



SLOVENSKI STANDARD
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Stationary source emissions - Determination of mass concentration of gaseous chlorides
expressed as HCl - Standard reference method

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von
gasförmigen Chloriden, angegeben als HCl - Standardreferenzverfahren

Emissions de sources fixes - Détermination de la concentration massique en chlorures
gazeux, exprimée en HCl - Méthode de référence normalisée

Ta slovenski standard je istoveten z: prEN 1911

ICS:

13.040.40 Ö{ ã ã Á ^] ! ^{ ã } ã ã] ç Stationary source emissions

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

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English Version

**Stationary source emissions - Determination of mass
concentration of gaseous chlorides expressed as HCl - Standard
reference method**

Emissions de sources fixes - Détermination de la
concentration massique en chlorures gazeux, exprimée en
HCl - Méthode de référence normalisée

Emissionen aus stationären Quellen - Bestimmung der
Massenkonzentration von gasförmigen Chloriden,
angegeben als HCl - Standardreferenzverfahren

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

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Foreword

This document (prEN 1911:2008) 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 1911-1:1998, EN 1911-2:1998, EN 1911-3:1998.

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SIST EN 1911:2011

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1 Scope

This European Standard describes the Standard Reference Method (SRM) with three alternative analytical techniques for determining gaseous chlorides content emitting to atmosphere from ducts and stacks. The specific components and the requirements for the measuring system are described. A number of performance characteristics with associated minimum performance criteria are specified for the measuring system (see tables 1 and 2 in 7.2). This European standard can be used as a SRM provided the overall uncertainty of the method is less than $\pm 30,0$ % relative at the daily Emission Limit Value (ELV) for incineration and large combustion plants or at the ELV prescribed by the specific regulations for other plants.

An Alternative Method to this SRM may be used provided that the user can demonstrate equivalence according to the Technical Specification TS 14793.

This method determines the concentration of chlorinated compounds that give Cl^- ions in the absorption solution. This Standard Reference Method has been evaluated during field tests on waste incineration. The method applies to waste gases in which chlorides concentration expressed as HCl may vary between $1 \text{ mg}\cdot\text{m}^{-3}$ and $5\,000 \text{ mg}\cdot\text{m}^{-3}$ under normal pressure and temperature conditions (see Note), and according to emission limit values laid down in the following Council Directives:

- Council Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants
- Council Directive 2000/76/EC on waste incineration plants.

NOTE The limit values of EU directives are expressed in mg HCl/m^3 , on dry basis, at the reference conditions of 273 K and 101,3 kPa and at the reference O_2 concentration.

2 Normative references

The following referenced documents are indispensable for the application 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 13284-1:2001, *Stationary source emissions – Determination of low range mass concentrations of dust – Part 1: Manual gravimetric method*

TS 14793:2004, *Stationary source emission - Intra-laboratory validation procedure for an alternative method compared to a reference method*

EN ISO 14956:2002, *Air Quality – Evaluation of the suitability of a measurement method by comparison with a stated measurement uncertainty*

ENV 13005:1999, *Guide to the expression of uncertainty in measurement (GUM)*

EN ISO 3696:1995, *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

EN ISO 10304-1:1995, *Water quality – Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulphate ions, using liquid chromatography of ions – Part 1: Method for water with low contamination (ISO 10304-1:1992)*

EN ISO 20988:2007, *Air quality – Guidelines for estimating measurement uncertainty*

EN 15259:2007, *Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report*

3 Definitions

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

3.1

absorber

device in which gaseous chloride is absorbed into an absorption liquid

3.2

absorption efficiency (ϵ)

ratio ϵ of quantity of the analyte q_1 collected in the first absorber divided by the quantity of the analyte collected in the first and the second absorber ($q_1 + q_2$)

$$\epsilon = q_1 / (q_1 + q_2)$$

3.3

automatic measuring system (AMS)

measuring system permanently installed on site for continuous monitoring of emissions

NOTE 1 An AMS is traceable to a standard reference method (SRM).

NOTE 2 Apart from the analyser, an AMS includes facilities for taking samples (e.g. probe, sample gas lines, flow meters, regulators, delivery pumps) and for sample conditioning (e.g. dust filter, moisture removal devices, converters, diluters). This definition also includes testing and adjusting devices that are required for regular functional checks.

3.4

calibration of an AMS

statistical relationship between values of the measurand indicated by the measuring system (AMS) and the corresponding values given by the standard reference method (SRM) used during the same period of time and giving a representative measurement on the same sampling plane

NOTE The result of calibration permits to establish the relationship between the values of the SRM and the AMS (calibration function).

3.5

chemical blank value

chloride ion content of an unexposed sample of the absorption solution, plus reagents that are added to the solution before analysis if necessary

3.6

analytical detection limit (D_L)

concentration value of the measurand below which there is at least 95 % level of confidence that the measured value corresponds to a sample free of that measurand

3.7

emission limit value (ELV)

emission limit value according to EU Directives on the basis of 30 min, 1 hour or 1 day

3.8

field blank

value determined by a specific procedure used to ensure that no significant contamination has occurred during all steps of the measurement and to check that the operator can achieve a quantification level adapted to the task

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3.9**isokinetic sampling**

sampling at a rate such that the velocity and direction of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point
[EN 13284-1]

3.10**measurand**

particular quantity subject to measurement
[VIM 2.6]

3.11**measurement series**

several successive measurements carried out on the same sampling plane and at the same process operating conditions
[EN 13284-1]

3.12**measuring system**

complete set of measuring instruments and other equipment assembled to carry out specified measurements
[VIM 4.5]

3.13**performance characteristic**

one of the quantities (described by values, tolerances, range...) assigned to equipment in order to define its performance

3.14**repeatability in the laboratory**

closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

NOTE 1 Repeatability conditions include:

- the same measurement procedure
- the same laboratory
- the same sampling equipment, used under the same conditions
- the same location
- repetition over a short period of time

NOTE 2 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

In this European Standard the repeatability is expressed as a value with a level of confidence of 95 %.
[VIM 3.6]

3.15**repeatability in the field**

closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with two equipments under the same conditions of measurement

NOTE 1 These conditions include:

- the same measurement procedure

- two equipments, the performances of which are fulfilling the requirements of the reference method, used under the same conditions
- the same location
- implemented by the same laboratory
- typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min)

NOTE 2 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

In this European Standard the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.

3.16

reproducibility in the field

closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with several sets of equipment under the same conditions of measurement

NOTE 1 These conditions are called field reproducibility conditions and include:

- the same measurement procedure
- several sets of equipment, the performance of which fulfils the requirements of the reference method, used under the same conditions
- the same location
- implemented by several laboratories

NOTE 2 Reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results.

In this European Standard the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %.

3.17

sampling location

specific area close to the sampling plane where the measurement devices are set up

3.18

sampling plane

plane normal to the centreline of the duct at the sampling position

[EN 13284-1]

3.1.21

sampling point

specific position on a sampling plane at which a sample is extracted

[EN 13284-1]

3.19

standard reference method (SRM)

measurement method recognised by experts and taken as a reference by convention, which gives, or is presumed to give, the accepted reference value of the concentration of the measurand (3.1.11) to be measured

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3.20**uncertainty**

parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

3.20.1**standard uncertainty u**

uncertainty of the result of a measurement expressed as a standard deviation u

3.20.2**expanded uncertainty U**

quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand

$$U = k \cdot u$$

NOTE In this European Standard, the expanded uncertainty is calculated with a coverage factor of $k=2$, and with a level of confidence of 95 %.

3.21**combined uncertainty u_c**

standard uncertainty u_c attached to the measurement result calculated by combination of several standard uncertainties according to GUM

3.22**overall uncertainty U_c**

expanded combined standard uncertainty attached to the measurement result calculated according to GUM

$$U_c = k \cdot u_c$$

3.23**uncertainty budget**

calculation table combining all the sources of uncertainty according to EN ISO 14956 or ENV 13005 in order to calculate the overall uncertainty of the method at a specified value

Add a sub-clause with symbols and abbreviations

4 Sampling**4.1 Sampling principle**

A known volume of flue gas is extracted representatively from a duct or a chimney during a certain period of time at a controlled flow rate with a temperature regulated probe. A temperature regulated filter removes the dust in the sampled volume, thereafter the gas stream containing gaseous chlorides is passed through a series of absorbers containing an absorption solution (chloride-free water).

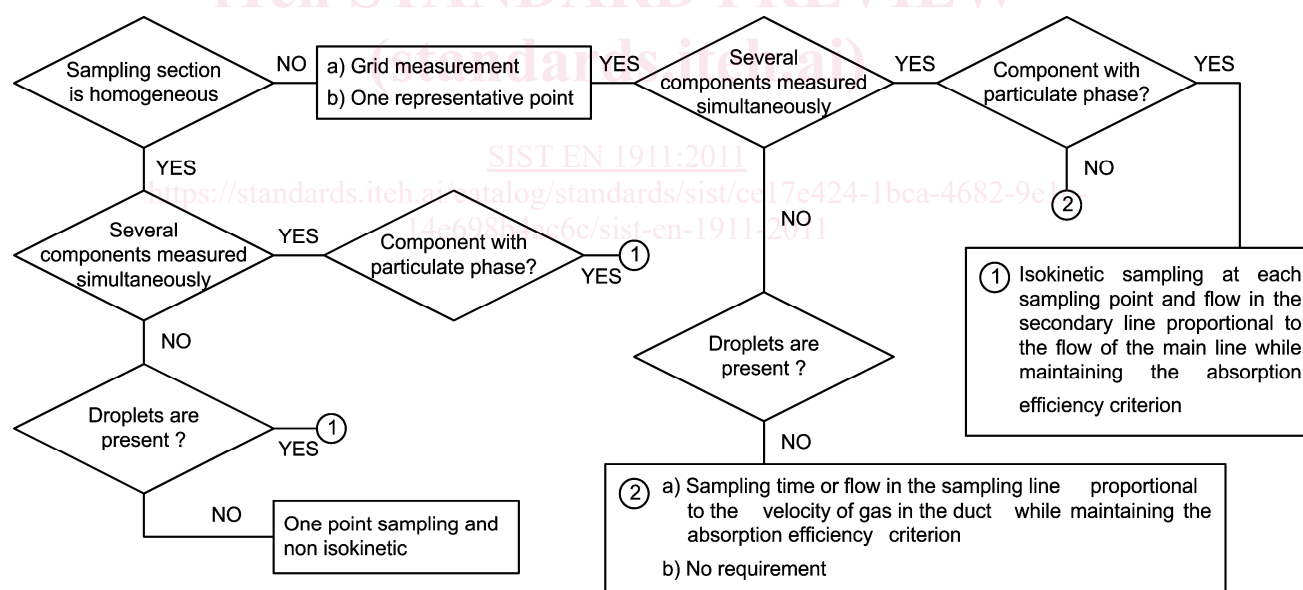
All compounds which are volatile at the temperature of filtration and produce chloride ions upon dissolution during sampling are measured by this method, which gives therefore the volatile inorganic chlorides content of gases expressed as HCl.

4.2 Sampling strategy**4.2.1 General**

The test programme shall be established on a sampling strategy that shall integrate at the same time:

- Quantification of several compounds simultaneously.
- The following compounds gaseous chlorides, HF, SO₂, NH₃ and H₂O can be sampled simultaneously in parallel side stream lines. If isokinetic sampling is required, because droplets are present, H₂O cannot be included in the measurement. Gaseous chlorides and dust can be sampled simultaneously in parallel side stream lines and require an isokinetic sampling with a probe equipped with a nozzle.
- Representativeness of the emission of the process. The following points should be considered when preparing the sampling programme:
 - the nature of the plant process e.g. steady state or discontinuous;
 - the expected concentration to be measured and any required averaging period, both of which can influence the measuring and sampling time. When a grid measurement is required, sampling time shall be in accordance with EN 13284-1 requirements related to the representativeness of the sample;
 - in the case of combination of several compounds measurement, each relevant SRM may give guidelines to get an acceptable sample;
 - EN 15259 deals with problem of the homogeneity of the gas effluents at the sampling sections. The test of homogeneity could be performed either by using an automatic HCl analyser or any other surrogates gases (e.g. O₂, CO₂, ...).

The diagram below describes the strategy of measuring to be followed according to the situation met.



In some cases, the waste gases to be analysed may be water vapour saturated or slightly supersaturated, thus containing droplets which may have a high chloride content (dissolved HCl and/or dissolved chlorides). For example, this may occur when sampling gases downstream a humid scrubber without subsequent reheating.

These droplets, sampled with the gas to some extent influence the results. It has been shown that, in such cases, the reproducibility of measurement is better by using an isokinetic sampling than by using classical gas sampling by a straight probe. Therefore, when the occurrence of droplets is suspected or known in the gas to be analysed, isokinetic sampling is required (see Note). When droplets are absent then non-isokinetic sampling may be used.

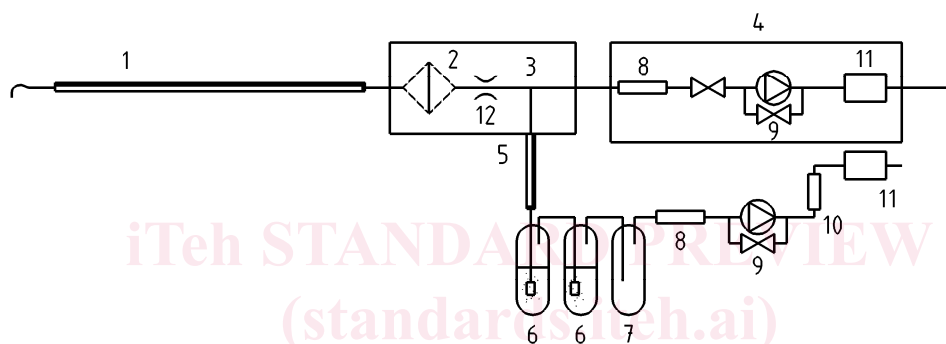
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NOTE When droplets are present and when a high heterogeneity has been demonstrated, the absorption efficiency may fail. In that case, instead of a isokinetic grid sampling the grid sampling is carried out with a sampling time at each point that is proportional to the local velocity.

4.2.2 Isokinetic sampling

Because probe nozzle diameters shall comply with EN 13284-1 and EN 15259 requirements isokinetic sampling requires usually volume flow rates much higher than those which can be admitted by the absorbers used for Gaseous chlorides collection. Therefore, downstream of the filter, only a part of the gases is drawn through the absorber(s) through a secondary line, the main line and the secondary line having their own gas metering systems and suction devices. The ratio between the main and the secondary line volume flow rates shall be kept constant. To make easier the control of this ratio, the measurement, by a diaphragm or any other appropriate device, of the total flow passing through the main line may be useful (see Figure 1).

NOTE A sampling system without any secondary line (side stream) can be used provided that the absorption efficiency requirements in 4.3.2.2.2 are fulfilled.



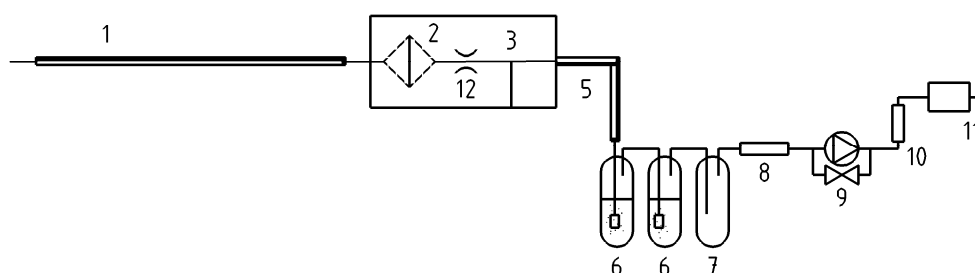
- | | |
|---|---|
| 1 nozzle and heated sampling probe | 7 guard bottle (optional) |
| 2 regulated temperature particle filter | 8 cartridge with desiccant (optional) |
| 3 heated T piece | 9 pump |
| 4 main flow unit for suction and measuring volume flow rate | 10 flow meter |
| 5 regulated temperature connecting line (optional) | 11 gas meter |
| 6 absorber(s) | 12 diaphragm for total flow rate measurement (optional) |

Figure 1 — Example of isokinetic sampling equipment

4.2.3 Non isokinetic sampling

Sampling shall be carried out at one or several points in the sampling section, in accordance with the result of the test of homogeneity carried out according to EN 15259.

Sampling may be carried out using a straight regulated temperature probe, without nozzle. Dust is removed by a high efficiency heated filter, then gaseous chlorides are collected in absorbers.



1 heated sampling probe	8 cartridge with desiccant (optional)
2 regulated temperature particle filter	9 pump
3 heated T piece	10 flow meter
5 regulated temperature connecting line (optional)	11 gas meter
6 absorber (s)	12 diaphragm for total flow rate measurement
7 guard bottle (optional)	

Figure 2 — Example of non-isokinetic sampling equipment

4.2.4 Losses of gaseous chlorides and side reactions during sampling

Attention is drawn to the risks of losses of gaseous chlorides in the sampling system, due to its high reactivity and solubility: All the parts of the sampling system upstream of the absorber shall be made of inert materials, and shall be heated in order to avoid cold points, which can lead to large losses of gaseous chlorides. Any parts that are not heated shall be rinsed.

Some kinds of waste gases (e.g. incinerator plants, etc.) may contain chemical species (e.g. calcium salts or hydroxide, ammonium salts or free ammonia, etc.) which can react with gaseous chlorides.

There are some experimental evidences that these reactions are strongly enhanced by filtration of sampled gases at temperature below 130 °C. Because most of these side reactions products are retained on the filter, this can lead to large underestimation of waste gases gaseous chlorides concentrations: it is the reason why this European standard requires a minimum filtration temperature of 160 °C, and 20 °C higher than the acid dew point of gases. When ammonia and chloride salts are present, a temperature of 180 °C is required to avoid formation of NH_4Cl on the filter.

4.3 Sampling equipment

4.3.1 Isokinetic sampling equipment

4.3.1.1 Main line

An example of the whole isokinetic sampling equipment is shown in Figure 1.

4.3.1.1.1 Probe

The length of the probe shall be enough to preheat the gas before entering the filter.

In order to access the representative measurement point(s) of the sampling plane, probes of different lengths and inner diameters may be used, but the residence time of the sample gas in the probe shall be minimised.

The probe may be marked before sampling in order to reach more easily the representative measurement point(s) in the measurement plane.