

5.2.6.6 UV detector, e.g. a spectrophotometer, operating over the wavelength range: 190 nm to 400 nm, optionally used in combination with a CD for the determination of nitrate or nitrite

5.2.6.7 Recording device, e.g. a computer with software for data acquisition and evaluation

5.2.6.8 Precolumns, if necessary

5.2.6.9 Suppressor device, if necessary

5.2.7 Inductively coupled plasma optical emission spectrometer system

In general, it consists of the following components:

5.2.7.1 Computer-controlled optical emission spectrometer with background correction

5.2.7.2 Radiofrequency generator

5.2.7.3 Mass-flow controller

A mass-flow controller on the nebulizer gas supply is recommended.

NOTE The plasma is very sensitive to variations in the gas flow rate of the nebulizer gas.