BS EN
14385:2004

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

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ICS 13.040.40

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British Standards

National foreword

This British Standard is the official English language version of EN 14385:2004.

The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/1, Stationary source emissions, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

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

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English version

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

Emissions de sources fixes - Détermination de l'émission totale de As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Tl et V

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

This European Standard was approved by CEN on 2 July 2003.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

This document (EN 14385:2004) 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of an identical text or by endorsement, at the latest by August 2004, and conflicting national standards shall be withdrawn at the latest by August 2004.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directives.

For relationship with EU Directives, see informative Annex ZA, which is an integral part of this document.

In this European Standard the Annexes A to E are informative.

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

Introduction

This European Standard specifies a method for the determination of the total mass concentration of specific elements in flue gases of waste incinerators. During the establishment of this European Standard field tests were performed in order to determine some performance characteristics. These tests showed that in the “gaseous” phase most of the elements can not 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 rather high level, based on the experiences of the absorption efficiencies in the field tests.

When this European Standard is applied for conditions that are different from those investigated during the field tests at municipal waste incinerators, the results may not be the same as experienced during these field tests described.

1 Scope

This European Standard specifies a manual reference method for the determination of the mass concentration of specific elements in exhaust gases from hazardous and municipal waste incinerators [1]. The method is applicable to each of the specific elements in the concentration range of 0,005 mg/m^3 to 0,5 mg/m^3. Unless otherwise stated, concentrations are expressed at volumes under dry conditions, normalised to 273 K, 101,3 kPa, and oxygen content with a volume fraction of 11 %.

Specific elements according to this European standard are antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), thallium (Tl), and vanadium (V).

This European Standard is also applicable for exhaust gases from other sources with a flue gas composition, similar to that given in Table 1. The performance characteristics of the method determined for waste incincerators cannot be extrapolated to be used for other types of matrix without any further validation work.

NOTE This European Standard has been validated with the described materials, equipment, sampling and digestion performances etc., followed by analyses with AAS and ICP. This does not exclude the use of other types that meet the requirements and proven to be equivalent to the described European Standard.

This European Standard has been validated for the determination of the mass concentration of metals in incineration exhaust gases, within the uncertainties stated in clause 9.

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

Table 1 — Exhaust gas matrix

Parameter to be determined	Mass concentration range		
total suspended matter	0 mg/m^3	to	20 mg/m^3
TOC[a)]	0 mg/m^3	to	20 mg/m^3
HCl	0 mg/m^3	to	20 mg/m^3
HF	0 mg/m^3	to	2 mg/m^3
SO_2	0 mg/m^3	to	100 mg/m^3
CO	0 mg/m^3	to	250 mg/m^3
NO_x as NO_2	0 mg/m^3	to	500 mg/m^3
Volume fraction range			
CO_2	3 %	to	15 % (dry, actual)
H_2O (ga)	10 %	to	35 % (actual)
O_2	3 %	to	17 % (dry, actual)
Temperature	60 °C	to	200 °C

a) total organic carbon

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 13284-1:2001, *Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method*

EN 13211:2001, *Air quality – Stationary source emissions – Manual method of determination of the concentration of total mercury*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results - Part 2 : Basic method for the determination of repeatability and reproducibility of a standard measurement method*

3 Terms and definitions, symbols and abbreviations

3.1 Terms and definitions

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

3.1.1
absorber
a device in which specific elements are absorbed into an absorption liquid

3.1.2
chemical blank
a solution used to check the purity of the chemicals employed by the laboratory

NOTE The chemical blank value is determined by analysing the chemical blank solution (produced as described in 5.2.10) for the specific elements. This chemical blank is to be used as blank for all digestions using acids from one and the same batch. Furthermore, this chemical blank should be used for dilution of laboratory standards.

3.1.3
filter blank
the filter blank value is 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. The treatment of the filter blank is specified in 8.7.3. The filter blank gives the blank values for the filter and treatment only. This value may be subtracted from the analytical value. The filter blank is **not** the same as the field blank (see 8.5)

3.1.4
field blank
samples of filter, absorption and rinsing solutions taken at sites without sampling gas and analysed as a normal sample (explanation see 8.5)

In every campaign of sampling, at least one sampling blank should be taken at each duct or chimney where sampling is to be carried out.

3.1.5
filtered material
materials collected on the filter

3.1.6
filter passing material
components passing the filter and recovered in the rest of the absorbing system

3.1.7
fritted gas distributor
a part of the absorber where the gas stream is distributed into the absorption liquid

3.1.8
representative sampling
sampling as stated in EN 13284-1:2001

3.1.9
specific elements
Antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), thallium (Tl), vanadium (V) and their compounds

3.1.10
total specific elements
sum of all specific elements of 3.1.9 apart from Cd and Tl contained in the exhaust gas, i.e. the sum of the filtered and filter passing parts of these elements

3.1.11
sampling campaign
sampling at one duct or location during one site visit

3.2 Symbols

3.2.1	A	Cross section area, in square metres (m^2)
3.2.2	Q	Flow rate of the sampled gas, in cubic metres per hour or litres per minute (m^3/h or l/min)
3.2.3	T	Temperature, in Kelvin (K)
3.2.4	V	Gas volume dry at standard conditions, in cubic metres or litres (m^3 or l)
3.2.5	L	Leakage rate (volume ratio)
3.2.6	O	Oxygen volume content of the flue gas, in percentage (%)
3.2.7	m	Mass, in milligrams (mg)
3.2.8	n	Number of absorption vessels
3.2.9	p	Pressure, in kilopascals (kPa)
3.2.10	β	Mass concentration, e.g. in milligrams per cubic metre (mg/m^3); grams per litre (g/l)
3.2.11	c	Mass concentration, in grams per litre (g/l)
3.2.12	ε	Absorption efficiency
3.2.13	w	Mass fraction in percent (%)
3.2.14	ρ_4^{20}	Density, in kilograms per litre (kg/l) at 20 °C related to the water of 4 °C
3.2.15	ρ	Specific conductivity, in micro-Siemens per metre (μSm^{-1})
3.2.16	κ	Specific resistance, in mega-Ohm and metre (MΩm)

3.3 Abbreviations

3.3.1	CRM	Certified reference material
3.3.2	El	Specific element
3.3.3	FEP	Polyperfluoroethene / -propene
3.3.4	PE	Polyethene
3.3.5	PFA	Perfluoroalkoxy compounds
3.3.6	PP	Polypropene
3.3.7	PTFE	Polytetrafluoroethene
3.3.8	amb	Ambient; index
3.3.9	gas	Gaseous; index
3.3.10	main	Main stream; index
3.3.11	side	Side stream; index
3.3.12	mes	Dry, temperature, pressure at measuring conditions; index
3.3.13	b	Humidity, pressure, temperature at measuring conditions; index
3.3.14	f	Wet at standard conditions; index
3.3.15	sol	Particle bound; index
3.3.16	norm	Normalized to a dry oxygen content of 11 % (volume fraction); index
3.3.17	per	Permitted; index
3.3.18	obs	Observed; index
3.3.19	int	Internal; index
3.3.20	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 or chimney during a certain period of time at a controlled flow rate following EN 13284-1:2001. 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 analyzed and the final result is expressed as the total mass concentration for each specific element and no distinction shall be made between filtered and filter passing fractions.

5 Apparatus, chemicals and gases

5.1 Apparatus

5.1.1 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 has to be taken to avoid contamination

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 13211 and EN 13284-1:2001.

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 13284-1:2001.

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

Temperature controlled

5.1.2.4 Absorbers

Fritted gas bubblers or impingers are to be used; for examples see annex A. For the main stream arrangement cooling of the absorbers to a temperature below 30 °C can be useful to avoid excessive evaporation from the first absorption bottle.

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 less than 1 m.

The total inner surface of all silicone tubing connections that can become exposed to the gases is limited in relation to the sampled gas flow rate. The flow rate dependent total inner surface (A/Q) of the exposed silicone tubing in the sampling equipment, shall be less than 0,003 3 $\text{m}^2/(\text{m}^3\ \text{h}^{-1})$ or 2 $\text{cm}^2/(l\ \text{min}^{-1})$ respectively.

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 low 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 the low pressure in the duct, should also be available.

If a variant of the sampling train with flow division is chosen, the ratio of the main and side streams has to be kept constant (± 10 %).

NOTE 1 Measures for the protection of the suction unit(s) such as filters, water traps etc. can be useful.

NOTE 2 Corrosion-proof and gas-tight flow meters (variable area meters, orifice plates etc.) are strongly recommended to check the sampling flow rate.

5.1.2.7 Gas volume metering

Two gas volume measuring methods may be used:

- gas flow measurement (Method I);
- gas volume measurement (Method II).

Both methods are described in EN 13284-1:2001. Method II is more accurate than method I.

5.1.2.7.1 Gas volume meters

The specifications for gas volume meters are given in EN 13284-1:2001, annex F (a wet gas volume meter may also be used).

Specifications for the gas volume measurement are:

a) When employing a dry gas volume meter a condenser and/or a gas drying system shall be used which can achieve a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10,5 °C or a volume content $\chi(H_2O) = 1,25$ %);

b) The gas volume meters (wet or dry) shall have a relative uncertainty not exceeding 2 % of the volume (actual conditions);

c) In order to calculate the gas volume at standard conditions the temperature measurement at the gas volume meter shall have an uncertainty not exceeding 2,5 K (i.e. 1 % of absolute temperature) and the pressure measurement at the gas volume meter shall have an uncertainty not exceeding 1 kPa (i.e. 10 mbar, or 1 %).

5.1.2.7.2 Gas flow meters

This is to be used for checking the actual volume flow rate. The measurement uncertainty of the flow meter shall be less than 5 %.

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 flasks

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 Storage flasks

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

5.1.3.5 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 recognised analytical grade are to be used (e.g. supra pure). All these materials are to have the lowest possible content of the elements to be determined. The chemicals used shall have a blank value for each of the elements of less than 1,0 µg/l.

WARNING Take care that all reagents used, are in accordance with the appropriate health and safety regulations. Carry out a risk assessment on the overall analytical protocol, which will include COSHH (Control of Substances Hazardous to Health) assessments for all reagents used. Particular attention is made to the use of hydrofluoric acid (HF) and develop a separate "safe working" protocol and used by the laboratory to address the unique safety issues relating to HF.

5.2.2 Filter

For any series of test, use only filters from one batch, which 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 µg/m³. Only flat filters made of quartz fibre, glass fibre or PTFE are to be used. For the filter efficiency, the same specifications as in EN 13284-1:2001 are required (see Note). This efficiency shall be certified by the supplier. The filter material shall be suitable for application up to the maximum temperature anticipated.

According to EN 13284-1:2001 the filter material shall have an efficiency of at least 99,5 % on a test aerosol with a maximum abundance at a particle diameter of 0,3 µm at the maximum flow rate anticipated, (or at least 99,9 % on a test aerosol of 0,6 µm mean diameter).

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

5.2.3 Hydrofluoric acid

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

5.2.4 Hydrogen peroxide

H_2O_2; mass fraction $w \approx 30$ %, $\rho_4^{20} = 1{,}11$ kg/l

5.2.5 Nitric acid

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

5.2.6 Hydrochloric acid

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

5.2.7 Water

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

5.2.8 Absorption solution

Prepare a mixture from equal volumes of nitric acid (5.2.5) and hydrogen peroxide (5.2.4) and dilute one volume part of this mixture with nine volume parts of water (5.2.7). This results in mass contents $w(HNO_3) \approx 3{,}3$ % and $w(H_2O_2) \approx 1{,}5$ %. As hydrogen peroxide tends to decompose with time then this solution should be prepared freshly. Keep a portion of the solution for analysis as a blank equivalent to the absorption solution used at site.

5.2.9 Boric acid solution (H_3BO_3)

To obtain a cold saturated boric acid solution with a mass content $w \approx 5$ %, dissolve 55 g of boric acid in 1 000 ml warm water (5.2.7) and let the solution cool down to room temperature.

5.2.10 Chemical blank solution for digestion

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). Fill up to 1 000 ml with water (5.2.7), and mix well. Transfer the mixture to a 1 000 ml storage bottle. Mark it ”chemical blank” and add any other relevant information (date etc.).

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

5.2.11 Rinsing acid

HNO_3, mass content $w \approx 25$ %, for rinsing the digestion equipment. Thoroughly mix about 275 ml of HNO_3 (5.2.5) with 300 ml of water (5.2.7) and make up to 1 l with water (5.2.7).

5.2.12 Standard solutions

These are to contain the specific elements to be determined with β(element) = 1 g/l; pH ≤ 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 Gases

These gases will depend on the chosen analytical technique and will be described in the manufacturer's operating instructions.

6 Sampling equipment

6.1 General requirements

The sampling equipment consists of:

- a temperature controlled sampling probe with the entry nozzle;

- a filter housing with filter support and filter

  The filter housing may be located either:

  – in the duct or chimney, mounted directly behind the entry nozzle (in-stack filtration); or

  – outside the duct or chimney, 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 13284-1:2001.

Only the additional specific requirements for the sampling of total specific elements are stated here.

Two types of absorber systems may be employed, a so-called 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 5.1.2.

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 13284-1:2001.

6.3 Absorbers

For an efficient absorption of gaseous phase metals, three absorbers shall be placed in series. The analytical procedures and/or sampling procedures shall be arranged in such a way that the detection limit for each element should be at least 1 µg/m³. If the element mass concentration of the third absorber is more than 10 % of the total concentration in the sampled gas for one or more elements then the overall result shall be rejected.

7 Cleaning of the sampling equipment prior to sampling

Those parts of the sampling train being in contact with the sampled gas 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).

Some examples of cleaning procedures are given in annex C.

8 Procedure

8.1 General requirements

The sampling shall be performed according to EN 13284-1:2001. This includes the procedure of the representative grid sampling, as well as maintaining isokinetism.

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 above the flue gas temperature, or 20 K above the dew point, whichever is the highest.

The sampling time shall meet legal or other regulatory requirements.

NOTE The sample volume taken should be sufficient to meet the required detection limit. 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 support or filter casetts are available the filters can be mounted in the filter housings in the laboratory, so that at the sampling site only the filter housings have to be changed.

8.2.2 Nozzle installation

The appropriate nozzle diameter shall be determined according to EN 13284-1:2001 and the nozzle 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.

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 have to be taken to avoid injury to persons and/or damage to the equipment in the event of breakage or leakage of the absorbers.

NOTE If there is a great amount of condensate, an empty absorber may be useful upstream of the first absorber filled with the absorption solution.

8.2.4 Leak test

Before each sampling the complete sampling train shall be leak tested.

WARNING Care has to be taken that no reflux of sorption solution towards the probe occurs.

This shall be done in one of the following three ways (other methods may be used, if they give equivalent results):

8.2.4.1 Method A

a) Assemble the complete sampler system, including charging the filter holder and absorbers;

b) Allow the sampler to warm up to its operating temperature;

c) Seal the nozzle inlet; close the nozzle and switch on the pump(s);

d) After reaching minimum pressure read the flow rate;

e) The leakage rate L_{per} shall not exceed 0,02 (2 %);

f) If the leak exceeds the criterion then check the system and locate the leak;

g) Repeat the leak test procedure until the criterion is satisfied.

8.2.4.2 Method B

a) Assemble the complete sampler system, including charging the filter holder and absorbers;

b) Allow the sampler to warm up to its operating temperature;

c) Seal the nozzle inlet;

d) Evacuate the sampling train to a low pressure of about 50 kPa to 75 kPa; the pressure should be nearly equivalent to that of the sampling;

e) Shut off the sampling train in front of the pump, note the pressure;

f) Read the pressure in the sampling train after 1 min;

g) Calculate the leak flow rate according to Equation (1)

$$\frac{\Delta p_{obs}}{\Delta t} = \frac{p_2 - p_1}{\Delta t} \qquad (1)$$

$$\frac{\Delta p_{per}}{\Delta t} = \frac{L_{per}}{V_{\mathrm{int}}} \cdot Q \cdot p_{amb} \qquad (1a)$$

where

Δp_{obs}	is the pressure increase, in kilopascals per minute (kPa/min)
p_1	is the pressure in the sampling train at time 0; step e – in kilopascals
p_2	is the pressure in the sampling train at time 1 – after 1 min; step f – in kilopascals
Δp_{per}	is the permitted maximum pressure increase
p_{amb}	is the ambient pressure in kilopascals
L_{per}	is the rate (100 % = 1) of permitted leakage of the sampling train
V_{int}	is the internal volume of the sampling train in litres
Q	is the flow rate anticipated for sampling in l/min

h) Compare the result Δp_{obs} with the respective curve in Figure 1 or the calculated Δp_{per}. ($\Delta p_{obs} \leq \Delta p_{per}$)

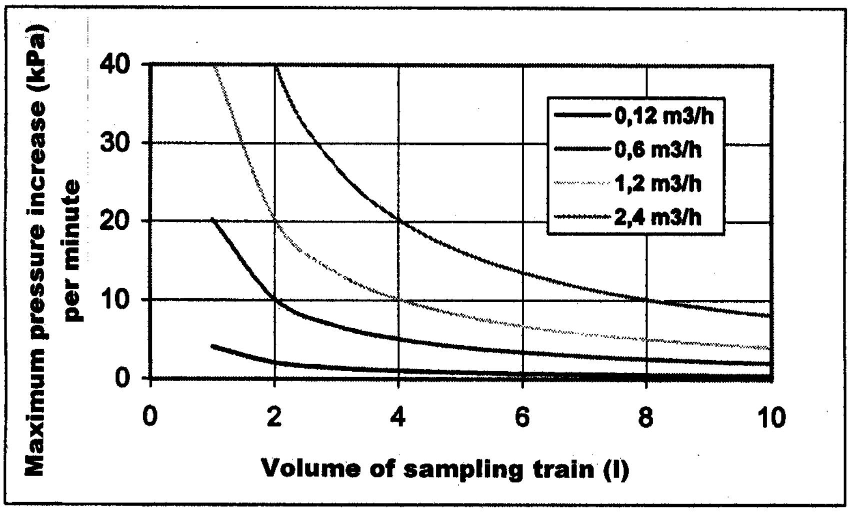


Figure 1 — Maximum allowable pressure increase per minute during a leak test at a leak of 2 %

EXAMPLE

internal volume of the sampling train	$V_{int} = 8\ l$
suction rate during sampling	$Q = 2{,}4\ \text{m}^3/\text{h}$ $= 40\ l/\text{min}$
minimum pressure during sampling	$p_1 = 50\ \text{kPa}$
pressure after sampling	$P_2 = 58\ \text{kPa}$
permitted leakage	$L_{per} = 0{,}02\ (2\ \%)$
ambient pressure	$p_{\text{amb}} = 102\ \text{kPa}$

Inserting these values into equations (1 and 1a) results in the permitted maximum pressure increase

$$\frac{\Delta p_{obs}}{\Delta t} = \frac{58 - 50\ kPa}{1\,\text{min}} = 8\ kPa/\text{min} \tag{2}$$

$$\frac{\Delta p_{per}}{\Delta t}\left(\frac{0{,}02}{8}\right)\cdot 40 \cdot 102 = 10\ kPa/\text{min} \tag{2a}$$

Leaktest is successful $\frac{\Delta p_{obs}}{\Delta t} \leq \frac{\Delta p_{per}}{\Delta t}$

i) If the leak exceeds the criterion then check the system and locate the leak;

j) Repeat the leak test procedure until the criterion is satisfied.

8.2.4.3 Method C

a) Assemble the complete sampler system, including charging the filter holder and absorbers;

b) Allow the sampler to warm up to its operating temperature;

c) Seal the nozzle inlet;

d) Open the by-pass valve, ensuring the main valve is closed. Switch on the sampling pump and slowly open the main valve. Once the main valve is fully open, slowly close the by-pass valve until the vacuum gauge reads about 50 kPa or the pressure drops to that expected during normal operations;

e) Allow the sampler to evacuate the system for 1 min;

f) Observe the dry gas meter and, using a stopwatch, note any movement of the meter over a period of no less than 1 min. The leak flow rate shall not exceed 0,02 (2 %) of the nominal sample gas flow rate, expected through the meter(s);

g) If the leak exceeds the criterion then check the system and locate the leak;

h) Repeat the leak test procedure until the criterion is satisfied.

8.2.5 Installation of equipment at chimney or duct

Install the completely mounted sampling equipment which has been leak proved and heated into the sampling port at the chimney or flue gas duct. Avoid back flow of absorption liquid into the sampling equipment in the case of low pressure in the chimney or duct. Ensure the sample nozzle entrance is in the same direction as the gas stream.

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

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

8.3 Performance of the sampling

Ensure the sampling equipment has reached the prescribed operating temperature range. Record the gas volume meters, rotate the probe so that the nozzle is facing the gas stream and start the measurement by extracting the flue gas from the duct. Note the start time. Record the pressure and the temperature at the gas volume meter(s). The relative deviation from the nominal flow rate value shall be in accordance with EN 13284-1:2001. During sampling, check at least every 5 min and adjust the flow rate for isokinetic sampling within – 5 % and + 15 %. Continuously monitor, or record at least every 5 min, the dynamic pressure measured by the Pitot tube or another suitable measurement system either installed at the fixed point or mounted on the sampling equipment.

Check the isokinetism at least once for each sampling point and adjust if necessary. Perform isokinetic and grid sampling according to EN 13284-1:2001.

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 sampling and note the time. Record the gas volume meters and the ambient pressure.

8.4 Disassembling the equipment

Disengage the complete sampling equipment from the chimney or flue gas duct. Disassemble the filter housing and absorbers.

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

8.4.1 Disassembling 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.

NOTE 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.

8.4.2 Rinsing of the sampling equipment

Rinse the nozzle, probe and filter housing after each measurement with rinsing acid (5.2.11). 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.

Rinse the nozzle, probe (inner tube) and filter housing with water (5.2.7) acetone (5.2.22) and let dry.

8.4.3 Rinsing of the connection tubing to the first absorber

After each measurement rinse the connection tubing (between the filter housing and the first absorber) into the first absorber with rinsing acid (5.2.11).

8.4.4 Handling of the absorption solutions from the absorbers

The content of all absorbers but the last one may be combined. The separate storage of the content of the last absorber shall be used for the control of the sufficient absorption efficiency.

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

Determine and record the weight or volume of the liquid. This may be performed directly on-site or afterwards.

NOTE The volume can be determined by filling the storage bottle to a constant and known volume.

WARNING Take special care during the rinsing of absorbers with fritted gas dividers. As absorption liquid is not easily rinsed from these devices, then rinsing needs to be thorough.

8.5 Field blanks

To check the procedure, for each campaign, at least one field blank shall be taken at site at each duct or chimney by the following procedures given in 8.2.1, 8.2.2, 8.2.3 and 8.4, but no flue gas shall be extracted from the chimney or flue gas duct. Filter, rinsing solutions and absorption solutions shall be collected for analyzing. Where multiple ducts are required to be sampled within a sampling campaign, the conditions at the different working environments shall be noted. Additional field blanks per sampling campaign can be required if the environmental conditions on site differ significantly between sampling locations If the result of the field blank is more than 10 % of the set regulatory emission value then the results of the corresponding part of the campaign shall be rejected.

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

8.6 Requirements for storage of the samples

Liquid samples are to be stored in PE bottles at a temperature of below 6 °C (e.g. in a refrigerator) (see also the warning in 8.2.3).

The liquid samples shall be analysed within two weeks after sampling.

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 8.7.2 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 analyzed separately.

8.7.2 Pre-cleaning of the digestion equipment

After cleaning in a laboratory dishwasher, 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 GLP (Good Laboratory Practice) procedure may be applicable.

8.7.3 Treatment of CRM and filter

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.

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 actual figures differ significantly from these values, the amounts of acids have to be changed proportionally.

CRM shall be digested together with an equivalent amount of the filter material following the same procedures as described for the filters. Due to the fact that for CRM's a minimum of 50 mg shall be used, five vessels, each with 1 filter and about 1/5 of the CRM, shall be digested and after that liquids shall be combined and made up to 500 ml. This is defined as the calibration control solution.

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

8.7.3.1 General procedure

a) Transfer the filter from the transport case (see 8.4.1) to the PTFE vessel. For this procedure a pair of tweezers (titanium, gold or plastic coated) shall be used. The filter may be folded some times 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 m*l* of HNO_3 (5.2.5) to the PTFE vessel;

e) Add 2,0 m*l* of HF (5.2.3) to the PTFE vessel. The filter has to 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 8.7.3.2. If a microwave oven is used go to 8.7.3.3.

8.7.3.2 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 20 ml of H_3BO_3 (5.2.9);

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. Fill up with water and mix well.

   For expected low concentrations in the filter a 50 ml volumetric flask may be used instead of a 100 m*l* flask;

f) (Optional) Transfer the digestion to a 100 ml storage bottle;

g) Mark the bottle with filter identification number etc.;

h) The digestion is now ready for analysis.

8.7.3.3 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 has to be changed accordingly, and as described by the manufacturer of the microwave oven.

a) Place the closed PTFE vessel in the microwave oven, and heat it according to the internal heating program, which should fulfil the minimum requirements given below:
   Minimum power used (in any part of the procedure): 800 W
   Minimum heating duration (excluding time without heating): 15 min at or above 200 °C;

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 20 ml of H_3BO_3 (5.2.9);

c) Place the closed PTFE vessel in the microwave oven and heat it again for 10 min;

d) Take out the PFTE vessel, and let it cool to room temperature. Open the PTFE vessel carefully and transfer the liquid quantitatively to a 100 ml volumetric flask;

e) Wash the inside of the PTFE vessel several times with water, and add it to the volumetric flask. Make up with water and mix well.

   For expected low concentrations in the filter a 50 ml volumetric flask may be used instead of a 100 ml flask;

f) Optional) Transfer the digestion to a 100 ml storage bottle;

g) Mark the bottle with filter identification number etc.

The digestion is now ready for analysis.

8.7.4 Pre-treatment of absorption solutions

It is not necessary to pre-treat the absorption solutions, expect that they have to be diluted with water to a known volume, or the volume has to be measured. Take a sub-sample and analyse according to 8.8.

8.7.5 Pre-treatment of rinsing solutions

The rinsing solutions are treated before digestion according to the following procedure:

a) Verify that the pH of the sample is 2 or lower. If it is not, acidify the samples by careful addition (with stirring) of concentrated HNO_3 (5.2.5) to pH ≈ 2;

b) Use water to rinse the sample into a beaker, and cover it with a ribbed watch glass;

c) Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling;

d) Digest the sample by quantitatively transferring the sample to the PTFE vessel, and carefully adding 3 ml of HNO_3 and 2 m*l* of HF;

e) Follow the procedures given in 8.7.3.2 or 8.7.3.3.

NOTE If the probe rinse is analysed together with the filter, both digestion solutions are mixed.

8.8 Analysis

The instrument (e.g. AAS, ICP-OES, ICP-MS) to be used to measure the samples should be checked for sensitivity, interference effects, linearity, detection limits and performance prior to measurement of the samples. Dilute samples as appropriate for the measurement equipment to be used.

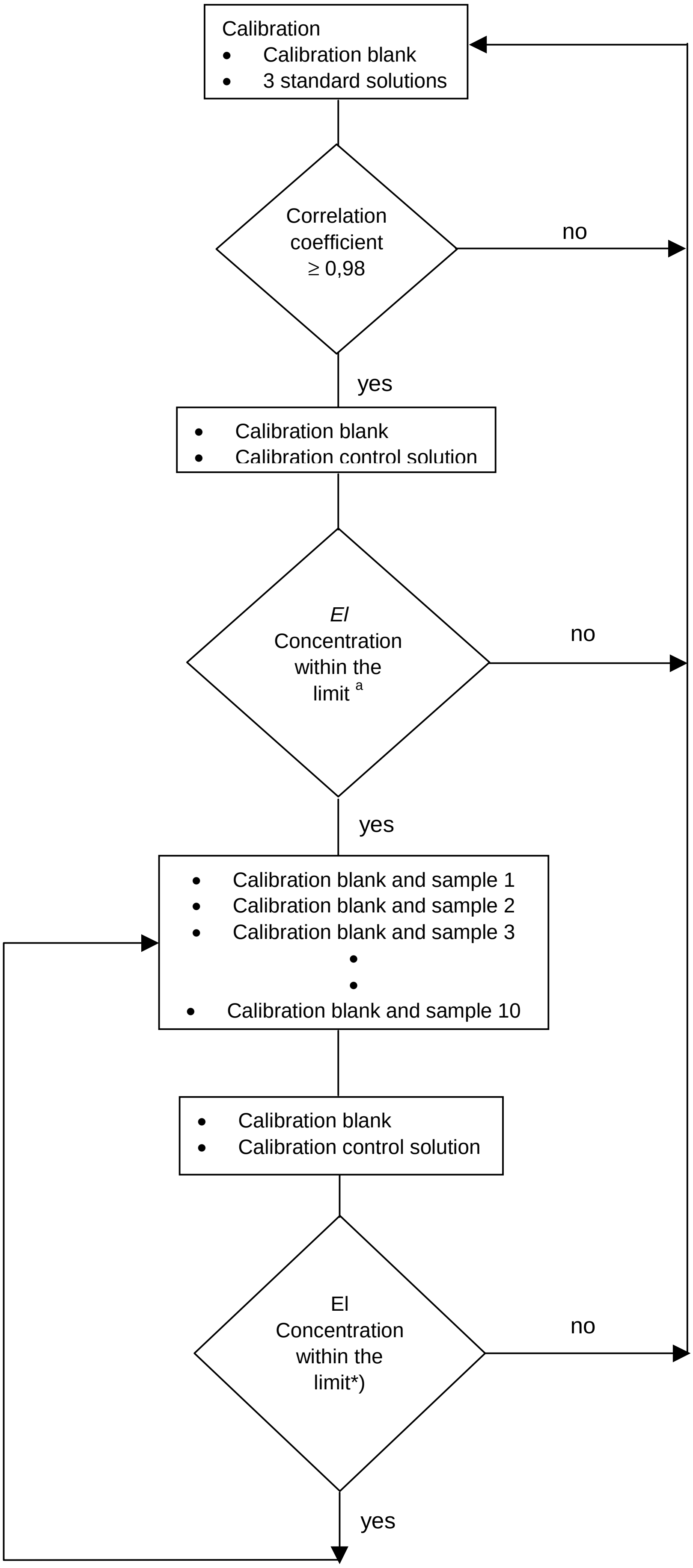
Prepare a series of calibration standards (preferably 3 standards and a calibration blank) in a suitable concentration range for the measurement equipment to be used and to cover the expected concentration range of elements to be measured. (see figure 2). The normal calibration range should be 0 to 250 µg/l. The standards should be prepared by diluting commercial available multi-element standards. The correlation coefficient of the calibration line shall be at least 0,98. If not, correct the problem and recalibrate.

The calibration line should be checked with a calibration control solution, prepared from the CRM material as described in 8.7.3. This solution is made from certified reference material which should have the same matrix as the samples. The concentrations of the elements in the calibration control solution should be in the upper half of the calibration range. Check the calibration line first with the blank solution and then run the calibration control solution. The measured concentrations of the elements of the calibration control solution shall not differ more than 10 % from the certified value or shall be within twice the uncertainty value quoted with the documentation provided with the CRM, depending on which value is higher. If not, correct the problem and re-analyse.

Start measuring the samples. After each 5th measurement run the blank solution to prevent contamination. The calibration control solution should be measured frequently (e.g. after 10 sample measurements) to check the instrument drift. If the results of the calibration control solution are not within 10 % of the certified values correct the problem. If necessary, recalibrate the instrument and re-analyse the samples, starting from the last determination when the drift was within the 10 % limit (see previous paragraph).

Follow the instructions provided by the manufacturer of the particular instrument.

Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects shall be investigated and established for each individual analyte line on that particular instrument.



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[a] The mean concentrations of the elements shall not differ more than 10 % from the certified value or shall be within twice the uncertainty value quoted with the documentation provided with the CRM, depending on which value is higher.

Figure 2 — Flowchart of the analytical procedure

9 Expression of results

9.1 Calculation

9.1.1 Gas volume at standard conditions

The conversion of the gas volume at measuring conditions to the volume at standard conditions is performed according to equation (2) by:

$$V_0 = V_{\text{mes}} \cdot \frac{T_0}{T_{\text{mes}}} \cdot \frac{p_{\text{mes}}}{p_0} \tag{2}$$

Abbreviations see 3.3.

NOTE From now on only volumes at standard conditions are used.

9.1.2 Total element content

The total mass concentration for each element in the flue gases is calculated as follows.

1) For the **side-stream arrangement** of the sampling equipment see equation (3):

$$\beta_{\text{El}} = \frac{m_{\text{El,sol}}}{V_{\text{main}} + V_{\text{side}}} + \frac{m_{\text{El,gas}}}{V_{\text{side}}} \tag{3}$$

where

$m_{\text{El,sol}}$	is the sum of the specific elements from the rinsing(s) of the main stream part of the sampling train and from the filter,
$m_{\text{El,gas}}$	is the sum of the specific elements from the rinsing(s) of the side stream part of the sampling train and from the absorbers:

2) For the **main-stream arrangement** of the sampling equipment use equation (4):

$$\beta_{\text{El}} = \frac{m_{\text{El,sol}} + m_{\text{El,gas}}}{V_{\text{main}}} \tag{4}$$

where

$m_{\text{El,gas}}$	is the sum of the specific elements from the rinsing(s) and from the absorbers.

9.1.3 Normalization to the dry oxygen content with a volume fraction of 11 %

For the comparison of the measured total mass concentration with the limit values of the corresponding EU incineration directive [1], the results of expressions (3) and (4) respectively have to be normalized to the dry oxygen content given in the directive. The normalized total mass concentrations of any element El_{norm} is calculated using Equation 5, where El is the measured total mass concentration, O_{mes} is the measured mean day oxygen content (volume content) during the sampling time and 11 is the dry oxygen content given in the directive for reporting normalized results.

$$\beta_{El_{\text{norm}}} = \frac{21-11}{21-0_{\text{mes}}} \cdot \beta_{El} \tag{5}$$

9.2 Performance characteristics

9.2.1 General

Many different sampling and analytical procedures were applied throughout Europe before the working group started. On the basis of four widely accepted sampling methods and two commonly employed analytical procedures for the measurement of metals and metalloids in very low concentrations pre-tests in different laboratories and preliminary tests at a plant are carried out. Following the results a sampling and analytical procedure and also a measuring plan for a field test have been drafted. With respect to the varying analytical equipment in the European laboratories and the detection limits necessary the full range from AAS through ICP-OES to ICP-MS should be allowed.

A very good waste incineration plant with low emissions would not be suitable because the measured values would be below the detection limits, so there would be difficulties to get reliable data with respect to performance characteristics. Another very important difficulty in defining an appropriate plant was the necessity for the presence of at least four sampling ports in the same cross-section of the duct; also this had to be in conjunction with a platform with enough space to accommodate four sampling trains and sampling teams. With respect to this it was very difficult to find a suitable plant with sufficiently high emissions for all the single metals and metalloids. In May 1998 a first series of field tests was carried out at a municipal incineration plant with different laboratories from six European countries. The trials to raise the emissions during the field test failed and therefore a lot of results lower than the detection limit occurred. The field test shows that the sampling methods yielded comparable results at the target concentration.

Having demonstrated applicability of the Standard, the working group then organized a second field validation trial whose aim was to confirm the repeatability standard deviation and the interlaboratory standard deviation of the methods (reproducibility). These validation measurements aimed to validate all of the sampling, extraction, clean-up, identification and quantification minimum requirements. After a long and time consuming search for a suitable plant the second validation trail was performed in June 2000. But unfortunately also at that plant the emissions during the field test were much lower than at the pre-test.

Also at that plant it was not possible to perform parallel double measurements with all four teams simultaneously due to space restrictions at the duct. As before, measurements were carried out in such a way that on two different days two different measuring teams performed double measurements and on two other days all four teams performed parallel single measurements.

The samples taken consisted of absorption solutions, dust filters and rinsings. The samples taken by the individual measuring teams were analysed at their own laboratories for the content of As, Cd, Cr, Co, Cu, Mn, Pb, Ni, Sb, Tl and V. The detailed results from the sampling and analysis and the calculations of the repeatability and reproducibility from both tests, are stated in separate reports (CEN/TC 264/WG 10 N 172 and N 173 [2]), taking into account ISO 5725-2.

The concentration levels for most of the elements in the waste gases during the tests were low. Due to this, a large number of results are below the detection limits of analysis. In order to avoid rejection of too many results for the calculation of repeatability and reproducibility, the working group has decided to perform calculations using values which are equal to half of the detection limit according to Resolution 59 of the working group, i.e.:

"WG 10 decides that for the report if the sample values or blank values are smaller than the detection limit, then the value of ½ detection limit is to be taken for calculation. If both the sample value and the blank value are below the detection limit then for calculation purposes the value shall be taken of ½ detection limit, but it should be understood that, the true value lies between 0 and the detection limit."

The regulator should give a clear instruction with respect to this item because this is not only essential for these pollutants but also for others e.g. like dioxins etc.

The repeatability has been calculated from the standard deviation of the results of the double measurements. The reproducibility has been calculated from the results of the parallel single measurements. Detection limits are in general fixed values for a certain amount of a (sub-) sample (e.g. amount of liquid in the absorber or the amount of filter material). Even when the concentration in the samples varies below the detection limit, the reported values will be the same (fixed) value. This implies that theoretically the repeatability will be zero. But in the field tests the detection limits are differing to more than factor 10, for a lot of elements more than factor 100. Therefore the reported repeatability should be greater than the reality.

The reproducibility is influenced in another way. This is illustrated by the following example. If teams A and B report true values for a sample and teams C and D report values below their detection limit, then the reproducibility will give higher values than if teams C and D would have lower detection limits and also report true values. The calculated reproducibility tends thus to a maximum value. Therefore the reported repeatability and reproducibility, given in tables D.2 and D.3, resulting from these calculations are, however, biased and shall be used only as indicative values.

In pre-tests the efficiency of the digestion and the performance of the analytical procedures were determined (see tables E.1 and E.2). The same solid mixture used in the pre-tests was to be analyzed from each team during the field tests (see table E.3). The calculated standard deviations of these results were helpful for estimating the repeatability and reproducibility for the whole process.

9.2.2 Pre-treatment and analysis

The analysis results strongly depend on the digestion quality, i.e. both the acids used (HF/HNO_3, HNO_3) and the ways of heating (microwave, oven, heating plate) influence the measurement results. Therefore, the procedures given in 8.7 and 8.8 shall strictly be followed.

9.2.3 Absorption efficiency

The absorption efficiencies for the different specific elements (see table D.1) depend on neither the element nor the type of sampling system arrangement (main-stream or side-stream). At concentrations above the detection limit the absorption efficiencies in most cases are better than 80 %. There is no correction to 100 % by calculation.

9.2.4 Detection limit

As given in 6.3 the analytical procedure and the volume sampled shall be arranged in such a way that the detection limit for each element, and each part of the sampling equipment, should be at least 1 µg/m^3. This would result in a detection limit for the whole sampling train of 5 µg/m^3.

This requirement corresponds with the monitoring of limit values of 0,05 mg/m^3 (for the sum of Cd and Tl) and 0,5 mg/m^3 (for the sum of As, Pb, Cr, Co, Cu, Mn, Ni and V) within the Directive on Hazardous Waste Incineration [3] and on Waste Incineration [1].

9.2.5 Repeatability and reproducibility

As discussed earlier, the results from the field tests given in tables D.2 and D.3 are reflecting the difficulties from very low metal concentrations and using two analytical methods with detection limits differing more than a factor of 10, often 100. Following the results from pre-tests and from analyzing the standard mixture during the field tests (see table E.3) for elements significantly above the detection limit repeatability and reproducibility should be between 30 % and 100 %.

10 Test report

The test report should include at least the following information:

a) reference to this European Standard;

b) identification and number of sample(s);

c) description of the plant and process;

d) plant operating conditions;

e) description of each sampling location;

f) number of sampling points in the sampling plane at each sampling location;

g) isokinetic/non-isokinetic sampling (performance of sampling (e.g. velocity in the duct, velocity at the entrance of the nozzle));

h) sampling time;

i) sampling volume(s);

j) isokinetism (results of sampling);

k) type of filter;

l) type of absorbers;

m) limits of detection;

n) type of absorption solution;

o) analysis procedure (reduction agent, manual or flow injection);

p) blank values;

q) total content of each element;

r) mass and concentration percentage of each element in the third absorber;

s) data for the performance characteristics in relation to the emission limit value (see 9.2.5);

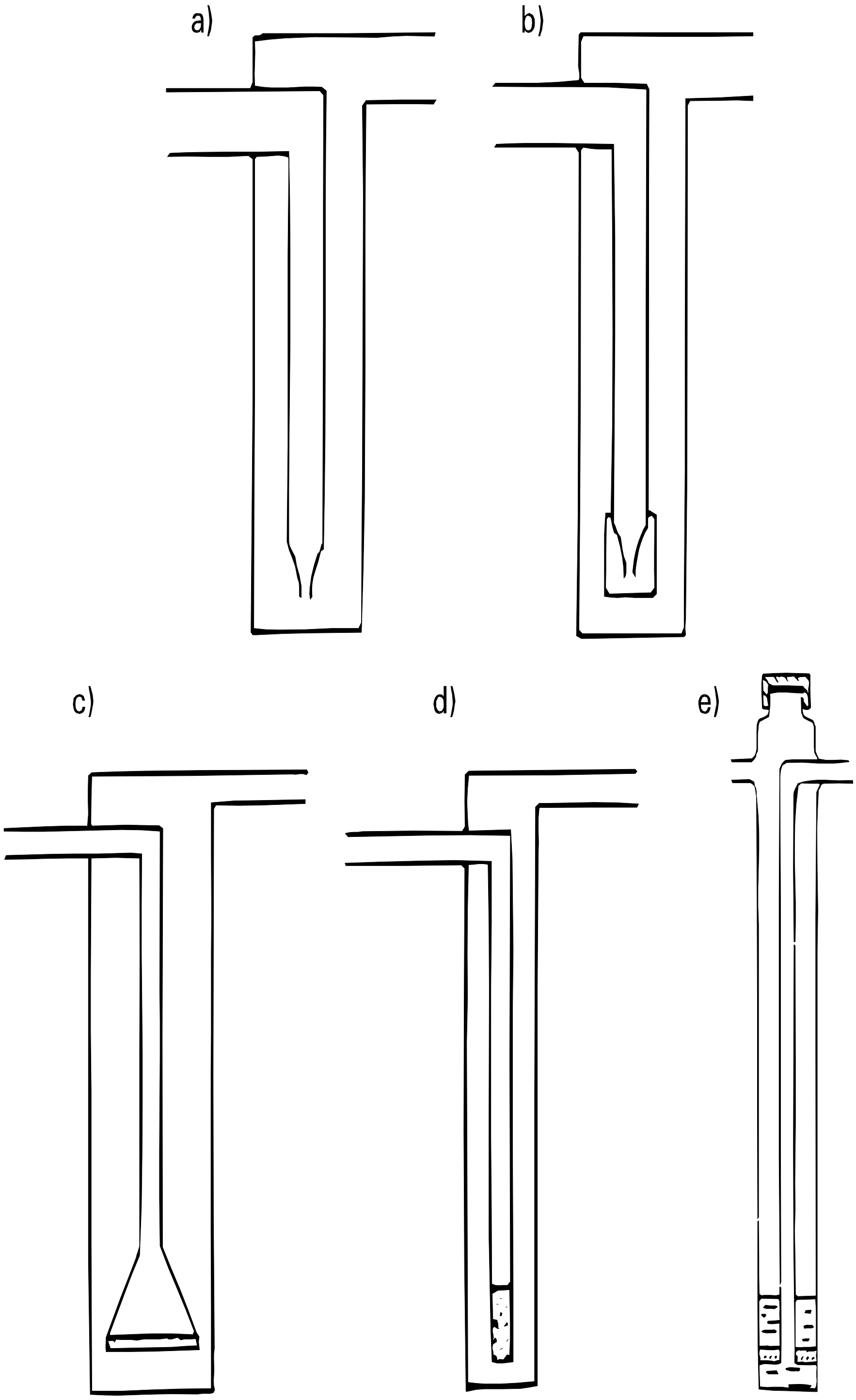
t) any deviations from this European Standard.

In case that additional QA/QC are obligatory in some member countries, these shall be considered.

Annex A
(informative)

Examples of absorption vessels

For high absorption efficiency it is advisable to distribute the gas stream in the absorption liquid as homogeneously as possible and have reasonably long contact time between gas and liquid. The absorption liquid is not carried over to the next absorber by the gas stream. In practice, sufficient free space should be present above the absorber liquid to avoid liquid transfer. This free space will also break down any foam which can be formed while the gas is bubbling through the liquid.



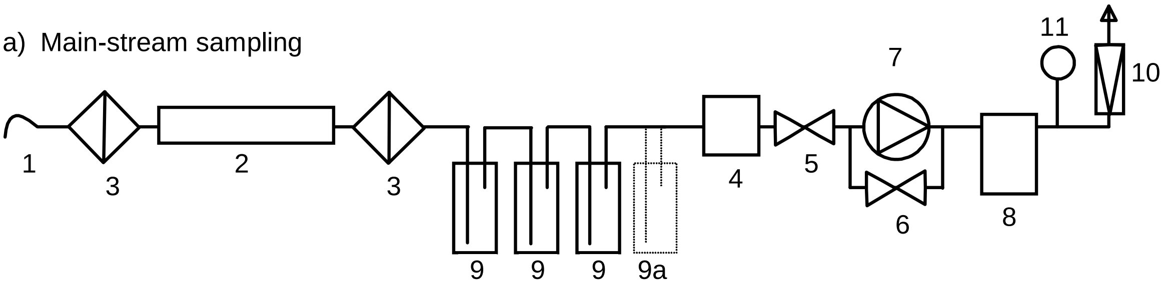
a) Midget impinger	Q ≈ 0,5 to 2 m^3/h
b) Greenburg-Smith impinger	Q ≈ 0,5 to 2 m^3/h
c)-e) fritted bubblers	Q ≈ 0,03 to 0,18 m^3/h (= 0,5 to 3 *l*/min)

Figure A.1 – Examples of impingers and fritted bubblers

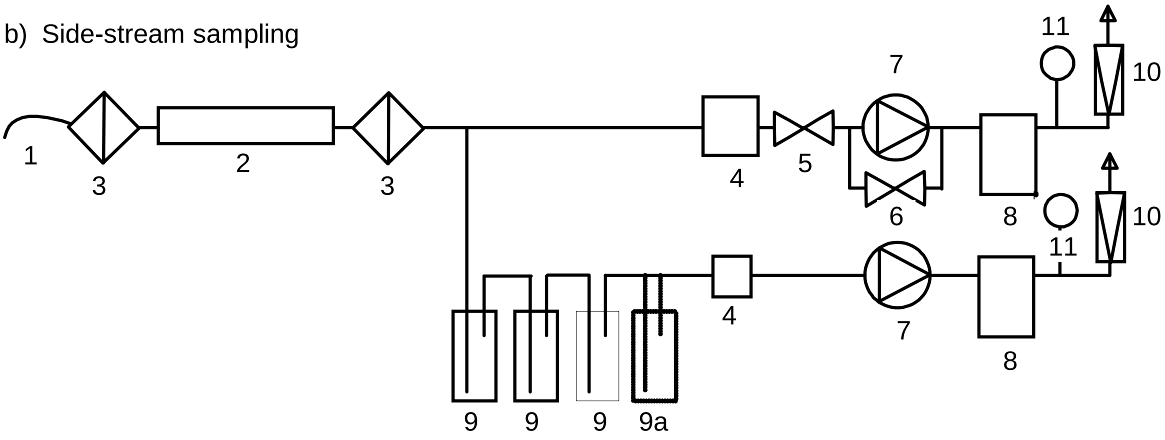
Annex B
(informative)

Types of isokinetic equipment

a) Main-stream sampling



b) Side-stream sampling



Key

1	Nozzle
2	Probe
3	Filter (either behind or in front of the probe)
4	Dryer
5	Main-stream valve
6	By-pass valve
7	Pump
8	Gas volume meter
9	absorber
9a	Safety bottle (optional)
10	Gas flow meter
11	Temperature and pressure measurement

Figure B.1 – Examples for isokinetic sampling equipment

Annex C
(informative)

Pre-cleaning procedures of the sampling equipment at the laboratory and determination of the absorption efficiency

The pre-cleaning shall be done in the laboratory according to good laboratory practice (GLP). In clauses C.1 and C.2 some possibilities are given for cleaning the equipment, washing and storage bottles.

C.1 Chemicals

The grade of purity of the chemicals is described in 5.2.

C.1.1 Rinsing solution

Prepare a mixture from equal volumes of nitric acid (5.2.5) and hydrogen peroxide (5.2.4) and dilute one volume part of this mixture with nine volume parts of water (5.2.7). This results in mass contents $w(HNO_3) \approx 4,5$ % and $w(H_2O_2) \approx 1,7$ %.

C.1.2 Aqua regia

Carefully mix three volume parts of hydrochloric acid (5.2.6) with one volume part of nitric acid (5.2.5). This solution is diluted with the same volume of water (5.2.7). This results in mass contents $w(HNO_3) \approx 11$ % and $w(HCl) \approx 15$ %.

C.1.3 Laboratory cleaning solution

Dilute nitric acid, HNO_3, mass content $w \approx 10$ %; for pre-cleaning those parts of the sampling equipment which come in contact with the sample gas. Thoroughly mix about 150 ml of HNO_3 (5.2.5) with 500 ml of water (5.2.7) and make up to 1 l with water (5.2.7).

C.1.4 Dilute hydrogen peroxide

H_2O_2; mass content $w \approx 3$ %. Thoroughly mix about 90 ml of H_2O_2 (5.2.4) with 500 ml of water (5.2.7) and make up to 1 l with water (5.2.7)

C.1.5 Rinsing acid

HNO_3, mass content $w \approx 25$ %, for rinsing the digestion equipment. Thoroughly mix about 275 ml of HNO_3 (5.2.5) with 300 ml of water (5.2.7) and make up to 1 l with water (5.2.7).

C.2 Equipment

C.2.1 Procedure A

The **nozzle**, **probe** (inner tube) and the **filter housing** are cleaned by circulating rinsing solution (C.1.1) for about 15 min at room temperature.

C.2.2 Procedure B

C.2.2.1 Filter housing

- Coarse cleaning in ultrasonic bath if necessary and drying;

- Rinse with laboratory cleaning solution (C.1.3) and water (5.2.7) and dry.

C.2.2.2 Probe, nozzle

- Circulate laboratory cleaning solution (C.1.3) for 1 h at room temperature and 10 min at 60 °C;
- Rinse with water (5.2.7);
- Dry with clean particle free air.

C.2.3 Procedure C

Any other GLP (Good Laboratory Practice) cleaning procedure.

C.3 Absorption and storage bottles

C.3.1 Procedure A

The **bottles** are rinsed with dilute hydrogen peroxide (C.1.4) and in an ultrasonic bath, if necessary.

C.3.2 Procedure B

- Coarse cleaning and rinsing with water (5.2.7);
- Fill bottles with aqua regiae (C.1.2) and leave them for one day;
- Pour out the aqua regiae and fill the bottles with water (5.2.7);
- Rinse bottles and frits with water (5.2.7);
- Dry the bottles.

C.3.3 Procedure C

- Fill the machine washed bottles with rinsing acid (C.1.5) over the sinter level;
- Shake the bottles;
- Shake the bottles again;
- Leave overnight at room temperature;
- Rinse the bottles with water (5.2.7);
- Repeat the procedure once;
- Dry the bottles in an oven at 110°C.

C.3.4 Procedure D

Any other GLP (good laboratory practice) cleaning procedure.

C.4 Determination of the absorption efficiency

The absorption efficiency is determined according to Equation C.1.

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

Annex D
(informative)

Measurement results of two field tests

D.1 Absorption efficiency

The absorption efficiencies in the bottles for the different specific elements established during field tests (see Table D.1) depend on neither the element nor the type of sampling system arrangement (main-stream or side-stream). They are generally relatively low and lie in the range between 39 % and 91 %. There is no correction to 100 % by calculation. The data of table D.1 consider only the absorption efficiency ratio of the metal content within the bottles; this absorption efficiency is not identical to the one mentioned in 9.2 and clause C.4.

Table D.1 — Mean values of the absorption efficiencies (fractions of elements in bottles 1 and 2, expressed as % of content of all three bottles)

	Team A		Team B		Team C		Team D	
Element	1. Field Test	2. Field Test	1. Field Test	2. Field Test	1. Field Test	2. Field Test	1. Field Test	2. Field Test
As	[a]	[a]	[a]	71	70	[a]	[a]	[a]
Cd	80	[a]	56	86	54	[a]	61	[a]
Co	[a]	[a]	65	80	51	[a]	[a]	[a]
Cr	91	79	55	52	71	[a]	[a]	[a]
Cu	69	77	75	66	63	[a]	[a]	66
Mn	80	78	66	66	65	[a]	[a]	[a]
Ni	69	71	[a]	72	57	71	[a]	[a]
Pb	69	79	65	89	47	76	70	[a]
Sb	[a]	80	69	76	64	87	[a]	[a]
Tl	[a]	[a]	39	[a]	[a]	[a]	[a]	[a]
V	[a]	86	83	69	85	[a]	[a]	[a]

[a] predominant results of the first two and the third bottle near or respectively below the detection limit

D.2 Repeatability

The repeatabilities have been calculated from the results of 12 double measurements of two respectively four teams during two interlaboratory field tests at two different waste incinerators. The results are shown in table D.2.

Table D.2 — Repeatability

First field test								
Element	Concentration		Number of Teams	Number of double measurements	Repeatability Standard Deviation	95 % Confidence Interval	Repeatability	
	range	average						
	µg/m³	µg/m³			µg/m³	µg/m³	µg/m³	%
As	1,6 to 10	5,3	2	12	1,6	3,4	4,8	91
Cd	0,35 to 5,2	2,9	2	10	0,75	1,7	2,4	81
Co	0,11 to 0,82	0,4	2	10	0,17	0,37	0,52	130
Cr	2,0 to 26	7,6	2	10	5,8	13	18	239
Cu	0,5 to 58	13	2	10	11	25	35	271
Mn	1,5 to 11	4,7	2	10	2,7	5,9	8,4	179
Ni	0,98 to 41	7,8	2	10	12	25	36	459
Pb	5,6 to 77	44	2	12	19	41	57	130
Sb	1,1 to 21	7,5	2	10	5,2	11	16	216
Tl	0,10 to 9,3	1,7	2	10	2,9	6,4	9,1	532
V	0,65 to 6,1	1,9	2	10	0,92	2,1	2,9	153
Second field test								
Element	Concentration range	average	Number of Teams	Number of double measurements	Repeatability Standard Deviation	95 % Confidence Interval	Repeatability	
	µg/m³	µg/m³			µg/m³	µg/m³	µg/m³	%
As	0,01 to 4,1	1,6	4	22	0,19	0,40	0,56	35
Cd	5,6 to 61	17	4	16	3,6	7,8	11	65
Co	0,01 to 2,8	1,1	4	22	0,23	0,47	0,66	60
Cr	1,3 to 42	7,7	4	22	5,8	12	17	221
Cu	14 to 95	53	4	16	5,8	12	17	32
Mn	1,4 to 21	5,8	4	22	3,7	7,8	11	190
Ni	1,0 to 9,8	3,9	2	11	1,2	2,5	3,6	92
Pb	143 to 820	378	4	21	33	67	95	25
Sb	3,4 to 45	17	4	22	5,7	12	17	100
Tl	0,01 to 42	10	4	22	1,7	3,6	5,1	51
V	0,09 to 8,7	2,0	4	22	1,2	2,4	3,4	170

D.3 Reproducibility

The reproducibilities have been calculated from the results of 12 repeated parallel measurements of four teams during two interlaboratory field tests at two different waste incinerators. The results are shown in table D.3.

Table D.3 – Reproducibility

First field test								
Element	Concentration		Number of Teams	Number of double measurements	Reproducibility Standard Deviation	95 % Confidence Interval	Reproducibility	
	Range	Average						
	$\mu g/m^3$	$\mu g/m^3$			$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	%
As	0,06 to 13	3,2	4	47	4,7	9,4	13	416
Cd	0,86 to 6,0	2,9	4	45	1,1	2,3	3,2	110
Co	0,15 to 3,37	0,4	4	45	0,60	1,3	1,8	450
Cr	1,3 to 13	3,4	4	45	2,7	5,4	7,6	224
Cu	3,7 to 38	11	4	45	5,8	12	16	149
Mn	2,4 to 8,3	4,0	4	45	1,1	2,1	3,0	75
Ni	0,85 to 11	2,8	4	47	2,0	3,9	5,5	196
Pb	6 to 73	47	4	46	12	24	34	73
Sb	0,48 to 16	5,8	4	45	2,8	5,5	7,8	134
Tl	0,01 to 0,77	0,4	4	47	0,30	0,60	0,90	225
V	0,17 to 6,9	1,5	4	47	2,0	4,0	5,6	373
Second field test								
Element	Concentration		Number of Teams	Number of double measurements	Reproducibility Standard Deviation	95 % Confidence Interval	Reproducibility	
	Range	Average						
	$\mu g/m^3$	$\mu g/m^3$			$\mu g/m^3$	$\mu g/m^3$	$\mu g/m^3$	%
As	0,10 to 5,1	1,4	4	42	1,7	3,5	4,9	350
Cd	2,5 to 29	7,6	4	42	5,6	11	16	207
Co	0,01 to 4,3	1,5	4	48	1,9	3,7	5,2	347
Cr	0,93 to 96	7,6	4	48	17	34	48	634
Cu	8,9 to 89	32	4	42	17	34	48	150
Mn	0,96 to 150	4,9	4	47	3,8	8,0	11	224
Ni	0,47 to 50	5,6	4	23	11	21	30	530
Pb	92 to 970	280	4	47	136	272	384	137
Sb	0,91 to 24	8,2	4	48	5,0	10	14	172
Tl	0,01 to 59	13	4	48	25	50	71	545
V	0,09 to 6,8	2,0	4	48	2,7	5,4	7,7	385

Annex E
(informative)

Pre-tests for the determination of the efficiency, of the digestion and of the performance of the analytical procedures

In pre-tests the efficiency of the digestions and of the performance of the analytical procedures were determined with a mixture of reference material BCR 176, diluted with quartz powder and a solution prepared from this mixture by digestion. For this, see the reference material BCR 176 and a mixture of this as well as a digestion solution were used.

Table E.1 – Reference sample (BCR, mixture and solution)

		Nominal value BCR 176 mg/kg	Nominal value Mixture [a] mg/kg	Nominal value Solution [b] µg/l
Elements to be determined	As	93,3	2,26	2,38
	Cd	470	11,39	11,99
	Co	30,9	0,75	0,79
	Cr	863	20,91	22,02
	Cu	1 302	31,55	33,22
	Mn	1 390	33,68	35,46
	Ni	123,5	2,99	3,15
	Pb	10 870	263,4	277,3
	Sb	412	9,98	10,51
	Tl	2,85	0,07	0,074
	V	–	–	–
Further elements	Hg	31,4	0,76	0,80
	Se	41,2	0,99	1,04
	Fe	21 300	516,1	543,5
	Zn	25 770	624,5	657,5

[a] prepared by mixing of 250 mg BCR and 10,0 g quartz powder
[b] prepared by digesting 1579,4 mg of the mixture in 15 portions and making up to 1 500 ml.

In a pre-test, the digestions of the mixture were prepared with different acid mixtures and the resulting solutions were analyzed. For testing the analytical procedure alone, also the solution described afore (see table E.1) has been analyzed. It was shown that a treatment with HNO_3/HF in a closed PTFE vessel (see table E.2) resulted in higher yields. The different analytical procedures – GF-AAS, ICP-OES and ICP-MS – gave equivalent results.

The standard deviations of the results for the digestion with HNO_3 HF in a closed PTFE vessel and for the solution described in table E.1 are listed in table E.2.

Table E.2 – Measurement results of BCR 176, mixtures and solutions

Elements		Nominal value Mixture [a] mg/kg	Standard deviation %	Nominal value Solution µg/l	Standard deviation %
Elements to be determined	As	2,26	20	2,38	57
	Cd	11,39	13	11,99	24
	Co	0,75	58	0,79	57
	Cr	20,91	22	22,02	9
	Cu	31,55	11	33,22	23
	Mn	33,68	9	35,46	23
	Ni	2,99	27	3,15	63
	Pb	263,4	16	277,3	10
	Sb	9,98	21	10,51	39
	Tl	0,07	110 [a]	0,074	132[a]
	V	3,80	109	5,50	32

[a] several measurement results below the detection limit

During the two field tests, the mixture described in table E.1 was analyzed together with the samples from the plant. They are reported together with the data from the pre-test in table E.3.

Table E.3 – Measurement results of the reference samples

Data from field tests					Data from pre-tests	
Element	Nominal value[a] mg/kg	Laboratory mean mg/kg	Standard deviation mg/kg	Standard deviation %	Laboratory mean mg/kg	Standard deviation %
As	2,26	2,24	1,17	52	2,50	20
Cd	11,39	10,6	2,4	23	9,90	13
Co	0,75	0,85	0,39	46	1,00	58
Cr	20,91	11,9	5,9	50	15,4	22
Cu	31,55	26,7	4,4	16	27,5	11
Mn	33,68	28,4	8,2	29	31,7	9
Ni	2,99	5,71	6,32	111	3,10	27
Pb	263,4	248	74	30	247	16
Sb	9,98	9,54	4,77	50	10,50	21
Tl	0,07	0,31	0,39	126	0,90	110
V	3,80	1,24	1,11	90	3,80	109

[a] mixture (see table E.1)

The nominal value of V is taken from the pre-tests.

Annex ZA
(informative)

Relationship with EU Directives

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of the EU Council Directive 94/67/EC on the Incineration of Hazardous Waste dated 1994-12-16 and of Directive 2000/76/EC of the European Parliament and of the Council on the Incineration of Waste dated 2000-12-04.

Warning Other requirements and EU Directives may be applicable falling within the scope of use of this European Standard.

Bibliography

[1] Directive 2000/76/EC of the European Parliament and of the Council of 04 December 2000 on the incineration of waste (Official Journal L 332, 28/12/2000 p. 91)

[2] CEN/TC 264/WG 10 N 172 and N 173, available through Kommission Reinhaltung der Luft – Normenausschuss KRdL, P.O Box 10 11 39, 40002 Düsseldorf, Germany.

[3] Council Directive 94/67/EC of 16 December 1994 on the incineration of hazardous waste (Official Journal L 365, 31/12/1994 p. 0034)

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