SLOVENSKI STANDARD
SIST EN 16913:2017

01-julij-2017

Zunanji zrak - Standardna metoda za merjenje NO $^{-}$, SO $^{2-}$, Cl^{-}, NH , Na , K , Mg^{2} , Ca^{2} v delcih PM2,5, zbranih na filtru

Ambient air - Standard method for measurement of NO $^{-}$, SO $^{2-}$, Cl^{-}, NH , Na , K , Mg^{2} , Ca^{2} in PM2,5 as deposited on filters

Außenluft - Messverfahren zur Bestimmung von NO $^{-}$, SO $^{2-}$, Cl^{-}, NH , Na , K , Mg^{2} , Ca^{2} in PM2,5 nach Abscheidung auf Filtern

Air ambiant - Méthode normalisée pour le mesurage de NO $^{-}$, SO $^{2-}$, Cl^{-}, NH , Na , K , Mg^{2} , Ca^{2} dans la fraction PM2,5

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EUROPEAN STANDARD

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English Version

Ambient air - Standard method for measurement of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in PM2,5 as deposited on filters

Air ambiant - Méthode normalisée pour le mesurage de NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} dans la fraction PM2,5 telle que déposée sur des filtres

Außenluft - Messverfahren zur Bestimmung von NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in PM2,5 nach Abscheidung auf Filtern

This European Standard was approved by CEN on 27 February 2017.

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European foreword

This document (EN 16913:2017) 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of an identical text or by endorsement, at the latest by December 2017, and conflicting national standards shall be withdrawn at the latest by December 2017.

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

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Introduction

This European Standard describes how to measure a specified range of anions and cations in $PM_{2,5}$ as deposited on filters.

The EU Air Quality Directive 2008/50/EC [1] 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.

Measurements of anions and cations in PM are being performed by the EMEP programme, mainly by using a filterpack with limited particle 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, are 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 European Standard as close as possible, the EMEP protocol has been taken as starting point for this European Standard. This European Standard 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 material) 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 sampling is usually done simultaneously.

1 Scope

This European Standard specifies a method for the determination of the mass concentration of water soluble NO_3^- (nitrate), SO_4^{2-} (sulphate), Cl^- (chloride), NH_4^+ (ammonium), Na^+ (sodium), K^+ (potassium), Mg^{2+} (magnesium), Ca^{2+} (calcium) in $PM_{2,5}$ as deposited on filters.

This European Standard describes the analytical procedures for determining anions and cations as part of the $PM_{2,5}$ particulate phase, sample extraction and analysis of anions and cations by ion chromatography. Sampling onto filters will be done in accordance with EN 12341 for $PM_{2,5}$.

NOTE 1 Alternatively, cations, excluding ammonium, can be analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). Ammonium can also be analysed by photometry or conductometry.

This European Standard can be used for the measurements of anions and cations as required by Directive 2008/50/EC. The method does not take into account the possible losses during sampling due to evaporation.

NOTE 2 NO_3^-, Cl^-, NH_4^+ are part of the volatile fraction of $PM_{2,5}$, and the concentrations determined using this standard can be used as minimum values for the concentrations of these ions in $PM_{2,5}$. NO_3^-, NH_4^+, Cl^- are usually up to 30 % underestimated due to evaporational losses from the filter during sampling.

This European Standard may be used at rural and urban background sites and road sites that are in accordance with the siting criteria of Directive 2008/50/EC.

This European Standard is applicable to the measurement of anion/cations in $PM_{2,5}$ samples corresponding to $PM_{2,5}$ mass concentrations between approximately 1 µg/m³ (i.e. the limit of detection of the standard measurement method (EN 12341) expressed as its uncertainty) up to 120 µg/m³.

The validated range of the anion and cation concentrations based on the field validation measurements is presented in Table 1.

Table 1 — Validated range of anions and cations

Component	Minimum µg/m³	Maximum µg/m³
Cl^-	0,001	1,4
NO_3^-	0,002	29
SO_4^{2-}	0,05	13
Na^+	0,003	1,9
NH_4^+	0,04	11
K^+	0,003	0,49
Mg^{2+}	0,001	0,38
Ca^{2+}	0,002	0,72

See Annex A for the statistical analysis of the field validation measurements.

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 and definitions

For the purposes of this document, the terms and definitions given in EN 12341:2014 and the following apply.

NOTE In particular, the following terms of EN 12341 are used in this document: calibration, combined standard uncertainty, coverage factor, expanded uncertainty, PM_x, standard uncertainty, uncertainty (of measurement).

3.1
field filter blank

filter that is taken through the same procedure as a sample, including transport to and from, and storage in the field, and analysis, but is not used for sampling air

Note 1 to entry: The filter is taken from the same batch as used for sampling.

3.2
laboratory filter blank

unused filter that does not leave the laboratory and is taken through the same procedure as a sample

Note 1 to entry: The filter is taken from the same batch as used for sampling.

3.3
reagent blank

solution that contains all the reagents used during the analysis of the sample, but without the sample and filter matrix

4 Symbols and abbreviations

For the purposes of this document, the following abbreviations apply.

EMEP	Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe
CD	Conductivity Detector
FEP	Fluorinated Ethylene Propylene
HDPE	High Density PolyEthylene
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
NIST	National Institute for Standards and Technology
PE	Polyethylene

PFA	Perfluoroalkoxy
PM	particulate matter
PP	Polypropylene
PTFE	Polytetrafluoroethylene

5 Principle

This method allows the determination of anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) 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 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 loaded filter is transported to the laboratory, where the anions and cations are extracted deionized water by ultrasonic extraction. The extraction solution is analysed separately for anions and cations by ion chromatography.

NOTE Alternatively, cations, excluding ammonium can be analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). Ammonium can also be analysed by photometry or conductometry.

6 Equipment

6.1 Sampling equipment

The performance requirements of the sampling instrument are described in EN 12341, including Annex B.

6.2 Laboratory equipment

6.2.1 General requirements

All surfaces in contact with the sample filters, sample and calibration solutions shall be made of inert material with respect to the analytes measured. 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 hexafluoro ethylene propene (FEP) may be advantageous. If cations are to be analysed, do not use glassware.

Wash all labware thoroughly and rinse with deionized water before use.

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

6.2.2 General labware

Ordinary labware like volumetric flasks, pipettes, dispensers, PE vessels for sample extraction, storage bottles (PE) for standard solutions and test tubes.

6.2.3 Filtration equipment

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

Alternatively, membrane filtration equipment (PE, PP or PTFE) and membrane filters of a median pore size 0,45 µm can be used.

6.2.4 Ion chromatography system

In general, it consists of the following components:

- eluent reservoir, and a degassing unit;
- metal-free high performance liquid chromatography (HPLC) pump;
- sample injection system, incorporating a sample loop of appropriate volume (e.g. 0,02 ml) or autosampler device;
- separator column, with the specified separating performance;
- conductivity detector (CD);
- recording device, e.g. a computer with software for data acquisition and evaluation;
- precolumns, if necessary;
- suppressor, if necessary.

7 Sampling

7.1 Filter material.

Quartz fibre filters shall be used for sampling.

It is recommended that filters used should be from a manufacturer who has determined the separation efficiency of the filter material according to standard methods such as EN 13274-7 [10] or EN 1822-1 [9].

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.

Brand related restrictions cannot be made, because brand specific qualities are bound to change in time. Currently the use of Whatman® QMA1) should be discouraged because of the high Na^+ blanks and the uncertainty to what level the water soluble Na^+ per batch may vary. Pallflex® Tissuequartz1) and Munktell® MK3601) are advised [2].

7.2 Sampling time.

Samples shall be taken for 24 h periods. In case of regulatory measurements filter exchange at midnight is required in order to obtain a calendar daily basis.

Due to evaporational losses, the yield of NH_4^+, NO_3^- and Cl^- on the filter is dependent on the start and stop time of the 24 h sampling period [2, 3, 4]. With respect to the diurnal variation of temperature, the lowest yield can be expected when filters are exchanged during relatively high temperature conditions (afternoon) and the highest yield at cold conditions (early in the morning). Therefore, it is at least important to have equal daily filter exchange times for sites that measure also PM mass concentration.

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1) Whatman® QMA, Pallflex® Tissuequartz and Munktell® MK360 are examples of suitable products available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products.

NOTE The filter exchange time may differ per application for practical reasons:

- in case of manually operated measurements, which is often the case for EMEP, it is best to synchronize with other measurement series preferably at a fixed time in the morning, i.e. 8 am;
- in case of PM measurements as part of a scientifically driven study, it is best to exchange filters early in the morning just after the expected coldest time of the day.

7.3 Field sampling and type of sampler.

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

7.4 Site types.

In Directive 2008/50/EC Annex IV the requirement for anions and cations measurements is set to “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, traffic related locations)". Hence, in view of consistency and comparability of methods this European Standard is for the use at rural sites as well as other types of monitoring sites, including suburban, urban background, urban roadside and industrial sites.

7.5 Filter environment during sampling.

The sampler can be located either indoors or outdoors. At this stage, no specific demands on temperature control beyond those given in EN 12341 are given.

8 Transport and storage

8.1 Handling

Filters shall be handled with clean tweezers, away from contamination sources.

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

8.2 Time and temperature limits

Filters shall not be kept longer than 16 days in the field. Transport and any laboratory storage shall be carried out at temperatures below 23 °C. Within 28 d 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.

9 Analysis

9.1 Reagents

Use only reagents of recognized analytical grade (see Annex C).

Use deionized water with a resistivity equal to or greater than 18 MΩ.cm at 25 °C, filtered to exclude particles larger than 0,45 µm.

9.2 Filter sub-sampling

For extraction of water-soluble constituents from $PM_{2,5}$ samples, the whole filter can be used or a sub-sample, representative of the filter as a whole, may be taken. This can be done by using an appropriate cutting device to obtain an accurately defined part of the exposed area of the sampled filter.

If sub-samples are to be analysed, perform a homogeneity check at least once for each type of sampler and for each type of sampling site (e.g. industrial, urban, traffic, rural).

9.3 Sample extraction

The filters are put into a sample tube and deionized water (9.1) is added.

The extraction volume shall be enough to cover completely the sample, typically at least 10 ml, for 47 mm filters.

The sample tubes shall be exposed in an ultrasonic bath for (30 ± 5) min to obtain complete extraction. Extraction should be performed at room temperature (no heating or cooling).

9.4 Sample preparation

If any filter material is expected to be present in the extract, the extracts shall be filtered or centrifuged prior to analysis to avoid problems with the analytical instrument.

NOTE To filter the sample solutions use, e.g. a disposable syringe filter (6.2.3).

9.5 Analysis of extracts

For the ion chromatography method, follow EN ISO 10304-1 [11] and EN ISO 14911 [12] for the analysis of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} or the procedure described in chapter 4.1 of the EMEP manual [5]. For other analytical methods, see Annex D.

The injection system of the ion chromatograph is rinsed with sample solution. A small volume of the sample solution, typically less than 0,05 ml, is then introduced into the injection system of an ion chromatograph. The sample is mixed with an eluent and pumped through the separation unit and detection unit of the ion chromatograph, i.e. a precolumn, a separation column, a suppressor device and a detector.

Match the matrices of the sample solutions, the calibration standard solutions and the reagent blank solution.

The ion chromatograph shall be calibrated with standard solutions containing known concentrations of the ions. At least five calibration solutions and one zero standard (reagent blank solution) shall be used to generate a suitable calibration curve. Prepare calibration solutions with ion concentrations distributed as evenly as possible over the expected working range.

Examples of the preparation of standard solutions are found in Annex C and Annex E.

NOTE 1 It can be advisable to match the matrix of the sample solutions, the calibration standard solutions and the reagent blank solution also with the eluent before analysis.

Any other analytical method shown to be equivalent using the EC equivalence procedure may be used [6].

NOTE 2 Further metal and metalloid constituents, including mineral dust constituents (e.g. Al, Zn, Fe), can be analysed with ICP–OES after digestion.