SLOVENSKI STANDARD

SIST EN 14385:2004

01-junij-2004

Emisije nepremičnih virov – Določevanje celotne emisije As, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Tl in V

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

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

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

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13.040.40	Emisije nepremičnih virov	Stationary source emissions

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

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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of an identical text or by endorsement, at the latest by August 2004, and conflicting national standards shall be withdrawn at the latest by August 2004.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 (m²)
3.2.2	Q	Flow rate of the sampled gas, in cubic metres per hour or litres per minute (m³/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 (m³ 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/m³); 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 $m^2/(m^3\ h^{-1})$ or 2 $cm^2/(l\ min^{-1})$ 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