



SLOVENSKI STANDARD

oSIST prEN 14385:2023

01-oktober-2023

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

Ta slovenski standard je istoveten z: prEN 14385

ICS:

13.040.40 Emisije nepremičnih virov Stationary source emissions

oSIST prEN 14385:2023

en,fr,de

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

DRAFT
prEN 14385

August 2023

ICS 13.040.40

Will supersede EN 14385:2004

English Version

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

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

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

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 264.

If this draft becomes a European Standard, 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.

This draft European Standard was established by CEN 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 CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.



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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Contents	Page
European foreword.....	5
Introduction	6
1 Scope.....	7
2 Normative references.....	7
3 Terms and definitions, symbols and abbreviations	7
3.1 Terms and definitions	7
3.2 Symbols.....	9
3.3 Abbreviations	9
4 Principle	10
5 Apparatus and Chemicals.....	10
5.1 Apparatus and Chemicals.....	10
5.2 Chemicals and filter material	13
6 Sampling equipment.....	15
6.1 General requirements	15
6.2 Isokinetic sampling equipment	15
6.3 Absorbers and absorption efficiency.....	16
7 Cleaning of the sampling equipment prior to sampling.....	17
8 Procedure.....	17
8.1 General requirements	17
8.2 Preparation and installation of equipment.....	17
8.3 Performance of the sampling.....	19
8.4 Disassembling the equipment.....	19
8.5 Field blanks	20
8.6 Requirements for storage of the samples	20
8.7 Pre-treatment before analysis	21
8.8 Analysis.....	23
9 Expression of results.....	25
10 Test report.....	28
Annex A (informative) Examples of absorption vessels.....	29
Annex B (informative) Types of isokinetic equipment and leak test methods.....	30
B.1 Types of isokinetic equipment.....	30
B.2 Leak test methods	31
Annex C (informative) Pre-cleaning procedures of the sampling equipment at the laboratory and determination of the absorption efficiency	35
C.1 General.....	35
C.2 Chemicals	35
C.2.1 General.....	35
C.2.2 Rinsing solution.....	35

C.2.3	Diluted Aqua regia.....	35
C.2.4	Laboratory cleaning solution.....	35
C.2.5	Dilute hydrogen peroxide.....	35
C.2.6	Rinsing acid.....	35
C.3	Equipment.....	35
C.3.1	Procedure A.....	35
C.3.2	Procedure B.....	36
C.3.2.1	Filter housing.....	36
C.3.2.2	Probe, nozzle.....	36
C.3.3	Procedure C.....	36
C.4	Absorption and storage bottles.....	36
C.4.1	Procedure A.....	36
C.4.2	Procedure B.....	36
C.4.3	Procedure C.....	36
C.4.4	Procedure D.....	37
Annex D (informative)	Measurement results of two field tests.....	38
D.1	Absorption efficiency.....	38
D.2	Repeatability.....	38
D.3	Reproducibility.....	40
Annex E (informative)	Pre-tests for the determination of the efficiency, of the digestion and of the performance of the analytical procedures.....	42
E.1	42	
E.2	Comments of Field Study Data.....	44
E.2.1	General.....	44
E.2.2	Pre-treatment and analysis.....	45
E.2.3	Absorption efficiency.....	46
E.2.4	Detection limit.....	46
E.2.5	Repeatability and reproducibility.....	46
Annex F (informative)	Example of assessment of compliance of the standard reference method.....	47
F.1	Introduction.....	47
F.2	Elements required for the uncertainty determinations.....	47
F.2.1	Model equation.....	47
F.3	Example of an uncertainty calculation in case of side-stream sampling system.....	47
F.3.1	General.....	47
F.3.2	Determination of the model equations.....	48

prEN 14385:2023 (E)

F.3.3	Equations for calculating combined uncertainties of gas volumes sampled in standardized conditions.....	50
F.3.4	Equations for calculating combined uncertainties of concentrations.....	51
F.3.5	Quantification of standard uncertainty components.....	54
F.3.5.1	Standards uncertainties of parameters taken into account in the volume gas uncertainties.....	54
F.3.5.2	Standard uncertainties of analysis:.....	54
F.3.5.3	Data for the uncertainty calculation example	55
F.4	Estimation of measurement uncertainty in case of main-stream sampling system...67	
F.4.1	General.....	67
F.4.2	Determination of the model equations	67
F.4.3	Equations for calculating combined uncertainties of gas volumes sampled in standardized conditions.....	68
F.4.4	Equations for calculating combined uncertainties of concentrations.....	68
Annex G (informative)	Determination and reporting of limits of detection and quantification	72
G.1	72	
G.2	Limit of detection (LoD).....	73
G.3	Limit of quantification (LoQ)	73
G.4	Rules to be adopted when Summing the Various Parts of a Metals Sample Train where the levels are at LoQ or below	74
Annex H (informative)	Alternative digestion method for the filters by use of an HF-free digestion Mixture [3],[4].....	77
H.1	77	
H.2	Reagents	77
H.3	Digestion of filter.....	77
H.4	Analysis.....	77
Bibliography.....		78

European foreword

This document (prEN 14385:2023) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 14385:2004.

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

- In the Scope: Range of specific elements widened from 0,5mg/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 Group 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 clearer and treatment of data where a wet gas meter has been used has been expanded. <https://standards.iteh.ai/catalog/standards/sist/8aad6491-f650-44e6-a61c-27f9e0483852>
- 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 given to CEN by the European Commission and the European Free Trade Association.

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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[oSIST prEN 14385:2023](https://standards.iteh.ai/catalog/standards/sist/8aad6491-f650-44e6-a61c-6ecade21f3a8/osist-pren-14385-2023)

<https://standards.iteh.ai/catalog/standards/sist/8aad6491-f650-44e6-a61c-6ecade21f3a8/osist-pren-14385-2023>

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) and tin (Sn)).

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 AAS and ICP. 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 13211, *Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury*

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 abbreviations

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

3.1 Terms and definitions

3.1.1

absorber

device in which specific elements are absorbed into an absorption liquid

prEN 14385:2023 (E)**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 chemical 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**

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

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

3.1.5**filtered material**

materials collected on the filter

3.1.6**filter passing material**

components 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**representative sampling**

sampling as stated in EN 13284-1 and EN 15259

3.1.9**Group A elements**

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

3.1.10**Group B elements**

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

3.1.11**sampling campaign**

sampling at one duct or location during one site visit

3.2 Symbols

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 Pressure, in kilopascals (kPa)
β	Mass concentration, e.g. in milligrams per cubic metre (mg/m ³); grams per litre (g/l)
c	Mass concentration, in 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 and metre (MΩm)
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 Abbreviations

CRM	Certified reference material
El	Specific element
FEP	Polyperfluoroethene /polyperfluoropropene
PE	Polyethene
PFA	Perfluoroalkoxy compounds
PP	Polypropene
PTFE	Polytetrafluoroethene
amb	Ambient; index
gas	Gaseous; index
main	Mainstream; index
side	Side stream; index

prEN 14385:2023 (E)

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 Apparatus and Chemicals****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 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;

prEN 14385:2023 (E)

- 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 meter, measurement of the flue gas water vapour content is required to allow the gas volume to be corrected to a dry gas sampled volume. 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.

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

See symbols 3.2 and abbreviations 3.3.

P_v = Partial of water in the gas meter;

P = Absolute Pressure in the Gas Meter;

H_m = Water content of gases entering wet gas meter.

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 $P_{sat}(T)$ of the water at the gas volume meter temperature:

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

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 It is the responsibility of the user to ensure 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 the need to 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 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 are to 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.