



BSI Standards Publication

**Stationary source emissions —
Determination of the total emission of As,
Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl and V**

National foreword

This British Standard is the UK implementation of EN 14385:2024. It supersedes BS EN 14385:2004, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/1, Stationary source emission.

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

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Emissionen aus stationären Quellen - Bestimmung der Gesamtemission von As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl und V

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (EN 14385:2024) 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of an identical text or by endorsement, at the latest by June 2025, and conflicting national standards shall be withdrawn at the latest by June 2025.

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

This document supersedes EN 14385:2004.

The main changes compared to the previous edition are listed below:

- in the Scope: Range of specific elements widened from 0,5 mg/m³ to 5 mg/m³;
- in the Scope: Table 1 Exhaust Gas matrix composition deleted;
- in Clause 3: Definitions clarified and widened;
- in Clause 3: Elements split into Groups A and B for clarity;
- in 5.1.2.7.2: Correction using a wet gas meter has been clarified;
- in Clause 5: Definitions of Chemicals and Quality have been clarified;
- in Clause 5: Leak check methods has been moved to Annex B;
- in Clause 8: Treatment of Data from field blanks has been clarified and made explicit;
- in Clause 9: Expression of results has been clarified and treatment of data where a wet gas meter has been used has been expanded;
- in Annex F: Example of an Uncertainty Budget Assessment of the Standard has been added;
- in Annex G: Determination and reporting of limits of detection and quantification added and information on how to deal with elements below the level of quantification;
- in Annex H: Alternative digestion method for filters by use of an HF-free digestion Mixture.

This document has been prepared under a standardization request addressed to CEN by the European Commission. The Standing Committee of the EFTA States subsequently approves these requests for its Member States.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and the United Kingdom.

Introduction

This document specifies a method for the determination of the total mass concentration of specific elements in waste flue gases. The document was validated for waste incinerators but is also applicable to other industrial processes. During the establishment of this document, field tests were performed in order to determine some performance characteristics. These tests showed that in the “gaseous” phase most of the elements cannot be determined quantitatively in the absorption solutions. Therefore, the results of this method are expressed as the total element mass concentrations (i.e. sum of gaseous, dissolved in droplets, solid and adsorbed on particles). This means that when the specific elements are mainly in the solid phase no significant losses (biases) should occur due to the poor absorption efficiency for the elements in the gaseous phase. The quality check requirement for approval of the results is the mass in the last absorber expressed as a minimum percentage of the total mass; this minimum is set at a high level, based on the experiences of the absorption efficiencies in the field tests.

1 Scope

This document specifies a manual reference method for the determination of the mass concentration of specific elements in stationary source emissions. The method is applicable to each of the specific elements in the concentration range of 0,005 mg/m³ to 5 mg/m³.

This document has been validated for the determination of the mass concentration of metals in incineration exhaust gases – applying the performance criteria stated in Clause 9 – for the following elements:

- arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), thallium (Tl), and vanadium (V) and their compounds.

The document can be used to determine metals other than those listed above (for example, selenium (Se) (ISO 17211), tellurium (Te), beryllium (Be), tin (Sn) and zinc (Zn)).

NOTE 1 These other metals mentioned above are commonly required by National Regulations, but this document currently has not yet been validated for these metals.

The document was validated for waste incinerators, but it is also applicable to other industrial processes, the practical experience shows that it can be applied over wide concentration ranges and various emission sources.

If mercury is intended to be determined as well, this can be sampled in a side stream arrangement of the sampling train (EN 13211) [5].

NOTE 2 This document has been validated with the described materials, equipment, sampling, and digestion performances etc., followed by analyses with atomic absorption spectroscopy (AAS) and inductively coupled plasma optical emission spectroscopy (ICP-OES,) or inductively coupled mass spectrometry (ICP-MS). This does not exclude the use of other types of equipment or analyses that meet the requirements and have been proven to be equivalent to the described European Standard.

2 Normative references

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

EN 13284-1:2017, *Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method*

EN 15259, *Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report*

3 Terms and definitions, symbols and abbreviated terms

3.1 Terms and definitions

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

3.1.1

absorber

device in which specific elements are absorbed into an absorption liquid

3.1.2

chemical blank

solution used to check the purity of the chemicals employed by the laboratory

Note 1 to entry: The chemical blank value is determined by analysing the solution (5.2.8) used for the absorption of the specific metal elements, plus any reagents that are added to the solution before analysis including the rinsing solution (5.2.11) if this is used at any stage in the sampling and analysis procedure. This chemical blank is to be used as a blank for all digestions using reagents all from the same batch. Furthermore, this chemical blank should be the same as the solutions used for dilution of laboratory standards, etc. It represents the potential background elements arising from the chemicals used in the analysis. This chemical blank can be subtracted if required from the analysis, if necessary, by the analytical laboratory. However, where it is subtracted this should be identified in the analytical report.

3.1.3

filter blank

value determined for each specific element by treatment and analysis of an unused filter which has been taken from the same batch as the sample filters

Note 1 to entry: Chemical blanks and filter blanks may be subtracted from the analysis and if the level is then below zero the level will be reported as the level of quantification. If chemical or filter blanks are repeatedly high requiring subtraction, then an investigation as to the quality of the reagents or filters should be conducted to ensure that subtraction of the chemical or filter blank is not masking the use of poor quality of reagents or filters.

3.1.4

field blank

sample of filter, absorption and rinsing solutions taken at site without sampling gas and analysed as a normal sample

Note 1 to entry: The field blank is not to be subtracted from the samples and shall be reported separately.

Note 2 to entry: An explanation is provided in 8.5.

3.1.5

filtered material

material collected on the filter

3.1.6

filter passing material

component passing through the filter and recovered in the rest of the absorption system

3.1.7

fritted gas distributor

part of the absorber where the gas stream is distributed into the absorption liquid

3.1.8

Group A elements

arsenic (As), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V) and their compounds

3.1.9

Group B elements

cadmium (Cd) and thallium (Tl) and their compounds

3.1.10**sampling**

<pollutants> process consisting of the collection of gas pollutants from process gases or the withdrawal or isolation of a fractional part of a larger volume of process gases

Note 1 to entry: To ensure sampling is representative the isokinetic sampling procedural requirements specified within EN 13284-1 and EN 15259 should be adopted.

3.1.11**sampling campaign**

sampling at one duct or location during one site visit

3.2 Symbols

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

A	Cross section area, in square metres (m^2)
Q	Flow rate of the sampled gas, in cubic metres per hour or litres per minute (m^3/h or l/min)
T	Temperature, in Kelvin (K)
V	Gas volume dry at standard conditions, in cubic metres or litres (m^3 or l)
L	Leakage rate (volume ratio)
O	Oxygen volume content of the flue gas, in percentage (%)
m	Mass, in milligrams (mg)
n	Number of absorption vessels
p	Pressure, in kilopascals (kPa)
P_v	Partial vapour pressure, in kilopascals (kPa)
C	Mass concentration, e.g. in milligrams per cubic metre (mg/m^3); grams per litre (g/l)
ε	Absorption efficiency
w	Mass fraction in percent (%)
ρ_4^{20}	Density, in kilograms per litre (kg/l) at 20 °C related to that of water at 4 °C
ρ	Specific conductivity, in micro-Siemens per metre (μSm^{-1})
κ	Specific resistance, in mega-Ohm-metre ($\text{M}\Omega\text{m}$)
H_m	Humidity, in percentage volume of gases at wet gas meter inlet
H_a	Humidity, in percentage volume of gases at required reporting conditions

3.3 Abbreviated terms

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

CRM	Certified reference material
El	Specific element
ELV	Emission limit value
FEP	Polyperfluoroethene/polyperfluoropropene

PE	Polyethene
PFA	Perfluoroalkoxy compounds
PP	Polypropene
PTFE	Polytetrafluoroethene
amb	Ambient; index
ave	Average
gas	Gaseous; index
main	Mainstream; index
side	Side stream; index
mes	Temperature, pressure at measuring conditions; index
b	Humidity, pressure, temperature at measuring conditions; index
f	Wet at standard conditions; index
sol	Particle bound; index
norm	Normalized to a reference dry oxygen content of x % (volume fraction); index
per	Permitted; index
obs	Observed; index
int	Internal; index
0	Temperature at standard condition of 273 K, pressure at standard condition of 101,3 kPa, dry volume at 273 K and 101,3 kPa; index

4 Principle

A known volume of flue gas is extracted isokinetically and representatively from a duct during a certain period of time at a controlled flow rate following EN 13284-1. The dust in the sampled gas volume is collected on a filter. Thereafter, the gas stream is passed through a series of absorbers containing absorption solutions and the filter passing fractions of the specific elements are collected within these solutions.

The filter, absorption solution and rinsing solutions are recovered for analysis.

The filter sample is digested in a closed PTFE vessel.

The absorption liquids and the rinsing solutions are prepared for analysis.

The samples are analysed and the final result is expressed as the total mass concentration for each specific element and no distinction is made between filtered and filter passing fractions.

5 Apparatus and chemicals

5.1 General

All parts coming into contact with the sample are to be made of corrosion resistant and inert material, i.e. borosilicate glass, quartz glass, PTFE, or titanium. As commercial titanium can contain some of the specific elements to be determined care shall be taken to avoid contamination.

All materials should be suitable for the temperature and flue gas composition they are likely to encounter during the sampling period and remain inert under these conditions and during recovery of the sample.

There have been reports that titanium can undergo thermal oxidation under some conditions and at temperatures above 300 °C and where fluoride levels are > 20 ppm and hence lead to contamination issues.

5.1.2 Apparatus for sampling

5.1.2.1 Nozzle, (see a) 1 of Figure B.1)

The diameter shall be chosen to be compatible with the required gas sampling volume flow rate; the choice of the nozzle shall be in accordance with EN 13284-1.

5.1.2.2 Filter housing and filter support, (see a) 3 of Figure B.1)

The filter housing and filter support shall be in accordance with EN 13284-1.

5.1.2.3 Sampling probe, (see a) 2 of Figure B.1)

5.1.2.4 Absorbers

Fritted gas bubblers or impingers are to be used; for examples see Annex A. The absorbers shall be cooled to a temperature less than or equal to 30°C to avoid excessive evaporation from the first absorption bottle and to aid absorption efficiency. A cooling/ice bath could be used to limit the temperature of the absorber which will improve the absorption efficiency and improve the drying of the gas stream prior to it reaching the dryer.

5.1.2.5 Connection fittings and tubing

Ball joints and other connectors made of the materials stated in 5.1.1 are allowed. PTFE lined seals are also allowed.

For the main-stream arrangement of the sampling equipment, the material requirements specified in 5.1.1 shall be applied from the nozzle to the last absorber; for the side-stream arrangement these materials shall be applied from the nozzle to the T-piece and from the T-piece to the last absorber in the side-stream sampling train.

The length of connections (such as tubing) from the sampling probe to the absorbers shall be minimized and less than 1 m.

5.1.2.6 Suction unit

Depending on the arrangement of the equipment (see Annex B) two suction units can be required for one sampling line.

The suction unit(s) shall be gas-tight, corrosion-proof, and capable of extracting at least the desired gas flow rate(s) at the pressure conditions present in the flue gas duct. Wide adjustments of the sample flow rate(s) shall be facilitated using regulating and/or by-pass valves. Shut-off valve(s) for stopping the gas flow or back flow, due to potentially low pressures in the duct, should also be available.

If a variant of the sampling train with flow division is chosen, the volume flow rate in the secondary line shall be taken into account in order to calculate the required volume flow rate in the main line.

NOTE Measures for the protection of the suction unit(s) such as filters, water traps, etc. can be useful.

Flow meters which are gas-tight and corrosion-proof (variable area meters, orifice plates, etc.) are strongly recommended to check the sampling flow rate.

5.1.2.7 Gas volume metering

5.1.2.7.1 General

In accordance with EN 13284-1 two kinds of systems may be used to measure the gas volume:

- volume measurements on a dry basis;
- volume measurements on a wet basis.

5.1.2.7.2 Gas volume meter

The requirements for the flow rate measurements on a dry basis are:

- atmospheric pressure measuring device;
- condenser and/or gas drying tower providing a residual humidity less than 10 g/m³ at the maximum flow rate;
- gas-tight suction device (such as compressed air ejector, pump, etc.);

NOTE 1 Gas-tightness is not necessary if the pump is positioned downstream of the metering device.

- flowmeter, in order to facilitate the flow rate adjustment, calibrated against the dry gas volume meter;
- dry gas volume meter providing gas volume measurement shall have a maximum expanded uncertainty of 5 % at the anticipated flow rate, incorporating the associated absolute pressure and absolute temperature measurement uncertainties (maximum expanded uncertainty of 2,0 % each);

The requirements for the flow rate measurements on a wet basis are:

- heated tubing, in order to prevent upstream condensation of the sample gas;
- heated orifice plate or equivalent device (flow meter), shall be calibrated within 10 % maximum expanded uncertainty of the anticipated flow rate; the uncertainty of temperature, pressure (absolute and differential) measurement shall be less than 2 %;
- gas-tight suction device (such as compressed air ejector, pump, etc.);

NOTE 2 Gas-tightness is not necessary if the pump is positioned downstream of the metering device.

- atmospheric pressure measuring device;
- when using a wet gas volume measurement system (gas volume meter, critical orifice, etc.), measurement of the flue gas water vapour content at the gas volume meter is required to allow the gas wet volume to be corrected to a dry basis, see Formula (1):

$$V_{mes}(dry) = V_{mes} \cdot \frac{P - P_v}{P} = V_{mes} \cdot \frac{100 - H_m}{100 - H_a} \quad (1)$$

See symbols 3.2 and abbreviations 3.3.

P_v is the partial vapour pressure of water in the gas meter;

P is the absolute pressure in the gas meter;

H_m is the water content of gases entering wet gas meter;

H_a is the water content at the reporting conditions.

In the particular case of a wet gas volume meter, it can be assumed that the gas is saturated at the gas volume meter temperature (T). The partial vapour pressure P_v is then equal to the saturation vapour pressure $P_{\text{sat}(T)}$ of the water at the gas volume meter temperature, see Formula (2):

$$V_{\text{mes(dry)}} = V_{\text{mes(wet)}} \cdot \frac{P - P_{\text{sat}(T)}}{P} \quad (2)$$

5.1.2.8 Storage bottles

The bottles for the storage of the unused absorption solutions (before sampling) as well as the exposed absorption solutions containing the absorbed elements (samples) shall be made of PE. The caps shall be made of PTFE, PFA, FEP, PP, or uncoloured PE.

WARNING Using the storage bottles with absorption solution see warning of 8.2.3.

5.1.3 Apparatus for analysis

5.1.3.1 Digestion device

Heating plate or microwave oven for digestion in a closed PTFE vessel at increased temperature and pressure.

5.1.3.2 Digestion PTFE vessels

Pressure tight PTFE vessels with lids to be used for sample digestion at increased temperature and pressure, matching the digestion device, capacity e.g. 100 ml to 200 ml.

5.1.3.3 Measuring cylinders

For the unused and exposed absorption solutions, the capacity will depend on their application, e.g. 50 ml, 100 ml, and 1 000 ml. The flasks are to be made of borosilicate glass, quartz glass, or PE.

5.1.3.4 Volumetric flasks

For the preparation of solutions, the capacity will depend on their application, e.g. 20 ml, 50 ml, 100 ml and 1 000 ml. They are to be made of borosilicate glass, quartz glass, or PE.

5.1.3.5 Storage flasks

For the digestion solutions, the capacity will depend on their application, e.g. 50 ml, 100 ml and 1 000 ml. Again, they are to be made of borosilicate glass, quartz glass, or PE.

5.1.3.6 Pipettes and dispensers

These are to be made of borosilicate glass, quartz glass, or PE.

5.2 Chemicals and filter material

5.2.1 General

Only reagents of recognized analytical grades are to be used. All these materials are to have a suitable content of the elements to be determined to enable the field blank criteria to be met (8.5).

WARNING The user should ensure that all reagents are used in accordance with the appropriate health and safety regulations. Risk assessment on the overall analytical protocol is required which will include COSHH (Control of Substances Hazardous to Health) assessments for all the reagents used. Particular attention should be made to the use of hydrofluoric acid (HF) and the need to develop a specific “safe working” protocol to address the unique safety issues relating to HF in the laboratory.

5.2.2 Filter

For any series of tests, use only filters from one batch, these should have a low and constant metal content. The filter material shall have a blank value for each of the elements (per cubic metre of sampled flue gas anticipated) of less than $1 \mu\text{g}/\text{m}^3$ or such that the field blank criteria (8.5) can be met. Only plane filters made of quartz fibre or PTFE shall be used. For the filter efficiency, the same specifications as in EN 13284-1 are required. This efficiency shall be certified by the supplier. The filter material shall be suitable for application up to the maximum temperature anticipated.

When using filters with organic binders, precautions shall be taken to ensure that during digestion all sampled elements attached to the filter material will be digested. The organic binders or the reaction products from these binders after digestion shall not influence the analysis.

NOTE 1 Generally, the use of filters with organic binders is not recommended.

NOTE 2 For long-term sampling (greater than 24 h) other filters could be considered as long as they allow the field blank criteria (8.5) to be met.

5.2.3 Hydrofluoric acid

HF; mass concentration $w \approx 40 \%$ (w/w), $\rho_4^{20} = 1,16 \text{ kg/l}$, for filter digestion.

5.2.4 Hydrogen peroxide

H_2O_2 ; mass concentration $w \approx 30 \%$ (w/w), $\rho_4^{20} = 1,11 \text{ kg/l}$.

5.2.5 Nitric acid

HNO_3 ; mass concentration $w \approx 65 \%$ (w/w), $\rho_4^{20} = 1,40 \text{ kg/l}$, for filter digestion.

5.2.6 Hydrochloric acid

HCl; mass concentration $w \approx 35 \%$ (w/w), $\rho_4^{20} = 1,18 \text{ kg/l}$.

5.2.7 Water

H_2O ; doubly distilled or of the same quality, specific conductivity $\rho < 10 \mu\text{Sm}^{-1}$ (i.e. specific resistance $\kappa > 0,1 \text{ MWm}$).

5.2.8 Absorption solution

Prepare a mixture of equal volumes of nitric acid (5.2.5) and hydrogen peroxide (5.2.4), pour one volume of this mixture into nine volume parts of water (5.2.7). This results in mass contents $w(\text{HNO}_3) \approx 4,4 \%$ and $w(\text{H}_2\text{O}_2) \approx 1,6 \%$. As hydrogen peroxide tends to decompose with time this solution should be prepared freshly on site. Keep a portion of the solution for analysis as a blank which is equivalent to the absorption solution used at site.

NOTE Alternatively, the nitric acid solution can be prepared in advance and the hydrogen peroxide added on site so avoiding the decomposition issue.

5.2.9 Boric acid solution (H_3BO_3)

To obtain a cold saturated boric acid solution with a mass content $w \approx 5 \%$ (m/v), dissolve an excess of boric acid ($\approx 50\text{--}55 \text{ g}$) in $1\,000 \text{ ml}$ warm water (5.2.7) and let the solution cool to room temperature. The supernatant liquid needs to be filtered or decanted for use.

5.2.10 Digestion Solution

To be obtained as follows: Add 200 ml of saturated H_3BO_3 (5.2.9), 30 ml of HNO_3 (5.2.5) and 20 ml HF (5.2.3) to a volumetric flask with approximately 700 ml of water (5.2.7). Make up to 1 000 ml with water (5.2.7) and mix well. Transfer the mixture to a 1 000 ml storage bottle. Label it “digestion solution” and add any other relevant information (date, etc.). Take approx. 50-100 ml of this solution into a further storage bottle and label it “digestion blank” along with any other relevant information (date, etc.)

The digestion solution shall be used as blank for all digestions by using acids from one batch. Furthermore, this chemical digestion solution shall be used for dilution of laboratory standards (3.1.3 and 8.7.3).

5.2.11 Rinsing acid

HNO_3 , mass content $w \approx 5\%$, for rinsing the digestion equipment. Add 80 ml of HNO_3 (5.2.5) carefully to 300 ml of water (5.2.7) and make up to 1 000 ml with water (5.2.7).

NOTE Alternatively the absorption solution can be used for rinsing the sampling train.

5.2.12 Standard solutions

These are to contain the specific elements to be determined with $C(\text{element}) = 1 \text{ g/l}$; $\text{pH} \leq 1$.

Use commercially available standard solutions and dilute them to the appropriate concentrations.

5.2.13 Certified reference material

Commercially available certified reference material (CRM), e.g. pulverized fly ash (BCR 038), shall be used.

5.2.14 Acetone

If acetone is used for pre-washing the nozzle and probe it shall be chosen such that it does not contribute to the overall analysis and such that the field blank criteria (8.5) can be met. This requires that high analytical grade acetone is used with low suspended and low residues on evaporation. The content of specific metals of Groups A and B metals (6.3) will need to be as low as possible. However, the specific levels will be dependent on the expected sample gas volume in a campaign.

The highest grade of analytical reagent is recommended with respect to metal content and will need verifying to ensure that the field blank criteria (8.5) can be met.

6 Sampling equipment

6.1 General requirements

The sampling equipment consists of:

- sampling probe with an entry nozzle suitable for isokinetic sampling conforming to the requirements specified in EN 13284-1;
- a filter housing with filter support and filter;
 - the filter housing may be located either:
 - in the duct, mounted directly behind the entry nozzle (in-stack filtration); or
 - outside the duct, mounted directly behind the suction tube (out-stack filtration).

In the latter case (out-stack filtration) the filter housing shall be temperature controlled.

- a series of at least three absorbers;
- suction unit(s) with gas metering device(s) and flow regulator(s).

6.2 Isokinetic sampling equipment

Sampling shall be carried out isokinetically according to EN 13284-1.

Only the additional specific requirements for the sampling of Group A elements and Group B elements (6.3) are stated here.

Two types of absorber systems may be employed, a main-stream or a side-stream arrangement. In the main-stream system all the sampled flue gas is passed through the absorbers, while in the side-stream arrangement only a part of the sampled flue gas is passed through the absorbers.

Examples of both systems of the isokinetic sampling equipment are given in Annex B.

The sampling probe shall be temperature controlled. In addition, when the out-stack filter arrangement is used the filter housing shall be temperature controlled too. In the case of the side-stream arrangement the T-piece (i.e. the connection to and the distribution T-piece itself), shall also be temperature controlled. Insulation without additional heating of these parts is not allowed.

NOTE Insulation alone of the connector and the T-piece is insufficient for maintaining the same gas temperature as in the sampling probe. The heat input from the sampled gas is insufficient to compensate for the thermal losses even with insulation.

The parts of the equipment that are in contact with the sampled flue gas shall only be composed of the specific materials prescribed in 5.1.

Additional measurement equipment is needed to monitor the isokinetic conditions. For the description of this equipment, and the associated specific requirements, reference is made to EN 13284-1.

6.3 Absorbers and absorption efficiency

For an efficient absorption of gaseous phase metals, three absorbers shall be placed in series.

A number of metals are often measured together as a group and are summed for comparison with an ELV for total metals. For example, metals are typically reported in two groups (see NOTE 1):

- Group A elements (As, Cr, Co, Cu, Mn, Ni, Pb, Sb and V)
- Group B elements (Cd and Tl)

The absorber efficiency test is applied separately to each group of metals.

The absorption efficiency is determined according to Formula (3).

$$\eta = 100 \times \left(1 - \frac{m_{\text{gas},3}}{m_{\text{sol}} + \sum_{i=1}^n m_{\text{gas},i}} \right) \quad (3)$$

where

- η is the absorption efficiency, in %;
- $m_{\text{gas},3}$ is the mass (in mg) of analyte in absorber 3 (absorber 4, if an optional absorber has been added where high moisture is anticipated in the gas stream);
- m_{sol} is the mass of analyte in solid phase, in mg;
- $m_{\text{gas},i}$ is the mass of analyte in all absorbers, in mg.

If one of the individual metal elements in the last absorber (e.g. Sb) is more than 10 % of the total combined mass for that individual element (i.e. the filter, probe rinse and absorbers) collected, then the result for all the metals in that group shall be rejected.

The absorber efficiency check becomes less effective as the concentration of the pollutant in a stack gas decreases, so for each group, the requirement to pass the absorber efficiency check shall not apply:

- to individual metal element(s), where the individual mass of the element in the final result is less than 1 % of the result for the total mass of metals in the group; or
- if the total combined result for the metals in the group is less than 30 % of the ELV.

EXAMPLE

- Group A elements (As, Cr, Co, Cu, Mn, Ni, Pb, Sb and V combined) – e.g. ELV: 0,5 mg/m³
- Group B elements (Cd and Tl combined) – e.g.: ELV: 0,05 mg/m³

For combined metals (As, Cr, Co, Cu, Mn, Ni, Pb, Sb and V) it would not be necessary for each individual element to comply with the less than 10 % in the last absorber criteria, if the overall combined result for the sample train was below 0,15 mg/m³ (i.e. < 30 % of the ELV).

For Cd and Tl combined it would not be necessary to comply with the less than 10 % in the last absorber criteria, if the overall combined Cd and Tl result for the sample train was below 0,015 mg/m³ (i.e. < 30 % of the ELV).

7 Cleaning of the sampling equipment prior to sampling

Those parts of the sampling train in contact with the sampled gas which form part of the sample shall be cleaned prior to sampling.

The following inner parts shall be cleaned: Nozzle, probe, filter housing, filter support, T-piece (if applied), absorbers, connection tubing, storage bottles for absorption solutions and samples, transport containers for filters (e.g. Petri dishes).

Examples of cleaning procedures are given in Annex C.

8 Procedure

8.1 General requirements

The sampling shall be performed according to the measurement and planning requirements of EN 15259 and the specific requirements of EN 13284-1. This includes, using grid sampling to obtain a representative sample, velocity traversing of the duct/stack, and determination of the gas density to ensure that isokinetic sampling can be achieved.

The sampling probe, the out-stack filter and the T-piece (see 6.2) shall be maintained at a temperature of at least 20 K (20 °C) above the flue gas temperature, or 20 K (20 °C) above the acid dew point (up to a maximum of 180 °C), whichever is the highest.

There may be legal or other regulatory requirements that affect the sampling time duration to ensure that the sample volume collected is sufficient.

The sample volume taken shall be sufficient to meet the required limits of quantification. This will depend on the analytical instrumentation used.

8.2 Preparation and installation of equipment

8.2.1 Filter installation

The filter shall be installed in the filter housing attached to the probe. Care shall be taken in handling the filter in order to avoid contamination.

NOTE If a sufficient number of filter supports or filter cartridges are available, the filters can be mounted in the filter housings at the laboratory, so that only the filter housings need to be changed at the sampling site.

8.2.2 Nozzle installation

The appropriate nozzle diameter shall be determined according to EN 13284-1. The nozzle is attached to the probe (for out-stack filtration) or to the filter housing (for in-stack filtration).

8.2.3 Installation of absorbers

The absorbers shall be filled with an appropriate amount (e.g. at least 25 % of the absorber volume) of absorption solution (5.2.8) so that sufficient gas/liquid contact is guaranteed in the absorbers. An empty absorber should be added behind the last filled absorber as a protection for the downstream suction equipment.

If a large amount of condensate is anticipated, an empty absorber may be installed upstream of the first absorber, so as to ensure that the absorber solution in absorber 1 is not unduly diluted. The contents of this additional absorber shall be combined with the absorber solution in absorber 1 along with rinsings of the additional absorber during recovery of the sample.

WARNING Do not fill glass absorbers or glass storage bottles at the laboratory because overpressure resulting from the decomposition of H_2O_2 during storage can result in an explosion. As the absorption liquids are highly corrosive, care and safety measures shall be taken to avoid injury to persons and/or damage to the equipment in the event of breakage or leakage of the absorbers.

8.2.4 Leak test

At the start of each sampling procedure the complete sampling train shall be leak tested.

This can be conducted using one of the three methods listed in Annex B (other methods may be used if they give equivalent results).

The leakage rate of the sample train shall not exceed 2,0 % of the expected sample gas flow rate.

Care shall be taken that no back flow of absorption solution towards the probe occurs when conducting the leak test. The sealing of the sample probe shall always be removed prior to turning off suction units.

It is recommended that the integrity of the sampling system could also be confirmed during sampling by measuring the concentration of a suitable stack gas component (e.g. oxygen) directly in the stack and downstream the sample gas line. Any systematic difference between those concentrations can indicate a leak in the system and can invalidate the test if this equates to a leakage rate which is > 2 % of the expected sample gas flow rate. This method will only show gross leaks and cannot be used as a primary leak procedure.

Where non-combustion processes are being monitored and there is effectively ambient levels of oxygen present particular care should be taken to ensure that no leaks occur during the sampling as the above procedure cannot be used.

8.2.5 Installation of equipment at duct

Install probe of the completely assembled sampling equipment which has been leak tested and heated into the sampling port at the duct. Avoid back flow of absorption liquid into the sampling equipment

in the case of low-pressure ducts. Ensure the sample nozzle opening is in facing into the direction of the gas stream.

The suction unit should be started as soon as possible to minimize exposure of the inner probe /nozzle surfaces.

Avoid contamination of the interior part of the nozzle with dust during insertion of the sampling equipment into the sampling port

WARNING Take care and safety measures as hazardous fumes can escape from the sampling port in the case of excess pressure in the duct and suitable PPE equipment should be used in accordance with appropriate risk assessments.

8.3 Performance of the sampling

Ensure the sampling equipment has reached the prescribed operating temperature range. Record the initial gas volume meter readings, start the measurement by extracting the flue gas from the duct. Note the start time.

Perform isokinetic and grid sampling according to EN 13284-1 including the sampling requirements regarding measurements of gas meter temperatures and pressures and frequency of these measurements.

Just before the end of the desired sampling time read the temperature and, if necessary, the pressure at the gas volume meter(s). Then stop the sampling and note the time. Record the gas volume meters and the atmospheric pressure.

8.4 Disassembling the equipment

8.4.1 General

Remove probe and nozzle from the duct and allow to cool. Disassemble the probe, filter housing and absorbers. Protect the internal surfaces of the sample train from external contamination.

WARNING Take care and safety measures as hazardous fumes can escape from the sampling port in the case of excess pressure during removal of the equipment.

8.4.2 Disassembly of the filter housing

Open the filter housing in an appropriate place where contamination of the filter can be avoided. Place the filter into a uniquely identified transport case.

If a sufficient number of filter housings are available then disassembling at the sampling site is not necessary and this operation can be done at the laboratory. Ensure that the filter housing is capped for transport to protect against contamination issues.

8.4.3 Rinsing of the sampling equipment

The upstream parts shall be rinsed at least after each measurement series on the same sampling plane and at least once a day. The metal concentration shall be attributed to individual tests in proportion to the sample volume for each of the samples.

Rinse the nozzle, probe and front portion of the filter housing with rinsing acid (5.2.11) or with absorption solution (5.2.8). Take care that a sufficient amount of rinsing liquid is used to wet to the total inner surface of the mentioned parts.

Store the used rinsing acid in a uniquely identified storage bottle. Determine and record the weight or volume of the liquid. This may be performed directly on-site or afterwards.

8.4.4 Rinsing of the connection tubing to the first absorber

After each measurement rinse the back section of the filter and the connection tubing (between the filter housing and the first absorber) into the first absorber with rinsing acid (5.2.11) or with absorption solution (5.2.8).

8.4.5 Handling of the absorption solutions from the absorbers

For each measurement series for each individual stationary source an absorber efficiency test (6.3) shall be conducted for at least one of the measurements (NOTE 1). For the other measurements the content of all absorbers may be combined. This should include any additional absorbers which have been inserted into the sampling train due to the high moisture content of the stack gases.

Rinse the absorbers and the surface of the connectors that come into contact with the stack gas after each measurement with rinsing acid (5.2.11) or with absorption solution (5.2.8) to ensure maximum capture of the metal species. Take care that a sufficient amount of rinsing liquid is used to wet to the total inner surface of the absorbers but that the amount used kept to a minimum or else dilution of the sample will occur affecting the limit of detection. The washings shall be added to the appropriate absorber solution bottle.

The absorption liquids from the absorbers are to be transferred into uniquely identified storage bottles.

A procedure should be in place to assess if any losses have occurred during transport of the absorber solutions (NOTE 2).

The volume of solutions can be determined on site by weighing or by any other suitable procedure, or the level of the solution can be marked on the storage bottle to check after transport that there have been no losses.

Take special care during the rinsing of absorbers with fritted gas dividers. As absorption liquid is not easily rinsed from these devices so this needs to be conducted carefully and thoroughly.

NOTE 1 Additional absorber efficiency tests on further measurements is not precluded by this document and can be beneficial where the tests are being conducted for regulatory purposes to minimize the requirements to conduct retesting of the process should an absorption efficiency test fail.

NOTE 2 Such procedures could include measuring the volume or mass of storage bottles before or after transport.

8.5 Field blanks

To check the procedure, for each campaign, at least one field blank shall be taken at the site sampling platform (if multiple ducts share the same sampling platform, a single field blank is required) by the following procedures given in 8.2.1, 8.2.2, 8.2.3, 8.2.4 and 8.4, but the probe is not inserted into the duct. Filter, rinsing solutions and absorption solutions shall be collected for analysis. The mean volume from the tests conducted in the campaign should be used if they are all similar. If one test is much shorter and is to be included in the test campaign, then the smallest volume sampled shall be used in determining the field blank. If the metal levels in the field blank is more than 10 % of the set regulatory emission value, then the results of that corresponding part of the campaign shall be rejected.

If the calculated value for a part of the sampling campaign is less than the preceding field blank value, the reported result is defined as less or equal to the blank.

The field blank shall not be subtracted from the samples and shall be separately reported.

The volume of gas which is collected when sampling should be considered during the planning of the sampling campaign to ensure that the requirements of the blank being less than 10 % of the ELV is easily achieved. In addition, the volume of the gas sampled needs to be sufficient that the potential interferants

or contaminants that arise from metals in the filter or on the glassware of the equipment are minimized and become effectively insignificant to the reported level for the sample.

8.6 Requirements for storage of the samples

Liquid samples are to be stored in PE bottles at a temperature of below 6 °C in the laboratory especially where there is a delay prior to analysis. However, during transportation and on-site the samples should be maintained below 25 °C.

The liquid samples shall be analysed within four weeks after sampling at the latest.

8.7 Pre-treatment before analysis

8.7.1 General

Before the different samples can be analysed some pre-treatment is necessary. This pre-treatment is described in 8.7.3 to 8.7.4. The pre-treated samples originating from the filter and absorption solution should be analysed separately, but in any event, the solution from the last absorber shall be analysed separately for at least one of the samples obtained during the campaign.

8.7.2 Pre-cleaning of the digestion equipment

After cleaning in a laboratory dishwasher or an appropriate procedure, the equipment used for the digestion is additionally cleaned by rinsing in a bath with rinsing acid (5.2.11) for 24 h. Afterwards the equipment is rinsed with water. Any other best practice procedure may be applicable.

8.7.3 Treatment of CRM and filter

8.7.3.1 General procedure

The sampling filter shall be digested in a closed PTFE vessel at increased temperature and pressure; PTFE filters are treated in the same way without dissolution of the filter material. This procedure describes how a sampling filter is dissolved by digestion with a mixture of HNO_3 and HF. After the digestion, boric acid is added to the liquid to form complexes with excess fluoride, at the same time the boric acid dissolves insoluble fluorides by complexation.

NOTE It is possible not to use boric acid provided that the results obtained are equivalent for the same type of filter used. For example, the use of an HF-resistant (e.g. PTFE) assembly at the sample introduction system in the ICP-MS eliminates the need to neutralize HF with boric acid.

The methods given are valid for plane filters of approximately 100 mg per filter, and a maximum of 10 mg of particulate matter collected on the filter. If the mass of the filter and / or the mass of particulate matter is higher the laboratory should assess whether the amounts of acid indicated in 8.7.3.2 are sufficient or should be increased.

A fly ash CRM with certificate values for the elements of interest shall be digested following the same procedures as described for the filters. The mass of CRM digested should be at least the minimum mass recommended on the CRM instructions. If the mass collected on the filter is higher than the recommended CRM minimum amount, a similar mass to that collected on the filter should be digested. This is defined as the calibration control solution.

If there is any elemental carbon present on the filter, this will not be digested by this method. If there is any visual evidence of elemental carbon in the digestion solution, then the liquid shall be filtered before analysis. This shall be stated in the final measurement report.

8.7.3.2 General procedure

- a) Transfer the filter from the transport case (see 8.4.2) to the PTFE vessel. For this procedure a pair of tweezers (titanium, gold, plastic or plastic coated) shall be used. The filter may be folded to fit in the PTFE vessel;
- b) Record the filter identification number and the vessel identification number on a working sheet. Note other relevant information as well;
- c) Clean the transport case with 1,5 ml of HNO_3 (5.2.5), and add it to the PTFE vessel;
- d) Add additional 1,5 ml of HNO_3 (5.2.5) to the PTFE vessel;
- e) Add 2,0 ml of HF (5.2.3) to the PTFE vessel. The filter shall be totally wetted;
- f) Assemble the PTFE vessel, as described in the manufacturer's instructions.

If an oven or a heating plate is used as heating source, continue with 8.7.3.3. If a microwave oven is used go to 8.7.3.4.

8.7.3.3 Heating in oven or heating plate

- a) Place the closed PTFE vessel in the oven, kept at a temperature of at least 160 °C for at least 8 h;
- b) take out the PTFE vessel, and let it cool to room temperature. Open the PTFE vessel carefully and add 20 ml of water (5.2.7) and with caution add 20 ml of H_3BO_3 (5.2.9);

Adding water will be to a concentrated acidic solution and hence there can be the risk and care should be taken in this operation.

- c) place the PTFE vessel into the oven at 150 °C for 2 h;
- d) take out the PTFE vessel, and let it cool to room temperature. Open the PTFE vessel carefully and transfer the liquid quantitatively into a 100 ml volumetric flask;
- e) wash the inside of the PTFE vessel several times with water and add it to the volumetric flask. Carefully make up with water and mix well;

Where low concentrations are on/in the filter a 50 ml volumetric flask may be used instead of a 100 ml flask, however larger volumes shall not be used or else detection requirements may not be met.

- f) mark the bottle with filter identification number, etc.;
- g) the digestion is now ready for analysis.

8.7.3.4 Heating in microwave oven

For digestion in microwave oven several individual procedures may be used by the laboratories. This subclause gives the minimum requirements to ensure a complete filter digestion.

The minimum requirements are based on one PTFE vessel in the microwave oven at the time. If two or more PTFE vessels are placed in the same oven, the procedure shall be changed accordingly, and as described by the manufacturer of the microwave oven.