



BSI Standards Publication

# Ambient air — Guide for the measurement of anions and cations in PM<sub>2,5</sub>

**National foreword**

This Published Document is the UK implementation of CEN/TR 16269:2011.

The UK participation in its preparation was entrusted to Technical Committee EH/2/3, Ambient atmospheres.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

© BSI 2011

ISBN 978 0 580 74622 2

ICS 13.040.20

**Compliance with a British Standard cannot confer immunity from legal obligations.**

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 30 September 2011.

**Amendments issued since publication**

Date	Text affected
------	---------------

---

ICS 13.040.20

English Version

## Ambient air - Guide for the measurement of anions and cations in PM<sub>2,5</sub>

Air ambiant - Guide pour le mesurage des anions et des  
cations dans la fraction PM<sub>2,5</sub>

Außenluft - Leitfaden zur Messung von Anionen und  
Kationen in PM<sub>2,5</sub>

This Technical Report was approved by CEN on 8 August 2011. 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, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.



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

**Management Centre: Avenue Marnix 17, B-1000 Brussels**

## Contents

Page

Foreword.....	3
Introduction .....	4
1 Scope .....	5
2 Terms and definitions .....	5
3 Symbols and abbreviations .....	6
4 Principle .....	8
5 Apparatus .....	8
6 Sampling, transport and storage .....	11
7 Analysis .....	11
8 Calculation of results .....	12
9 Quality control.....	15
10 Measurement uncertainty .....	17
11 Artefacts and interferences .....	17
12 Reporting of results.....	18
Annex A (informative) Example of a closed vessel microwave digestion procedure to determine elements in the water-insoluble fraction of PM <sub>2,5</sub> .....	19
Annex B (informative) Preparation of stock standard solution .....	21
Annex C (informative) Uncertainty budget.....	22
Annex D (informative) Data quality objectives .....	24
Annex E (informative) Reagents .....	26
Bibliography .....	31

## **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.

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.

## Introduction

This CEN Technical Report describes how to measure a specified range of anions and cations in PM<sub>2,5</sub>.

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<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> in PM<sub>2,5</sub> 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<sub>2,5</sub>, 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<sub>2,5</sub> 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  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  in  $\text{PM}_{2,5}$  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  $\text{PM}_{2,5}$  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<sup>3</sup>/h

[EN 14907]

### 2.3

#### **low volume sampling method**

##### **LVS**

method for sampling particulate matter with a flow rate of 2,3 m<sup>3</sup>/h

[EN 14907]

### 2.4

#### **PM<sub>2,5</sub>**

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<sub>10</sub>**

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

$\gamma_{\text{amb}}$  mass concentration of anions or cations in ambient air, in  $\mu\text{g}/\text{m}^3$

$\delta_i$  deviation of the  $i^{\text{th}}$  calibration point from the best-fit calibration relationship

$I_i$  peak area on the ion chromatogram for the relevant ion generated from measurement  $i$

$I_{\text{sam}}$  peak area on the ion chromatogram for the relevant ion measured on the sampled filter

$\bar{I}$  average of  $n$  measurements of  $I_i$

$\bar{I}_{\text{blk}}$  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

$m_{\text{blk},i}$  mass of anions or cations measured on the  $i^{\text{th}}$  blank filter in a set of  $n$ , in  $\mu\text{g}$

$\bar{m}_{\text{blk}}$  average of  $n$  measurements of  $m_{\text{blk}}$

$m_{\text{ext t}}$  mass of extraction solution, in g

$m_{\text{ion}}$  filter blank corrected mass of anions or cations measured in the PM on the sampled filter, in  $\mu\text{g}$

$m_{\text{MDL}}$  method detection limit, expressed in  $\mu\text{g}$

$r$  ratio of sub-sampled filter area to the total filter area, in  $\text{m}^2/\text{m}^2$

$R$  peak resolution



- $\sigma_R$  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  $i^{\text{th}}$  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
- $V_{\text{amb}}$  volume of ambient air sampled, in  $\text{m}^3$
- $\dot{V}_{\text{cal}}$  gradient of calibration curve (sensitivity) produced by the ion chromatograph, in  $\text{g}/\mu\text{g}$
- $\dot{V}_{\text{cal}, t=0}$  measured sensitivity of the instrument at time  $t = 0$
- $\dot{V}_{\text{cal}, t=t}$  measured sensitivity of the instrument at time  $t$
- $\Delta\dot{V}_{\text{cal}}$  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  $i$
- $x_{\text{ext}}$  filter blank corrected mass fraction of anions or cations in the PM extract, in  $\mu\text{g}/\text{g}$

### 3.2 Abbreviations

- CD conductivity detector
- EA European cooperation for accreditation
- FEP hexafluoroethene propene
- HDPE high density polyethylene
- 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  $\mu\text{m}$ .

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  $\text{PM}_{2,5}$ , 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  $\pm 5\%$ .

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  $w(\text{HNO}_3) = 1\%$ ) 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.

#### 5.2.7.4 Nebulizer, with variable speed peristaltic pump

Common nebulizers are the concentric nebulizer (e.g., Meinhard), the cross-flow nebulizer, the V-groove nebulizer and a cyclonic chamber with or without baffles. Other types of nebulizers may also be used if it can be shown that they are fit for purpose.

#### 5.2.7.5 Ultrasonic nebulizer

If very low concentration measurements are to be achieved, ultrasonic nebulizers are recommended. In this special type of nebulizer the sample solution is pumped through a tube that ends near the transducer plate that vibrates at an ultrasonic frequency. The amount of aerosol produced (the efficiency) is typically 10 % to 20 % of the quantity of the pumped solution. As this is very high, the aerosol needs to be dried (desolvated) before being introduced into the plasma, which otherwise would be extinguished. The aerosol is transported to the plasma by the nebulizer gas.

Disadvantages of the ultrasonic nebulizer include its greater susceptibility to matrix effects, diminished tolerance to high dissolved solid contents (approximately > 0,5 % m/v) and a longer rinsing time. Vapour generation apparatus for hydride or cold vapour can also be used for sample introduction.

#### 5.2.7.6 Argon gas supply

Argon gas with a sufficient purity grade, for instance > 99,95 %.

## 6 Sampling, transport and storage

Sampling, as well as transport and storage of unloaded filters, should be performed according to EN 14907.

NOTE EN 14907 is under revision and will be included in the forthcoming revision of EN 12341.

## 7 Analysis

### 7.1 Filter sub-sampling

For extraction of water-soluble constituents from the PM<sub>2,5</sub> filters, 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.

### 7.2 Sample extraction

The filters are put into a sample tube and deionised water is added.

The extraction volume should be as small as possible, but enough to completely cover the sample, typically at least 10 ml, for 47 mm filters.

The sample tubes should be exposed in an ultrasonic bath for at least 30 minutes to obtain complete extraction.

### 7.3 Sample preparation

If any filter material is expected to be present in the extract, the extracts should be filtered or centrifuged prior to analysis.

## 7.4 Analysis of extracts

The analysis of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  should follow EN ISO 10304-1 and EN ISO 14911 for ion chromatography or the procedure described in chapter 4.1 of the EMEP manual. A small volume of the sample, typically less than 0,5 ml, is introduced into the injection system of an ion chromatograph. The sample is mixed with an eluent and pumped through a guard column, a separation column, a suppressor device and a detector.

The ion chromatograph should be calibrated with standard solutions containing known concentrations of the ions. At least five calibration solutions and one zero standard (blank solution of only deionized water) should be used to generate a suitable calibration curve. The concentration range depends on the sample; the calibration curve should cover concentrations lower and higher than the measured concentration.

NOTE 1 The calibration standards may contain 0, 0,5, 1,0, 2,5, 5,0 and 10,0 mg/l of the different ions. An example of the preparation of standard solutions is found in Annex B.

Special attention should be paid to control contamination from ammonia in the laboratory air. All reagents should be of recognized analytical grade. The water used for dilution should be deionized and filtered.

NOTE 2 Any other analytical method shown to be equivalent using the EC equivalence procedure may be used [11]

NOTE 3 Further metal and metalloid constituents, including mineral dust constituents (e.g. Al, Zn, Fe), can be analysed with ICP-OES after digestion. A suitable digestion procedure is given in Annex A.

## 8 Calculation of results

### 8.1 General

It is intended that the following equations for the calculation of results be applied to samples of  $\text{PM}_{2,5}$ , collected according to EN 14907.

The data quality objectives of Directive 2008/50/EC shall be met at all times.

### 8.2 Calculation of anion and cation mass concentration in ambient air

The mass concentration of anions and cations in ambient  $\text{PM}_{2,5}$  using this standard method may be described by the following equation:

$$\gamma_{\text{amb}} = \frac{m_{\text{ion}}}{V_{\text{amb}}} \quad (1)$$

where

$\gamma_{\text{amb}}$  is the mass concentration of anions or cations in ambient air, in  $\mu\text{g}/\text{m}^3$ ;

$V_{\text{amb}}$  is the volume of ambient air sampled, in  $\text{m}^3$ ;

$m_{\text{ion}}$  is the filter blank corrected mass of anions or cations measured in the PM on the sampled filter, in  $\mu\text{g}$ .

NOTE 1 It is assumed that sampling is carried out according to EN 14907 and that sampled PM is analysed as received. Therefore no term is included to account for any loss of volatile material during sampling, or for any deviation from the sampling of  $\text{PM}_{2,5}$  by the standard method.

Furthermore, the mass of anions or cations measured on the sampled filter may be calculated by:

$$m_{\text{ion}} = \frac{m_{\text{ext}} x_{\text{ext}}}{r} \quad (2)$$

where

$x_{\text{ext}}$  is the filter blank corrected mass fraction of anions or cations in the PM extract, in  $\mu\text{g/g}$ ;

$m_{\text{ext}}$  is the mass of extraction solution, in g;

$r$  is the ratio of sub-sampled filter area to the total filter area, in  $\text{m}^2/\text{m}^2$ .

NOTE 2 If the sampled filter is not sub-sampled prior to analysis then  $r$  will be equal to unity with no uncertainty and may be neglected.

Furthermore, the mass fraction of anions and cations in the PM extract may be calculated by:

$$x_{\text{ext}} = \frac{I_{\text{sam}} - \bar{I}_{\text{blk}}}{\dot{V}_{\text{cal}}} \quad (3)$$

where

$I_{\text{sam}}$  is the peak area on the ion chromatogram for the relevant ion measured on the sampled filter;

$\bar{I}_{\text{blk}}$  is the average peak area on the ion chromatogram for the relevant ion measured on a given number of blank filters;

$\dot{V}_{\text{cal}}$  is the gradient of calibration curve (sensitivity) produced by the ion chromatograph, in  $\text{g}/\mu\text{g}$ .

Equation (3) assumes that the same mass of solution is used to extract the sampled filter and the blank filter. If this is not the case an appropriate correction based on the differences in solution masses should be applied to Equation (3).

### 8.2.1 Blank correction for ionic content in filter material

It is important to note that the ionic content of the blank filters used to sample the ambient PM may be significant. It is therefore important that a blank correction is made for this value as shown in Equation (3). Given that it is not possible to measure the blank content of the individual filters used to perform sampling, it is important that a number of filters from the same batch are measured in order to obtain a mean blank value and the variability in this value.

Determinations of the mass of ions on a blank filter may be made using the analogous relationships to Equations (2) and (3), but in this case considering the blank filter as the sample and the extraction medium as the blank.

### 8.3 Method detection limit

The method detection limit,  $m_{\text{MDL}}$ , expressed in  $\mu\text{g}$ , is defined as:

$$m_{\text{MDL}} = 3 \sqrt{\frac{\sum_{i=1}^n (\bar{m}_{\text{blk}} - m_{\text{blk},i})^2}{n-1}} \quad (4)$$

where

$m_{\text{blk},i}$  is the mass of anions or cations measured on the  $i^{\text{th}}$  blank filter in a set of  $n$ , in  $\mu\text{g}$ ;

$\bar{m}_{\text{blk}}$  is the average of  $n$  measurements of  $m_{\text{blk}}$ ;

NOTE This may be converted into a method detection limit in mass concentration terms by dividing  $m_{\text{MDL}}$  by the volume of ambient air sampled during a normal sampling period.

#### 8.4 Repeatability

The repeatability is the closeness of agreement of successive measurements of the same measurand carried out under the same conditions of measurement. Quantitatively this can be expressed as the relative standard deviation of a set of repeat measurements, thus:

$$\sigma_{\text{R}} = \frac{1}{\bar{I}} \sqrt{\frac{\sum_{i=1}^n (\bar{I} - I_i)^2}{n-1}} \quad (5)$$

where

$\sigma_{\text{R}}$  is the relative standard deviation of a set of  $n$  measurements;

$I_i$  is the peak area on the ion chromatogram for the relevant ion generated from measurement  $i$ ;

$\bar{I}$  is the average of  $n$  measurements of  $I_i$ .

#### 8.5 Drift in instrument sensitivity

The drift in the sensitivity of the ion chromatograph,  $\Delta \dot{V}_{\text{cal}}$ , over a time,  $t$ , is given by:

$$\Delta \dot{V}_{\text{cal}} = \frac{\dot{V}_{\text{cal},t=0} - \dot{V}_{\text{cal},t=t}}{\dot{V}_{\text{cal},t=0}} \quad (6)$$

where

$\dot{V}_{\text{cal},t=0}$  is the measured sensitivity of the instrument at time  $t = 0$ ;

$\dot{V}_{\text{cal},t=t}$  is the measured sensitivity of the instrument at time  $t$ .

To express this quantity in percentage terms, the value  $100 \Delta \dot{V}_{\text{cal}}$  needs to be calculated.



## 9 Quality control

### 9.1 Reagent blank

A reagent blank check should be carried out periodically to assure the quality of the reagent being used. Plot control charts and if the results indicate reagent blank levels are elevated, investigate the reasons for this and take corrective action.

### 9.2 Field filter blank check

The field filter blank is used only for quality assurance purposes. If the field filter blank exceeds significantly the average laboratory filter blank, investigate the reasons for this and take corrective action.

### 9.3 Analytical repeatability

The relative standard deviation,  $s$ , of the measured analytical response in the centre of the application range based on 10 repeat measurements should conform to the limits given below:

- $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ :  $s < 2\%$ ;
- $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ :  $s < 2\%$ .

### 9.4 Calibration

No point on the calibration relationship should deviate by more than the standard deviation of the measured analytical response at the concentration in question, such that:

$$\frac{\delta_i}{s_i} \leq 1 \quad (7)$$

where

$\delta_i$  is the deviation of the  $i^{\text{th}}$  calibration point from the best-fit calibration relationship;

$s_i$  is the standard deviation of the measured analytical response for the  $i^{\text{th}}$  calibration point.

The calibration range should cover the vast majority of the measured sample concentrations, and ideally should be centred at about the average measured sample concentration.

The calibration relationship should comprise a minimum of five points (not including the zero point).

### 9.5 Ion chromatography analysis

Demonstrate that the ion chromatography is able to separate the peak of interest successfully by ensuring that the peak resolution for successive peaks is greater than 1. The peak resolution may be calculated thus:

$$R = 2 \frac{t_2 - t_1}{w_1 + w_2} \quad (8)$$

where

$R$  is the peak resolution;

$t_1$  is the retention time of the first peak, in s;

$t_2$  is the retention time of the second peak, in s;

$w_1$  is the peak width on the time axis of the first peak, in s;

$w_2$  is the peak width on the time axis of the second peak, in s.

NOTE Peak widths are measured at the base of each peak, and are calculated by constructing isosceles triangles over the Gaussian peak shapes.

## 9.6 Filter extraction reproducibility

The relative standard deviation,  $s_D$ , of the measurements of multiple extractions of sub-samples from the same filter, as a measure of filter extraction reproducibility should conform to the limits given below:

—  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ :  $s_D < 5\%$ ;

—  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ :  $s_D < 5\%$ .

## 9.7 Method detection limit

Requirements for method detection limits, based on laboratory filter blanks, depend on the range of concentrations measured. For measurements at rural background sites the method detection limit  $m_{\text{MDL}}$  should conform to the limits given below:

—  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ :  $m_{\text{MDL}} < 500$  ng/filter (for 47 mm filters);

—  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ :  $m_{\text{MDL}} < 500$  ng/filter (for 47 mm filters).

## 9.8 Certified reference materials

Appropriate certified reference solutions should be analyzed on a regular basis to provide continuous validation for the analysis step of the standard method.

Where appropriate certified reference materials in comparable matrices are available, these should be extracted and analyzed on a regular basis to provide continuous validation for the standard method.

## 9.9 External quality assessment

If users of this technical report carry out analysis of anions and cations in particulate matter on a regular basis it is recommended that they participate in relevant external quality assessment schemes or proficiency testing schemes.

## 9.10 Accreditation

In order to fulfill the requirement of Directive 2008/50/EC the laboratories using this Technical report will have to demonstrate accordance with the requirements of EN ISO/IEC 17025. One of the ways of demonstrating compliance with these requirements is through formal accreditation by an accreditation body falling under the Multi-Lateral Agreement (MLA) of the European Cooperation for Accreditation (EA).

## 10 Measurement uncertainty

Equations (1), (2) and (3) may be combined to give:

$$\gamma_{\text{amb}} = \frac{m_{\text{ext}} (I_{\text{sam}} - \bar{I}_{\text{blk}})}{V_{\text{amb}} r \dot{V}_{\text{cal}}} \quad (9)$$

An individual laboratory may produce an assessment of the uncertainty of any individual measurement by performing a full ISO GUM treatment on Equation (6). This yields a combined relative standard uncertainty in the measured ambient mass concentration,  $\frac{u_c(\gamma_{\text{amb}})}{\gamma_{\text{amb}}}$ , of:

$$\frac{u_c(\gamma_{\text{amb}})}{\gamma_{\text{amb}}} = \sqrt{\frac{u^2(m_{\text{ext}})}{m_{\text{ext}}^2} + \frac{u^2(I_{\text{sam}}) + u^2(\bar{I}_{\text{blk}})}{(I_{\text{sam}} - \bar{I}_{\text{blk}})^2} + \frac{u^2(V_{\text{amb}})}{V_{\text{amb}}^2} + \frac{u^2(r)}{r^2} + \frac{u^2(\dot{V}_{\text{cal}})}{\dot{V}_{\text{cal}}^2}} \quad (10)$$

Where  $u(x)$  is the estimated standard uncertainty in  $x$ . If the sampled filter is not sub-sampled prior to analysis then  $u(r) = 0$ .

The relative expanded uncertainty,  $U_r$ , of the measurement result is then calculated by:

$$U_r = k \frac{u_c(\gamma_{\text{amb}})}{\gamma_{\text{amb}}} \quad (11)$$

where

$k$  is the coverage factor to provide a 95 % level of confidence, usually assumed to be equal to 2.

For an exemplar uncertainty budget, see Annex C.

## 11 Artefacts and interferences

### 11.1 Sampling

Various sampling artefacts may affect the quality of data obtained using the present CEN Technical Report. These artefacts notably include wall losses, losses of particulate semi-volatile matter due to temperature changes and to gas adsorption in the sampler both affecting gas/particle equilibria, as well as adsorption of inorganic gaseous compounds (e.g. SO<sub>2</sub>, NH<sub>3</sub>, and HNO<sub>3</sub>) onto the filter. The importance of such sampling artefacts primarily depends on the nature of the apparatus surface material, on the length of the connecting pipework, on the used filter type, on possible filter clogging, and on temperature changes during sampling (as well as during transport and storage). It is expected that sampling artefacts mainly affect the determination of ammonium nitrate and ammonium chloride. However, it is not possible here to give specific recommendations to lower the influence of sampling artefacts as validation studies are necessary to achieve this goal.

NOTE According to the EMEP protocol, the most accurate measurements of anions and cations can be obtained using "denuder-filterpack systems". The use of on-line automated analysers may also minimize the influence of sampling artefacts on the data accuracy.

## 11.2 Analysis

Any species with a retention time similar to that of the main ions could interfere when ion chromatography is used. With the exception of  $\text{NO}_2^-$ , precipitation and filter extracts do normally not contain such species. In some systems a negative water dip in the start of the chromatogram may interfere with the  $\text{Cl}^-$  determination. This can be avoided by adding a small amount of concentrated eluent to all samples and calibration standards to match the eluent concentration.

NOTE For coastal or marine sites, an interference between sodium and ammonium can occur, so the choice of chromatographic column is critical.

## 12 Reporting of results

The report should include the following information:

- reference to this CEN Technical Report;
- identification of the sampling location;
- description of the sampling system that was used;
- sampling frequency and period;
- results of the determination of anions and/or cations expressed in  $\mu\text{g}/\text{m}^3$ ;
- any unusual features noted during the determination;
- method detection limit;
- expanded uncertainty and how this was calculated;
- short description of analysis procedure including analytical technique.

## Annex A (informative)

### Example of a closed vessel microwave digestion procedure to determine elements in the water-insoluble fraction of PM<sub>2,5</sub>

#### A.1 General

Mineral dust may often contribute significantly to particle mass. To generate a total mass closure, it is important to determine this fraction. Monitoring of air pollution has mainly been focused on anthropogenic sources, mineral dust has therefore traditionally not been measured because of its more natural origin, even though atmospheric dust can be an indirect result of land use and human activities. Mineral dust is a mirror of the earth's crust and consists mainly of silicates and oxides of silicon, aluminium and iron. There are also water-insoluble portions of alkali metals and alkaline earth metals in mineral dust. The relative importance of mineral dust in particulate matter depends on location, season and particle size. It is mainly concentrated in the coarse fraction. There can be large local variations depending on the source, e.g. Saharan dust can make a large contribution of the PM<sub>2,5</sub> concentration in southern Europe. Mineral dust has in general low solubility and is therefore difficult to analyze without digestion procedures. To dissolve the mineral dust it is usually necessary to use strong solvents as hydrofluoric acid.

#### A.2 Power controlled microwave digestion with HNO<sub>3</sub> / H<sub>2</sub>O<sub>2</sub> / HF

The digestion procedure given in this Annex was used by some laboratories participating in field validation tests and is given for illustrative purposes. It will not be applicable to all digestion systems. Before using this procedure, refer to the manufacturer's instructions.

##### A.2.1 Reagents

For the determination of some elements the degree of purity "for analysis" may be sufficient. However, higher purity requirements may be necessary depending on the measuring task at hand. The reagents used should be examined regularly for their blank values.

- **Concentrated nitric acid**, HNO<sub>3</sub>, mass content,  $w(\text{HNO}_3) \sim 65 \%$ ,  $\rho = 1,40 \text{ kg/l}$ ;
- **Diluted nitric acid (1 %)**, HNO<sub>3</sub>, mass content,  $w(\text{HNO}_3) \sim 1 \%$ , 15,4 g (11 ml) of the concentrated nitric acid are filled to 1 l with water;
- **Hydrofluoric acid**, HF, mass content  $w(\text{HF}) \sim 40 \%$ ;
- **Hydrogen peroxide solution**, H<sub>2</sub>O<sub>2</sub>, mass content  $w(\text{H}_2\text{O}_2) \sim 30 \%$ .

##### A.2.2 Cleaning of microwave digestion vessels

Clean microwave digestion vessels before use by taking them through the same procedure used for sample digestion (see A.2.3), but adding just 8 ml concentrated nitric acid and 2 ml hydrogen peroxide to the vessels. Afterwards rinse the vessels three times with water (E.2.1). Shorter cleaning times or alternative cleaning procedures may be used if it can be demonstrated that they are effective. If there are tide mark residues from the previous digestion, try to remove them by following the manufacturer's cleaning instructions or e.g. by using an ultrasonic bath.

### A.2.3 Sample digestion

- If necessary, take a sub-sample from the filter using an appropriate cutting tool. Take care not to contaminate the sub-sample with wear from the punching tools or support plate under the punch. Transfer the sub-sample into the digestion vessel. To ensure complete submersion of filter in the digestion acid, first fold the filter or cut it into small pieces using a cutting implement that will not contaminate the sample.
- Carefully add 8 ml of concentrated nitric acid and 2 ml of hydrogen peroxide to the vessel (for a 50 mm diameter filter). The addition of hydrofluoric acid allows significantly higher recovery rates to be achieved for some elements e.g.. Al and Cr. Depending on the measuring task, 0,5 ml hydrofluoric acid is added to the sample and the digestion vessel is closed with the corresponding cap. The digestion vessel is placed in the microwave digestion system in accordance with the manufacturer's instructions.
- For microwave digestion apparatus, a distinction is made between temperature/pressure controlled systems and systems in which the microwave power is programmed. It is not possible to specify general operating parameters for the different microwave systems because they depend on the equipment. A microwave digestion system with temperature control was used for the digestion described below.
  - Digestion vessels: 12 fortified fluorocarbon polymer vessels;
  - Volume of digestion vessels: 100 ml;
  - Digestion matrix: 8 ml concentrated nitric acid + 2 ml hydrogen peroxide + 0,5 ml hydrofluoric acid;
  - Digestion programme:

**Table A.1 — Digestion programme**

Time ramp in min	Temperature in °C	Hold time in min	Description
3	130	2	Heating
3	180	2	Heating
3	200	20	Hold temperature
-	to 50	> 20	Cooling

For systems that measure the pressure and temperature of one control vessel, it should be checked that none of the other vessels holds a critical mixture with respect to the pressure build-up. For the same reason, the control vessel should not contain any blanks, as the presence of blanks results in a lower positive pressure than is the case with samples having the relevant dust mass.

- Also after the cooling phase there will still be pressure in the digestion vessels. Therefore, they should only be opened within a closed fume hood with the necessary caution. After opening, the contents of the digestion vessel are transferred to a PFTE beaker. The solution is evaporated to dryness. Then the sample is re-dissolved with diluted nitric acid. Depending on the selection of the analytical method (e.g. ICP-MS) the diluted nitric acid is spiked with internal standards. After the residue, if any, has settled, the clear supernatant solution is prepared for analysis with ICP-OES or the ICP-MS apparatus. The solution may have to be filtered. In case that no hydrofluoric acid is added, the content of the digestion vessel can be directly transferred to a 50 ml or 100 ml measuring flask. Then, optionally, internal standard is added and diluted to the mark with diluted nitric acid.

## Annex B (informative)

### Preparation of stock standard solution

Stock standard solutions e.g. 1 000 mg (of element)/litre, may be purchased as certified solutions from different manufacturers or NIST (National Institute for Standards and Technology, USA), or prepared from salts or oxide dried in the prescribed way, dissolved and diluted to 1 000 ml as listed in Tables B.1 and B.2

**Table B.1 — Preparation of anion stock standard solutions**

Salt	Weight (g)	Drying temperature (°C)	Drying time (h)
NaCl	1,6485	150	1
Na NO <sub>3</sub>	6,0679	105	2
Na <sub>2</sub> SO <sub>4</sub>	4,4299	105	24

The salt amount indicated gives 1 000 mg of the anions per litre.

**Table B.2 — Preparation of cation stock standard solutions**

Salt	Weight (g)	Drying temperature (°C)	Drying time (h)
NH <sub>4</sub> Cl	3,8190	105	1
NaCl	2,5421	150	2
KCl	1,9067	105	1
CaCO <sub>3</sub>	2,4971	180	1
MgO	1,6581	-	

The salt amount indicated gives 1 000 mg of the cations per litre.

The CaCO<sub>3</sub> should be added to approximately 600 ml of water. Then add concentrated hydrochloric acid (HCl) slowly until the entire solid has dissolved, and dilute to 1 000 ml with water. The MgO should be dissolved in 10 ml concentrated nitric acid (HNO<sub>3</sub>) before diluting to 1 000 ml with water. The other salts should be dissolved directly in water. These stock standards are stable for at least 1 year.

## Annex C (informative)

### Uncertainty budget

**Table C.1 — Exemplar uncertainty budget, calculating the combined standard uncertainty, for a measurement of anions in PM made using this standard method**

Symbol	Quantity	Units	Estimate	Sensitivity coefficient	Uncertainty	Probability distribution	Divisor	To Standard uncertainty
<b>Uncertainty in the mass concentration of anions in ambient air</b>								
$V_{amb}$	Volume of ambient air sampled	m <sup>3</sup>	24,00	-0,07	1,20	Rectangular	√3	-0,046
$m_{ext}$	Mass of extraction solution	g	10,00	0,16	0,01	Normal	1	0,002
$R$	Ratio of the sub-sampled filter area to the total filter area	m <sup>2</sup> /m <sup>2</sup>	0,50	-3,21	0,01	Ractangular	√3	-0,019
$I_{sam}$	Peak area on the ion chromatogram for the relevant ion measured on the sampled filter	1	20,00	0,08	0,50	Normal	1	0,042
$\bar{I}_{blk}$	Average peak area on the ion chromatogram for the relevant ion measured on a given number of blank filters	1	0,75	-0,08	0,05	Normal	1	-0,004
$\dot{V}_{cal}$	Gradient of calibration curve	g/μg	10,00	-0,16	0,25	Normal	1	-0,040
$\gamma_{amb}$	Mass concentration of anions in ambient air and the standard uncertainty in this value	μg/m <sup>3</sup>	1,60	-	-	-	-	0,080



Some guidance is given in estimating the standard uncertainties of these components:

- $u(m_{\text{ext}})$  can be estimated from the uncertainty of repeat weighing, and the calibration of the analytical balance.
- $u(V_{\text{amb}})$  is defined in EN 14907 as a maximum of  $5/\sqrt{3}$  % (including flow rate calibration, drift in sampling flow rate during measurement, etc).
- $u(r)$  is a measure of the uncertainty in the ratio of the area of the sub-sample (if taken) to the area of the sampled filter. This may also include a component of uncertainty to recognise that a sub-sample may not be representative of the filter as a whole.
- $u(\dot{V}_{\text{cal}})$  may be estimated by weighted regression software but will be approximately equal to the repeatability of the instrument response at the centre of the calibration range added in quadrature to the uncertainty in the composition of the calibration standards at this concentration (including consideration of the uncertainty of gravimetric preparation and the purity of the salts used).
- $u(I_{\text{sam}})$  can be estimated from the repeatability of measurements using the ion chromatograph at the appropriate measured concentration level.
- $u(\bar{I}_{\text{blk}})$  can be estimated from the standard deviation of measurements of a number of blank filters.

Expected relative expanded uncertainties for this method, using a coverage factors of  $k=2$ , at the 95 % level of confidence, are expected to be in the range 10 % to 20 %.

For more details about the calculation of uncertainty in this context, see [1].

## Annex D (informative)

### Data quality objectives

#### D.1 EU Air Quality Directive 2008/50/EC

##### D.1.1 Annex I: Data quality objectives for ambient air quality assessment of particulate matter (PM<sub>10</sub>/PM<sub>2,5</sub>)

###### Fixed measurements

Uncertainty	: 25 %
Minimum data capture	: 90 %

###### Indicative measurements

Uncertainty	: 50 %
Minimum data capture	: 90 %
Minimum time coverage	: 14 % (one measurement a week at random, evenly distributed over the year, or eight weeks evenly distributed over the year)

###### Modelling uncertainty

Daily averages	: not yet defined
Annual averages	: 50 %
Objective estimation Uncertainty	: 100 %

The uncertainty for modelling is defined as the maximum deviation of the measured and calculated concentration levels for 90 % of individual monitoring points, over the period considered, by the limit value (or target value in the case of ozone), without taking into account the timing of the events. The uncertainty for modelling should be interpreted as being applicable in the region of the appropriate limit value (or target value in the case of ozone). The fixed measurements that have to be selected for comparison with modelling results should be representative of the scale covered by the model.

The uncertainty for objective estimation is defined as the maximum deviation of the measured and calculated concentration levels, over the period considered, by the limit value (or target value in the case of ozone), without taking into account the timing of the events.

The requirements for minimum data capture and time coverage do not include losses of data due to the regular calibration or the normal maintenance of the instrumentation.

##### D.1.2 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 also in urban areas.

###### B. Substances

Measurement of PM<sub>2,5</sub> must 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 should be included: SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>, organic carbon (OC) and elemental carbon (EC)

**C. Siting**

Measurements should be taken in particular in rural background areas (in accordance with parts A, B and C of Annex III. Assessment criteria)

## **Annex E** **(informative)**

### **Reagents**

#### **E.1 General**

For the determination of ions and elements at trace and ultra-trace level, use reagents of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined. Use only reagents of recognized analytical grade. Although the chemicals and concentrations to be used for preparing eluent solutions and regeneration solutions are normally given by the manufacturers of the different separation columns, the reagents listed in this Annex may be considered representative examples for the preparation of eluents for anion determination and cation determination with ion chromatography.

#### **E.2 Anion determination by ion chromatography**

**E.2.1 Water, distilled or deionised, with a conductivity of <0,1 µS/cm at 25 °C and particles no larger than 0,45 µm**

**E.2.2 Sodium hydrogencarbonate, NaHCO<sub>3</sub>**

**E.2.3 Sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>**

**E.2.4 Sodium hydroxide, NaOH**

**E.2.5 Potassium hydroxide, KOH**

**E.2.6 Chloride, nitrate, and sulfate stock standard solutions, ρ = 1 000 mg/l each**

Single anion and mixed anion stock solutions with adequate and required specification may be purchased as certified solutions from different manufacturers. These solutions are considered to be stable for several months.

**E.2.7 Chloride, nitrate, and sulfate standard solutions**

**E.2.7.1 General**

Depending on the concentrations expected, prepare single or mixed standard solutions, of chloride, nitrate and sulfate concentrations from the stock standard solution (E.2.6) by diluting with water (E 2.1). Store the standard solutions in polyethylene (PE) bottles.

**E.2.7.2 Example for a chloride, nitrate and sulfate mixed standard solution, ρ = 10 mg/l each.**

Pipette 1,0 ml of each of the stock standard solutions (E.2.6) into a 100 ml volumetric flask, and dilute to volume with water (E.2.1).

## E.2.8 Chloride, nitrate and sulfate calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (E.2.7.2) to prepare 5 calibration solutions distributed as evenly as possible over the expected working range.

Proceed as follows for the range 0,1 mg/l to 0,5 mg/l:

Pipette, into a series of 20 ml volumetric flasks, the following volumes: 200  $\mu$ l, 400  $\mu$ l, 600  $\mu$ l, 800  $\mu$ l or 1 000  $\mu$ l of the standard solution (E.2.7.2) and dilute to volume with water (E.2.1). The concentrations of the anions in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l or 0,5 mg/l, respectively.

Prepare the calibration solutions on the day of use.

## E.2.9 Blank

Fill a volumetric flask (e.g. 100 ml flask) with water (E.2.1).

## E.2.10 Eluents

### E.2.10.1 General

Degas all water used for eluent preparation. In order to minimise the growth of bacteria or algae, prepare eluents freshly after 3 days.

The choice of eluent depends on the chosen column and detector (e.g. ultraviolet (UV) or conductivity). Seek advice from the column supplier. The example for the eluent composition in E.2.10.3 refers to the conductivity detector (CD) suppressor technique only. Nevertheless, the non-suppressed CD technique (as well as UV detection) is included in this method.

A selection of reagents for common eluents is given in E.2.2 to E.2.5.

NOTE Preparing the eluent from concentrates has proved to be successful. Alternately, automatic eluent generators (e.g. for KOH eluents) can be used

### E.2.10.2 Sodium carbonate/sodium hydrogencarbonate concentrate

For the eluent concentrate preparation:

Transfer 28,6 g of sodium carbonate (E.2.3) and 8,4 g of sodium hydrogencarbonate (E.2.2) into a 1 000 ml volumetric flask.

Dissolve in water (E.2.1) and dilute to volume with water. The solution contains 0,27 mol/l of sodium carbonate and 0,1 mol/l of sodium hydrogencarbonate.

This solution is stable for several months if stored at 2 °C to 8 °C in glass or PE bottles.

### E.2.10.3 Sodium carbonate/sodium hydrogencarbonate eluent

The following eluent is applicable for the determination of the anions according to this standard:

Pipette 20 ml of the concentrate (E.2.10.3) into a 2 000 ml volumetric flask and dilute to volume with water (E.2.1). The solution contains 0,002 mol/l of sodium carbonate and 0,001 mol/l of sodium hydrogencarbonate.

### E.3 Cation determination by ion chromatography

**E.3.1 Water, distilled or deionised, with a conductivity of <math><0,1 \mu\text{S}/\text{cm}</math> at 25 °C and particles no larger than 0,45  $\mu\text{m}$**

**E.3.2 DL-2,3-Diaminopropionic acid monohydrochloride (DAP),  $\text{C}_3\text{H}_8\text{N}_2\text{O}_2\cdot\text{HCl}$ , purity  $\geq 99,0 \%$**

**E.3.3 Hydrochloric acid solution, HCl,  $c(\text{HCl}) = 7,7 \text{ mol/l}$ , mass content  $\sim 28 \%$**

**E.3.4 Methanesulfonic acid,  $\text{CH}_3\text{SO}_3\text{H}$ , purity  $\geq 99,0 \%$ ,  $\rho^{25} = 1,481 \text{ g/ml}$**

**E.3.5 Pyridine 2,6-dicarboxylic acid (PDA),  $\text{C}_7\text{H}_4\text{NO}_4$ , purity  $\geq 99,5 \%$**

**E.3.6 Nitric acid solution,  $\text{HNO}_3$ ,  $c(\text{HNO}_3) = 1 \text{ mol/l}$**

**E.3.7 Tartaric acid,  $\text{C}_4\text{H}_6\text{O}_6$**

**E.3.8 Cation stock standard solutions of ammonium ( $\text{NH}_4^+$ ), calcium ( $\text{Ca}^{2+}$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), Na,  $\rho = 1\ 000 \text{ mg/l}$  each.**

Single-ion stock solutions with adequate specification may be purchased as certified solutions from different manufacturers. These solutions are considered to be stable for several months.

#### **E.3.9 $\text{NH}_4^+$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ standard solutions**

##### **E.3.9.1 General**

Depending on the concentrations expected, prepare single or mixed standard solutions, of  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  concentrations from the stock standard solution (E.3.8) by diluting with water (E.3.1) Alternately, standard solutions and calibration solutions can be prepared by diluting the stock standard solution (E.3.8) with the eluent used (e. g. methanesulfonic acid (E.3.12.2.2)). In the latter case, matrix matching of the sample extracts prior to analysis is recommended. Store the standard solutions in PE bottles.

##### **E.3.9.2 Example for a $\text{NH}_4^+$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ mixed standard solution, $\rho = 10 \text{ mg/l}$ each.**

Pipette 1,0 ml of each of the stock standard solutions (E.3.8) into a 100 ml volumetric flask. Add 0,1 ml of nitric acid (E.3.6). Make up to volume with water (E.3.1) and transfer to a suitable storage bottle.

##### **E.3.10 $\text{NH}_4^+$ , $\text{Ca}^{2+}$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ calibration solutions**

Depending on the concentrations expected in the sample, use the standard solution (E.3.9) to prepare 5 calibration solutions distributed as evenly as possible over the expected working range.

Proceed as follows for the range 0,1 mg/l to 0,5 mg/l:

Pipette, into a series of 20 ml volumetric flasks, the following volumes: 200  $\mu\text{l}$ , 400  $\mu\text{l}$ , 600  $\mu\text{l}$ , 800  $\mu\text{l}$  or 1 000  $\mu\text{l}$  of the standard solution (E.3.9.2). Add 0,02 ml of nitric acid (E.3.6). Make up to volume with water (E.3.1). The concentrations of the cations in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l or 0,5 mg/l, respectively.

Prepare the calibration solutions on the day of use.

### **E.3.11 Reagent blank solution**

Transfer 1,0 ml of nitric acid (E.3.6) and 1 000 ml of water (E.3.1) into an high density polyethylene (HDPE) or polypropylene (PP) container. Prior to analysis, make sure that the acid matrix and concentration of the reagent blank solution is the same as in the standard and sample solutions. If standard solutions and calibration solutions are prepared by diluting the stock standard solution (E.3.8) with the eluent used (e. g. methanesulfonic acid (E.3.12.2.2)), use the eluent as the reagent blank solution.

### **E.3.12 Eluents**

#### **E.3.12.1 General**

Degas all water used for eluent preparation. In order to minimise the growth of bacteria or algae, prepare eluents freshly after 3 days.

The choice of eluent depends on the chosen column. Seek advice from the column supplier.

The examples for the eluent composition in E.3.12.2 refer to the suppressor technique only. The examples for the eluent composition in E.3.12.3 refer to the non-suppressed technique.

A selection of reagents for common eluents is given in E.3.2 to E.3.7.

#### **E.3.12.2 Examples of eluents for ion chromatography using the suppressor technique**

##### **E.3.12.2.1 Hydrochloric acid / DAP eluent**

Transfer 5,2 ml of a hydrochloric acid solution (E.3.3) and 0,562 g of DAP (E.3.2) into a 1 000 ml volumetric flask and dilute to volume with degassed water.

The solution contains 0,04 mol/l of hydrochloric acid and 0,004 mol/l DAP. Store the solution at 4 °C to 6 °C, renew it every 7 days.

##### **E.3.12.2.2 Methanesulfonic acid eluent**

Transfer 1,3 ml of methanesulfonic acid-solution (E.3.4) into a 1 000 ml volumetric flask and dilute to volume with degassed water.

The solution contains 0,02 mol/l of methanesulfonic acid. Renew the eluent every 3 days.

#### **E.3.12.3 Examples of eluents for ion chromatography without using the suppressor technique**

##### **E.3.12.3.1 Tartaric acid/PDA concentrate**

The eluent concentrate has proved to be successful for the eluent preparation:

Transfer 1,671 g of PDA (E.3.5) in a beaker of capacity 1 000 ml, add approximately 500 ml of water (E.3.1). Stir and dissolve by heating (60 °C to 80 °C). After cooling add 6,003 g tartaric acid (E.3.7) and transfer the cool solution into a 1 000 ml volumetric flask and dilute the volume with water.

The solution contains 0,01 mol/l PDA and 0,04 mol/l tartaric acid and is stable for one month if stored at 4 °C to 6 °C.

##### **E.3.12.3.2 Tartaric acid/PDA eluent**

Transfer 100 ml of the concentrate (E.3.12.3.1) into a 1 000 ml volumetric flask and dilute to volume with water.

The solution contains 0,001 mol/l PDA and 0,004 mol/l tartaric acid. The eluent pH is 2,8. Renew the eluent every 3 days.

#### **E.3.12.3.3 Nitric acid eluent**

Transfer 500 ml of water (E.3.1) into a 1 000 ml volumetric flask, add 20 ml of the nitric acid solution (E.3.6) and dilute to volume with water.

The solution contains 0,02 mol/l nitric acid. Renew the eluent every 3 days.

### **E.4 Cation determination by inductively coupled plasma optical emission spectrometry (ICP-OES)**

#### **E.4.1 Nitric acid, $\rho$ (HNO<sub>3</sub>) = 1,4 g/ml.**

#### **E.4.2 Element stock standard solutions of Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, $\rho$ = 1 000 mg/l each.**

Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique may be purchased as certified solutions from different manufacturers. These solutions are considered to be stable for several months.

#### **E.4.3 Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> standard solutions**

##### **E.4.3.1 General**

Depending on the concentrations expected, prepare single or mixed standard solutions, of Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> concentrations from the stock standard solution (E.4.2).

Store the standard solutions in PE bottles.

##### **E.4.3.2 Example for a Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> mixed standard solution, $\rho$ = 10 mg/l each.**

Pipette 1,0 ml of each of the stock standard solutions (E.4.2) into a 100 ml volumetric flask. Add 0,5 ml of nitric acid (E.4.1). Make up to volume with water (E.2.1) and transfer to a suitable storage bottle.

#### **E.4.4 Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> calibration solutions**

Depending on the concentrations expected in the sample, use the standard solution (E.4.3.2) to prepare 5 calibration solutions distributed as evenly as possible over the expected working range.

Proceed as follows for the range 0,1 mg/l to 10 mg/l:

Pipette, into a series of 20 ml volumetric flasks, the following volumes: 200  $\mu$ l, 400  $\mu$ l, 600  $\mu$ l, 800  $\mu$ l or 1 000  $\mu$ l of the standard solution (E.4.3.2). Add 0,1 ml of nitric acid (E.4.1). Make up to volume with water (E.2.1). The concentrations of the cations in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l or 0,5 mg/l, respectively.

Prepare the calibration solutions on the day of use.

#### **E.4.5 Reagent blank solution**

Transfer 50 ml of nitric acid (E.4.1) and 1 000 ml of water (E.2.1) into an HDPE or PP container. Prior to analysis, make sure that the acid matrix and concentration of the reagent blank solution is the same as in the standard and sample solutions.



## Bibliography

- [1] R.J.C. Brown and P.R. Edwards, *Measurement of anions in ambient particulate matter by ion chromatography: A novel sample preparation technique and development of a generic uncertainty budget*, *Talanta*, 2009, 80, 1020-1024. doi:10.1016/j.talanta.2009.07.042
- [2] EN 14907, *Ambient air quality — Standard gravimetric measurement method for the determination of the PM<sub>2,5</sub> mass fraction of suspended particulate matter*
- [3] EN 1822-1, *High efficiency air filters (EPA, HEPA and ULPA) — Part 1: Classification, performance testing, marking*
- [4] EN 13274-7, *Respiratory protective devices — Methods of test — Part 7: Determination of particle filter penetration*
- [5] EN ISO 10304-1, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate*
- [6] EN ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*
- [7] EN ISO 14911, *Water quality — Determination of dissolved Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> using ion chromatography - Method for water and waste water*
- [8] JCGM 200:2008, , *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*
- [9] EN ISO/IEC 17025 *General requirements for the competence of testing and calibration laboratories*
- [10] EN 12341 *Ambient air quality —Standard gravimetric measurement method for the determination of the PM<sub>10</sub> and PM<sub>2,5</sub> mass fraction of suspended particulate matter.*
- [11] *Guide to the demonstration of equivalence of ambient air monitoring methods*, Report by an EC Working Group on Guidance for the Demonstration of Equivalence, January 2010





# British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

## About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards-based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

## Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at [bsigroup.com/standards](http://bsigroup.com/standards) or contacting our Customer Services team or Knowledge Centre.

## Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at [bsigroup.com/shop](http://bsigroup.com/shop), where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

## Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to [bsigroup.com/subscriptions](http://bsigroup.com/subscriptions).

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

**PLUS** is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit [bsigroup.com/shop](http://bsigroup.com/shop).

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email [bsmusales@bsigroup.com](mailto:bsmusales@bsigroup.com).

## BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

## Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

## Copyright

All the data, software and documentation set out in all British Standards and other BSI publications are the property of and copyrighted by BSI, or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use. Except as permitted under the Copyright, Designs and Patents Act 1988 no extract may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, photocopying, recording or otherwise – without prior written permission from BSI. Details and advice can be obtained from the Copyright & Licensing Department.

## Useful Contacts:

### Customer Services

**Tel:** +44 845 086 9001

**Email (orders):** [orders@bsigroup.com](mailto:orders@bsigroup.com)

**Email (enquiries):** [cservices@bsigroup.com](mailto:cservices@bsigroup.com)

### Subscriptions

**Tel:** +44 845 086 9001

**Email:** [subscriptions@bsigroup.com](mailto:subscriptions@bsigroup.com)

### Knowledge Centre

**Tel:** +44 20 8996 7004

**Email:** [knowledgecentre@bsigroup.com](mailto:knowledgecentre@bsigroup.com)

### Copyright & Licensing

**Tel:** +44 20 8996 7070

**Email:** [copyright@bsigroup.com](mailto:copyright@bsigroup.com)



...making excellence a habit.™