

BS EN 1911:2010



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

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National foreword

This British Standard is the UK implementation of EN 1911:2010. It supersedes BS EN 1911-1:1998 and BS EN 1911-2:1998 and BS EN 1911-3:1998 which are withdrawn

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

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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

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Foreword

This document (EN 1911:2010) 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of an identical text or by endorsement, at the latest by February 2011, and conflicting national standards shall be withdrawn at the latest by February 2011.

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

This document supersedes EN 1911-1:1998, EN 1911-2:1998 and EN 1911-3:1998.

Annex E provides details of significant technical changes between this European Standard and the previous edition.

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

Introduction

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 8.2). This European Standard can be used as an SRM provided the overall uncertainty of the method is less than 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 CEN/TS 14793.

1 Scope

The method described in this European Standard determines the concentration of chlorinated compounds in a flue gas that – after passage of the sampling system including a particle filter – 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 mg·m⁻³ and 5 000 mg·m⁻³ under normal pressure and temperature conditions (see Note 1), and according to emission limit values laid down, for example, in the Council Directive 2000/76/EC on waste incineration plants.

NOTE 1 The limit values of this European Standard are expressed in mg HCl/m³, on dry basis, at the reference conditions of 273 K and 101,3 kPa and at the reference O₂ concentration.

NOTE 2 The required uncertainty results from the capacity of the method tested in the field (Annex D) and in the laboratory (see performance characteristics in Tables 1 and 2 and Annex C).

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 concentration of dust — Part 1: Manual gravimetric method*

ENV 13005, *Guide to the expression of uncertainty in measurement*

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

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

EN ISO 10304-1, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (ISO 10304-1:2007)*

EN ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)*

3 Terms, definitions and abbreviations

3.1 Terms and definitions

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

3.1.1 absorber

device in which gaseous chloride is absorbed into an absorption solution

3.1.2 chemical blank

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

3.1.3
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

3.1.4
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

3.1.5
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 13284-1:2001]

3.1.6
measurand

particular quantity subject to measurement

[ISO/IEC Guide 99:2007, 2.6]

3.1.7
measurement series

several successive measurements carried out on the same sampling plane and at the same process operating conditions

[EN 13284-1:2001]

3.1.8
performance characteristic

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

3.1.9
analytical repeatability

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

NOTE 1 Analytical repeatability conditions include:

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

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

[ISO/IEC Guide 99:2007, 3.6]

NOTE 3 In this European Standard the analytical repeatability is expressed as a value with a level of confidence of 95 %.

3.1.10

repeatability in the field

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

NOTE 1 These conditions include:

- the same measurement procedure;
- two sets of equipment, 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 over 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.

NOTE 3 In this European Standard the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.

3.1.11

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.

NOTE 3 In this European Standard the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %.

3.1.12

sampling location

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

3.1.13

sampling plane

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

[EN 13284-1:2001]

3.1.14

sampling point

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

[EN 13284-1:2001]

3.1.15

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 to be measured

3.1.16

uncertainty

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

3.1.17

standard uncertainty

u

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

3.1.18

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

NOTE 1 $U = k.u$

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

3.1.19

combined uncertainty

u_c

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

NOTE
$$u_c = \sqrt{\sum_{i=1}^N u_i^2}$$

3.1.20

overall uncertainty

U_c

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

NOTE $U_c = k \times u_c$

3.2 Abbreviations

C_{Ag} concentration of silver nitrate solution, in moles per litre (mol/l)

CI_r repeatability confidence interval

CI_R reproducibility confidence interval

C_{corr}	corrected concentration of measurand
C_{actual}	concentration of measurand at actual O ₂ concentration
$C_{chlorides(Cl)}$	chlorides content expressed in milligrams Cl ⁻ per cubic metre
$C_{chlorides(HCl)}$	chlorides content expressed in milligrams HCl per cubic metre
D_L	analytical detection limit
M_{Cl}	molar mass of chloride
M_{HCl}	molar mass of hydrogen chloride
$m_{chlorides}$	quantity of gaseous chlorides collected in the sampling device, , in milligrams Cl
$O_{2,meas}$	dry oxygen content
$O_{2,ref}$	oxygen reference concentration
P	absolute pressure in kilopascals (kPa) at the gas volume meter; P is equal to the sum of relative pressure measured at the gas volume meter P_{rel} plus atmospheric pressure P_{atm}
P_{rel}	relative pressure measured at the gas volume meter in kilopascals (kPa)
P_{atm}	atmospheric pressure in kilopascals (kPa)
$p_s(H_2O)$	saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa)
p_{res}	residual vapour pressure, in kilopascals (kPa)
S_r	repeatability standard deviation
S_R	reproducibility standard deviation
$t_{0,95;np-1}$	student factor for a level of confidence of 95 % and a degree of freedom of np-1
T	actual temperature, in Kelvins (K)
u	standard uncertainty
u_c	combined uncertainty
U	expanded uncertainty
U_c	overall uncertainty
V_{std}	volume of gas sampled under standard conditions and dry basis, in cubic metres (m ³)

V_s	volume of absorption solution S_e , in millilitres (ml)
$V_{s,a}$	aliquot portion of S_e used for analysis, in millilitres (ml)
V_{AgNO_3}	volume of the Ag NO ₃ solution used for dosing the solution S_e , in millilitres (ml)
$V_{o,AgNO_3}$	volume of the Ag NO ₃ solution used for taking into account the chemical blank value, in millilitres (ml)
$V_{T,p}$	volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m ³)

4 Principle

This European Standard describes the Standard Reference Method (SRM) for determining chloride ions content, expressed as HCl, 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 8.2). These performance characteristics and the overall uncertainty of the method shall meet the specifications given in this European Standard.

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 heated probe. A heated 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 the waste gas. The results shall be expressed as HCl.

After sampling the solutions are analysed by one of the following methods:

- silver titration: potentiometric method (Method A);
- mercuric-thiocyanate spectrophotometry (Method B);
- ion-exchange chromatography (Method C).

5 Sampling

5.1 Sampling strategy

5.1.1 General

The test programme shall be established following the advice and requirements described in EN 15259:2007 (5.4, Clauses 6, 7 and 8).

- Quantification of several compounds simultaneously, if relevant.

NOTE 1 Compounds such as gaseous chlorides, HF, SO₂, NH₃ and water vapour, can be sampled simultaneously in parallel side stream lines.

NOTE 2 When performing isokinetic sampling the presence of water droplets means water vapour cannot be measured simultaneously in the same equipment.

NOTE 3 Gaseous chlorides and dust can be sampled simultaneously and require an isokinetic sampling with a probe equipped with a nozzle.

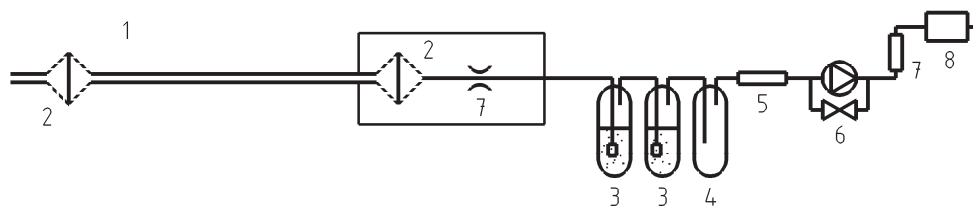
b) Representativeness of the emission of the process. The following points shall be considered when preparing the sampling programme:

- 1) the nature of the plant process, e.g. steady state or discontinuous;
- 2) the homogeneity of the gas effluents at the sampling sections can be performed either by using an automatic HCl analyser or any other relevant surrogates gases (e.g. O₂, CO₂, etc.). When droplets are present, it is not necessary to perform the homogeneity test because a grid sampling is performed;
- 3) 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;
- 4) In some cases where flue gases are treated by a wet scrubber, they may be 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 and the accuracy of the 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.

5.1.2 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 heated probe, without nozzle. Dust is removed by a high efficiency heated filter, and then gaseous chlorides are collected in absorbers (see Figure 1).



Key

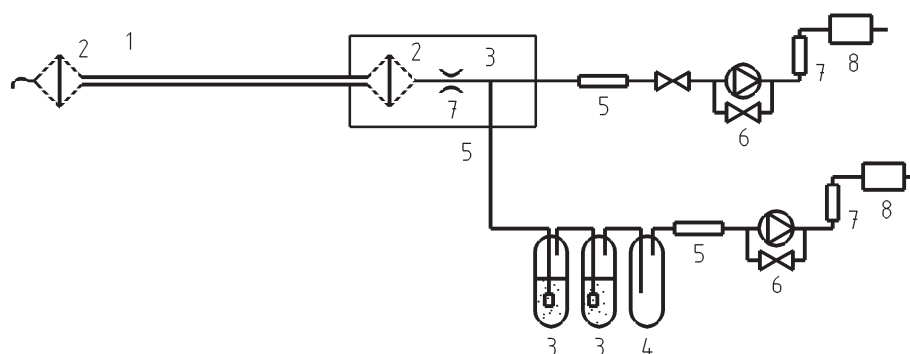
- | | |
|---|---|
| 1 heated sampling probe | 5 cartridge with desiccant (optional) |
| 2 heated particle filter (alternatives) | 6 pump |
| 3 absorber(s) | 7 flow meter behind the filter (e.g. diaphragm) or before the gas meter |
| 4 guard bottle (optional) | 8 gas meter |

Figure 1 — Example of non-isokinetic sampling equipment

5.1.3 Isokinetic sampling

5.1.3.1 Isokinetic sampling with a side stream

Because probe nozzle diameters shall comply with EN 13284-1, isokinetic sampling often requires 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 measurement of the flow in the main line can be measured either by a diaphragm or any other appropriate device, placed behind the filter and before the T piece or before the volume meter (see Figure 2).



Key

1 heated sampling probe	5 cartridge with desiccant (optional)
2 heated particle filter (alternatives)	6 pump
3 absorber(s)	7 flow meter behind the filter (e.g. diaphragm) or before the gas meter
4 guard bottle (optional)	8 gas meter

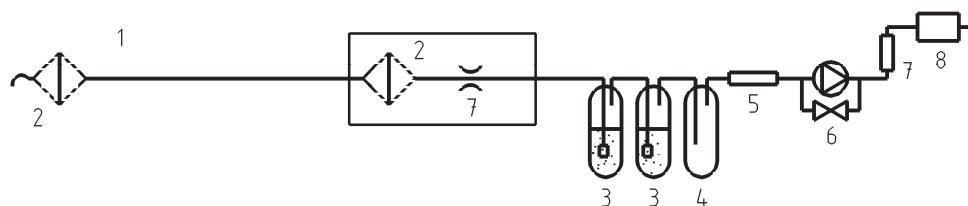
Figure 2 — Example of isokinetic sampling equipment with a side stream

For practical reasons it is difficult to adjust the secondary line volume flow rate quickly at each sampling point. Therefore, in the cases where the concentration is homogeneous in the sampling section, the flow rate can be kept constant. However, if the concentrations across the sampling section are not homogeneous, then the laboratory shall decide, depending on the measuring quality objectives to be reached, to fulfil or not the requirement EN 15259 of a flow rate proportional to the local velocity at each sampling point. The respect of EN 15259 is much easier using an isokinetic sampling system without any side stream (see 5.1.3.2).

5.1.3.2 Isokinetic sampling without any side stream

A sampling system without any secondary line (side stream) can be used provided that the absorption efficiency requirements in 5.2.1.2.2 are fulfilled.

NOTE An advantage of an isokinetic sampling without a side stream is that a flow rate proportional to the local velocity at each sampling point can be maintained more easily when a non homogeneity is detected in the sampling section.



Key

1 heated sampling probe	5 cartridge with desiccant (optional)
2 heated particle filter (alternatives)	6 pump
3 absorber(s)	7 flow meter behind the filter (e.g. diaphragm) or before the gas meter
4 guard bottle (optional)	8 gas meter

Figure 3 — Example of isokinetic sampling equipment without any side stream

5.1.4 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.

5.2 Sampling equipment

5.2.1 Isokinetic sampling equipment.

The items described hereafter assume that a side stream is used. If it is not the case, the absorbers and other components described in 5.2.1.2.2 to 5.2.1.2.5 are used.

NOTE An example of the whole isokinetic sampling equipment is shown in Figures 2 and 3.

5.2.1.1 Main line.

5.2.1.1.1 Probe.

The heated probe and entry nozzle shall be designed in accordance with EN 13284-1. However, since these parts are often made of borosilicate glass, which is difficult to manufacture to close tolerances, requirements may be less stringent concerning the edge of the entry nozzle. 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.

5.2.1.1.2 Filter housing.

The filter housing is located just before the probe (in-stack filtration) or directly behind the probe (out-stack filtration).

The filter housing for out-stack filtration shall be heated at a controlled temperature of at least 20 °C above the dew point. It shall be connected to the probe without any cold path between the two.

In-stack filtration is possible with effluent without droplets and if gas temperature is at least 20 °C above the dew point.

NOTE 1 The filter housing may be jointed with the probe thereby avoiding leaks.

NOTE 2 A stop valve after the filter housing can be useful to prevent back flush of absorption solution into the probe or into the filter when sampling in flue gases under unfavourable conditions (e.g. high depression in the duct).

NOTE 3 In special cases where the sample gas temperature is > 200 °C, the heating jacket around the sampling probe, filter housing and connector line may be switched off. However the temperature in the sampled gas just after the filter housing should not fall below 20 °C above the dew point temperature.

5.2.1.1.3 Particle filter.

The efficiency of the filter material shall be better than 99,5 % on a test aerosol of 0,3 µm mean diameter (or 99,9 % on a test aerosol of 0,6 µm mean diameter), for the maximal actual volume flow rate of the filter, to avoid measurement errors due to fine particles of chloride salts which could be collected in the absorbers and analysed as gaseous chlorides.

Filters with the most suitable properties for this purpose are plane filters: convenient borosilicate glass and quartz fibres filters of different diameters and certified efficiency are commercially available.

Diameters of about 40 mm to 160 mm are generally convenient.

Filters of different designs may be used, but the residence time of the sample gas shall be minimised. For plants with dust concentration less than 5 mg/m³, a simplified filtration technique can be used (e.g. quartz wool plugs in a heated housing).

5.2.1.1.4 Temperature controller.

A temperature controller is required for the probe and filter housing. It shall be capable of controlling temperature with an uncertainty of 2,5 K or better (uncertainty of calibration).

5.2.1.1.5 Suction and volume flow meter.

The unit for suction and metering the volume flow rate in the main line shall have an adjustable volume flow rate and flow meter, in order to comply with isokinetic criteria.

Various kinds of devices may be used, for instance:

- volume flow rate measurement on wet basis using an heated orifice plate followed or not by a compressed air ejector acting as suction device;
- water vapour removing device (condenser, dryer, etc.), leak tight pump, volume and flow meter.

If the flow meter is placed just after the filter, it shall be calibrated and data corrected (temperature, pressure, humidity) to fulfil the isokinetic criterion. If the flow meter is placed just before the volume meter, the volume flow rate in the secondary line shall be taken into account in order to calculate the total volume flow rate in the main line.

5.2.1.2 Secondary line (optional for Isokinetic sampling without any side stream).

5.2.1.2.1 Connection to the main line.

A tee piece ensures the division of the sample between the secondary line which allows a gas volume flow rate that fulfils the collection efficiency criteria and the main line.

NOTE A flow of about 2 l·min⁻¹ to 3 l·min⁻¹ is generally used.

Care shall be taken to design the sampling system in such a way that no condensation shall occur between the filter and the tee connection.

A line connecting the heated separator to the absorber is made of borosilicate glass or PTFE. Parts of the line which are not rinsed shall be heated to avoid condensation. This line shall be as short as possible, in order to minimise the residence time of the gas.

5.2.1.2.2 Absorbers.

To achieve an efficient absorption, at least two absorbers shall be placed in series.

A cooling system may be used to reduce the evaporation in the first absorber.

NOTE 1 Downstream of these absorbers, an extra empty absorber may be used as a liquid trap and as a protection for the downstream equipment.

NOTE 2 Sintered frits are often used in order to achieve fine bubbling of gas into the absorption reagent. Annex A describes two types of suitable absorber.

The absorbers are made of borosilicate glass, polytetrafluoroethylene (PTFE) or polyethylene (PE) (see an example in Annex A).

Condensate recovery is facilitated when the absorber is fitted with a vertical inlet tube. The absorber geometry and the quantity of water contained shall enable gaseous chlorides absorption efficiency:

- of not more than 5 % to be retained in the last absorber in the range of concentration examined;
- or the content in the last absorber corresponds to a concentration lower than a concentration corresponding to five times the analytical detection limit.

The absorption efficiency shall be determined for each measuring campaign.

The absorption is tested as follows:

- Carry out sampling in normal conditions.
- Remove the absorbers from the sampling train and transfer the sample solution from last absorber into a separate sample bottle. If a trap is used behind the absorbers to collect any solution carry-over, its contents shall be combined with the sample of downstream bottle. Rinse each absorber with the absorption solution (5.2.4) thoroughly and particularly the fritted glass dividers, if they are used to recover the absorption solution trapped in it and add the rinsing solutions to the appropriate absorber sample. Rinse all the unheated parts of the sampling system between the filter and the absorber 1 and add the rinsing to the content of the first bottle(s).
- Analyse samples of the first(s) absorber(s) and of the last absorber separately as described in Clause 6 to determine the chloride content, qs_1 and qs_2 . Check that the content in the last absorber is less than required.

5.2.1.2.3 Sampling pump.

Leak-free pump capable of sampling gas at a set flow rate.

NOTE A rotameter (optional) facilitates the adjustment of the nominal sampling flow rate.

5.2.1.2.4 Gas volume meter.

Any dry or wet gas volume meter may be used providing the volume is measured with a relative uncertainty of calibration not exceeding 2 % at actual conditions.

The gas volume-meter shall be equipped with a temperature measuring device (uncertainty of calibration less than 2,5 K). The absolute pressure at the gas volume meter (uncertainty of calibration less than 1,0 %) can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than $10 \text{ g}\cdot\text{m}^{-3}$ (equivalent to a dew point of $10,5 \text{ }^\circ\text{C}$ or a volume content $\chi(\text{H}_2\text{O}) = 1,25 \text{ } \%$).

NOTE 1 For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at $110 \text{ }^\circ\text{C}$ for at least 2 h.

When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

$$\text{For "dry" gas meter: } V_{std} = V_{T,p} \times \frac{273}{T} \times \frac{p - p_{res}}{101,3} \quad (1)$$

$$\text{For "wet" gas meter: } V_{std} = V_{T,p} \times \frac{273}{T} \times \frac{p - p_s(\text{H}_2\text{O})}{101,3} \quad (2)$$

where

V_{std} is the volume under standard conditions and dry basis, in cubic metres (m^3);

$V_{T,p}$ is the volume under actual conditions of temperature and pressure, on dry basis with "dry" gas meter or wet basis with "wet" gas meter, in cubic metres (m^3);

T is the actual temperature, in Kelvins (K);

p is the total pressure in kilopascals (kPa) (i.e. atmospheric pressure + static pressure) at the gas meter;

$p_s(\text{H}_2\text{O})$ is the saturated vapour pressure at the temperature of the gas meter, in kilopascals (kPa);

p_{res} is the residual vapour pressure, in kilopascals (kPa).

NOTE 2 The relative pressure can be neglected if the gas volume meter is the last equipment of the sampling chain.

5.2.1.2.5 Optional additional apparatus.

- A shut-off device for the secondary line that allows isolation of the sampling line may be used. If such a device is used, it shall be capable of being rinsed completely after each sampling operation.
- An additional bottle may be located just before the main absorber; this arrangement prevents liquid being sucked back in the event of mishandling, but condensation often occurs in it. If such a device is used, it shall be rinsed completely after each sampling operation, along with the tubes connecting it. In this case, the rinsing solution shall be incorporated with the solution contained in the main absorber. Such a device shall not be used for measuring concentrations lower than $30 \text{ mg}\cdot\text{m}^{-3}$.
- Guard bottle, without sintered frit, that can be positioned after the secondary absorber to collect any reagent carry over.

- A cartridge filled with desiccant is normally located just before the unit for suction, in order to prevent any further moisture condensation.
- A diaphragm or any other appropriate device, to measure the total flow passing through the main line may be useful to control the isokinetic rate and the ratio between the flow rate of the main line and the flow rate of the secondary line. The system can be placed behind the filter and before the tee piece.
- A cooling bath could be used to limit the temperature of the absorbers.

5.2.2 Non isokinetic sampling equipment.

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

The sampling probe is a straight tube of about 5 mm to 8 mm internal diameter. The probe shall be temperature-controlled as indicated in 5.2.1.1.4, and designed in order to minimise unheated zone near the connection to the filter housing.

The particle filter shall be as described in 5.2.1.1.3.

Care shall be taken in order to avoid condensation by heating all the parts of the connecting line which are not rinsed after sampling.

The absorbers are described in 5.2.1.2.2 and optional apparatus in 5.2.1.2.5.

The unit for suction and metering the volume flow rate is described in 5.2.1.1.5.

5.2.3 Materials.

All the parts of the sampling equipment which are in contact with the gases to be analysed upstream of the absorbers, including probe nozzle, seals and flexible connections shall be resistant to corrosion and temperature. They shall not adsorb or react with gaseous chlorides and other compounds in the gases being sampled.

Borosilicated glass and titanium are convenient, and PTFE may also be used (seals, flexible connections, etc.).

Stainless steel shall not be used, since it is known to give gaseous chlorides losses in some cases.

Requirements are of course less stringent for parts of sampling system which are downstream the absorbers (pumps, flow rate meters, etc.), but the use of corrosion resistant materials is recommended.

5.2.4 Absorption solution.

Chloride-free water of at least grade 2 purity according to EN ISO 3696:1995 shall be used (conductivity less than $100 \mu\text{S}\cdot\text{m}^{-1}$).

5.3 Sampling procedure

5.3.1 Preparation and installation of equipment

5.3.1.1 Sampling location

The sampling location is chosen according to EN 15259.

5.3.1.2 Sampling point(s)

The sampling point(s) shall be chosen according to EN 15259.

5.3.2 Sampling procedure

5.3.2.1 Preparation

Taking into account the results of the preliminary survey (see EN 15259) and the planned test programme (see 5.1.1), prepare the required equipment in a clean working environment, either on-site or beforehand.

Use equipments with a valid calibration (flow, pressure, temperature and volume measuring devices).

Prior to each series of measurement, clean the probe and the filter holder.

Change the filter at least for each measurement series. For dust concentrations above 100 mg/m^3 , the filter shall be changed before each individual measurement.

Thoroughly wash the line and the absorber(s) to be used with the absorption solution (see 5.2.4).

NOTE 1 As far as possible, the use of the same pieces of equipment indiscriminately to measure low and high concentrations should be avoided (for example measurement upstream and downstream of a scrubber).

Sintered glass tips or plates may be heavily contaminated by chlorides, and shall be rinsed carefully.

Fill the absorber(s) with the same quantity of absorption solution as that used during the absorption efficiency checks (e.g. 40 ml to 100 ml for the absorbers shown in Annex A).

NOTE 2 It is a good practice to "passivate" the sampling line: install the probe in the duct, and condition the sampling system for not less than 10 min, in order to bring the whole sampling train up to the working condition and ensure that it operates correctly.

5.3.2.2 Checks

Check the velocities of flow at the sampling points, and calculate the sampling parameters to be achieved at each point (volume flow rate, sampling time), if required.

Ensure that the sampling train has been correctly assembled, and is leak tight, performing leak tests described in 5.3.3.2 before (and/or during) each. It is recommended to perform a leak test after sampling when a grid measurement has been performed.

Before each measuring series, and at least once a day, determine also the field blank (see 5.3.3.3).

5.3.2.3 Sampling

Taking into account the expected concentration to be measured and the analytical detection limit of the available analytical method, calculate the required sampled volume and sampling time. Calculate also, if relevant, the required sampling parameters (volume flow rate or sampling time) for each sampling point in the duct.

When carrying out isokinetic sampling using a side stream, the secondary volume flow rate in the absorber(s) can be kept constant.

The sampling procedure depends slightly on the kind of device used for suction and metering the volume flow rate (see 5.2.1.2 and 5.2.1.1.5).

The following sampling procedure shall be used when using equipment shown in Figures 1 and 2:

- a) preheat the probe and the filter housing;
- b) insert the probe in the duct;

- c) record gas meter values. Start the pumps and adjust volume flow rates to their required values;

NOTE 1 Care should be taken to prevent sucking back of the content of absorbers, due to negative pressure in the duct and to pressure variations in the sampling line when starting the pumps.

- d) periodically check volume flow rates and temperature during sampling, and adjust them if necessary.

Record the pressure, temperature and flow meters or gas meter readings. If sampling is carried out at several points of the duct section, move the probe from point to point within the duct without stopping the pumps, and then adjust the sampling parameters related to isokinetic sampling (flow rates) or to non iso-kinetic sampling (flow rate or sampling time). When a change of the measurement port is required, shut-off of the pump or the sampling line is necessary. When performing isokinetic sampling, the secondary volume flow rate can be kept constant;

- e) at the end of sampling period, record the final gas meter readings;
- f) dismantle the absorbers;
- g) rinse the absorbers and the connecting line with the absorption solution and collect the solution into a flask for analysis.

NOTE 2 If gas to be analysed is expected to have a very low gaseous chlorides content, special care should be taken to avoid excessive dilution caused by high rinsing volumes.

5.3.2.4 Other parameters to be recorded

Depending on the objective of the test programme, it may be necessary to measure or record other parameters during sampling period, e.g.:

- velocities and temperature in the stack, including continuous monitoring at a reference point if flow conditions are not steady;
- water vapour content and CO₂ or O₂ concentration, since these indications are often necessary to express gaseous chlorides concentrations under standard conditions.

NOTE Using continuous monitors of CO₂ or O₂ allows identification of leaks during sampling (see 5.3.3.2).

5.3.3 Validation of results

5.3.3.1 Parameters depending on the stationary source

It may occur that no suitable location exists in the plant, and/or that measurements have been performed during insufficient steadiness of the plant, which leads to an increase of the uncertainty of the measurements.

In such a case, it shall be clearly indicated in the test report that any deviation in the measurements is not in accordance with this European Standard, and details on the characteristics of the flow at the sampling location and/or on the variations of the volume flow rate in the duct while sampling shall be added in the test report.

5.3.3.2 Leak tests

Perform a leak test on the sampling train. Check the sampling line for leakage according to the following procedure or any other relevant procedure:

- assemble the complete sampling system, including charging the filter housing and absorbers;
- seal the nozzle or the probe inlet;
- switch on the pump(s);

— after reaching minimum pressure read the flow rate.

Leak flow rate shall be measured (e.g. by a rotameter) and shall not exceed 2 % of the expected sample gas flow rate.

Perform the leak test at the operating temperature unless this conflicts with safety requirements.

The integrity of the sampling system can be also tested during sampling by continuously measuring the concentration of a suitable stack gas component (e.g. O₂) directly in the stack and downstream the sampling line. Any systematic difference between those concentrations indicates a leak in the system.

It is recommended to perform a leak test after sampling if a grid measurement has been performed.

5.3.3.3 Field blank

This procedure is used to ensure that no significant contamination has occurred during all the steps of the measurement.

NOTE This includes for instance the equipment preparation in laboratory, its transport and installation in the field as well as the subsequent analytical work in the laboratory.

A field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this European Standard and including the sampling procedure described in 5.3.2.1 and 5.3.2.3 without the suction step, i.e. without starting and operating the suction device.

A field blank shall be carried out before each measurement series and after the series if the glassware is rinsed and re-used on site. The field blank taken after a measurement series may be used as the field blank taken before the following measurement series.

When equipment in contact with the measured component is not cleaned for reuse in the field (i.e. only prepared in laboratory or rinsed at the end of a series), if two or several measurement series are performed with equipment prepared at the same time and according to the same procedure, and if the measurements are performed on the same industrial process or on several lines of the same industrial process, then a single field blank shall be performed.

The average sampling volume shall be used for calculation of the field blank value expressed in mg·m⁻³.

The field blank shall be less than 10 % of the emission limit value (ELV). If the calculated value of the measurement is less than the field blank, the measured value result shall be reported as less or equal to the field blank. If the field blank is > 10 % of ELV, then the measurement is invalid.

5.3.3.4 Other elements

The operating conditions of the plant process during sampling, and any special circumstances and incidents which might have influenced the results shall be reported.

If it has been necessary to modify the method for any reason, then this modification shall be reported.

6 Analysis

6.1 Introduction

After sampling the solutions shall be analysed by one of the following methods:

— silver titration: potentiometric method (Method A);

- mercuric-thiocyanate spectrophotometry (Method B);
- ion-exchange chromatography (Method C).

The method to be used depends on the anticipated range of chloride concentration to be measured, therefore on HCl concentration in sampled gases, on sampled gas volumes, and on the final solution volumes (absorption solution and rinses).

Because the analytical detection limit of method A is approximately $0,5 \text{ mg}\cdot\text{l}^{-1}$ to $1 \text{ mg}\cdot\text{l}^{-1}$, this method shall not be used for the measurement of chloride concentrations less than $2 \text{ mg}\cdot\text{l}^{-1}$, which corresponds usually to gaseous chlorides concentrations in gases less than $1 \text{ mg}\cdot\text{m}^{-3}$ (sampled volume $0,2 \text{ m}^3$, solution volume approximately 100 ml).

Methods B and C, which have an analytical detection limit approximately $0,05 \text{ mg}\cdot\text{l}^{-1}$ to $0,1 \text{ mg}\cdot\text{l}^{-1}$, may be used in any case, if necessary after dilution of the solution to be analysed; their results may be considered as equivalent (see Annex B).

Any other method can be used provided its equivalence with one of these methods has been demonstrated.

6.2 Reagents and samples to be analysed

6.2.1 Reagents for analysis

All reagents shall be of analytical grade. The reagents common to the three methods are:

- chloride-free water of at least grade 2 purity according to EN ISO 3696:1995 (conductivity less than $100 \mu\text{S}\cdot\text{m}^{-1}$);
- stock solution of sodium chloride. Dissolve 1,603 g of sodium chloride previously dried 2 h at $110 \text{ }^\circ\text{C}$ in 1 l of water. 1 ml of solution corresponds to 1 mg gaseous chlorides;
- reference solution of sodium chloride freshly prepared by taking 10 ml of stock solution and diluting to 1 000 ml. This solution then corresponds to a concentration in gaseous chlorides of $0,01 \text{ mg}\cdot\text{ml}^{-1}$.

Other reagents for particular analytical methods are specified in 6.3.2 and 6.4.3.

6.2.2 Samples to be analysed

6.2.2.1 Absorption solutions (S_e)

Content and the rinses are poured into a flask after sampling. They are made up to a known volume (250 ml for example).

To determine absorption efficiency, the second absorber content can be analysed separately.

6.2.2.2 Samples of field blank

These samples are to make up to a known volume.

6.3 Silver titration: potentiometric method

6.3.1 Apparatus

6.3.1.1 Potentiometric determination system including a silver electrode and a reference electrode, or a combined silver electrode.

These electrodes shall release no chloride during the determination.

6.3.2 Reagents and solutions

6.3.2.1 Silver nitrate, reference solution $0,1 \text{ mol}\cdot\text{l}^{-1}$: it shall be freshly prepared e.g. from commercially available ampoules, and shall be kept in a brown bottle.

6.3.2.2 Silver nitrate, reference solution, $0,02 \text{ mol}\cdot\text{l}^{-1}$ freshly prepared by dilution to 1/5 of solution (see 6.3.2.1) and kept in a brown bottle.

6.3.2.3 Nitric acid solution, approximately $1 \text{ mol}\cdot\text{l}^{-1}$ prepared by diluting 70 ml of HNO_3 ($\rho = 1,42 \text{ g}\cdot\text{cm}^{-3}$) to 1 000 ml with water.

6.3.3 Procedure

Pipette an aliquot of solution to be analysed into a titration flask and add 5 ml of nitric acid (see 6.3.2.3).

Lower the electrodes into the liquid.

If necessary, add sufficient chloride free water (see 6.2.1) to allow the electrode to be covered.

Stir the medium with a magnetic bar.

According to the type of potentiometric determination system used, use the appropriate procedure as follows:

- record the whole potential titration curve and determine the volume at the inflexion point (see 6.3.4.2);
- using potentiometry with a predetermined final potential, i.e. determine, the final potential prior to the measurements, under measurement conditions, on a known quantity of chloride;
- continuously add identical volumes of titrate and determine the volume resulting in maximum potential increment.

Titrate the sample with silver nitrate solution described in 6.3.2.1 (see 6.3.2.2 in the case where using $0,1 \text{ mol}\cdot\text{l}^{-1}$ solution results in the use of small volume which cannot be determined accurately).

Repeat the procedure with chloride free water, in order to take into account the chemical blank value.

6.3.4 Interferences

6.3.4.1 Any ions reacting with silver ions (such as Br^- , I^- , CN^- , S^{2-} , SO_3^{2-} , SCN^-) may be interferent.

6.3.4.2 The recording titration curve method (see 6.3.3) allows the presence of interferents to be established, if any, when the curve shows more than one inflexion point.

When bromides and iodides have the same order of concentration as chlorides, recorded titration provides separate measuring spots and separate estimation. The measurement is carried out in the following order: iodide or bromide then chloride.

6.3.4.3 Interference by sulphides and sulphites can be eliminated by adding a few drops of concentrated hydrogen peroxide solution (30 %).

6.3.4.4 Interference from cyanides can be eliminated by adding formaldehyde.

Where thiocyanates are present as a result of the presence of both sulphides and cyanides, those ions can be eliminated by oxidation under heat using hydrogen peroxide solution at pH 10 in an ammoniacal medium. After oxidation, the aliquot solution shall be acidified by adding HNO_3 before titration.

6.3.5 Calculations

The gaseous chlorides quantity in the absorption solution is calculated using the following formula:

$$m_{\text{chlorides}} = \frac{V_s}{V_{s,a}} \times (V_{\text{AgNO}_3} - V_{o,\text{AgNO}_3}) \times C_{\text{Ag}} \times 36,5 \quad (3)$$

where

- $m_{\text{chlorides}}$ is the quantity of gaseous chlorides collected, expressed in milligrams HCl;
- V_s is the volume of absorption solution S_e (see 6.2.2.1), in millilitres (ml);
- $V_{s,a}$ is the aliquot portion of S_e (see 6.2.2.1) used for analysis, in millilitres (ml);
- V_{AgNO_3} is the volume of the Ag NO₃ solution used for dosing the solution S_e (see 6.2.2.1), in millilitres (ml);
- V_{o,AgNO_3} is the volume of the Ag NO₃ solution used for taking into account the chemical blank value, in millilitres (ml);
- C_{Ag} is the concentration of silver nitrate solution, in moles per litre (mol/l);
- 36,5 is the molar weight of gaseous chlorides.

6.4 Mercuric-thiocyanate spectrophotometry

6.4.1 Warning

WARNING — The use of mercury-containing solutions necessitates the observance of precautions for the handling and disposal of dangerous substances.

6.4.2 Apparatus

6.4.2.1 Spectrophotometer able to operate at 460 nm, with cells of optical path lengths of 1 cm to 5 cm.

6.4.3 Reagents

6.4.3.1 Mercuric-thiocyanate solution.

Dissolve 0,5 g of Hg(SCN)₂ in 100 ml of methanol.

6.4.3.2 Nitric acid approximately 6 mol·l⁻¹.

Dilute 400 ml of nitric acid ($\rho = 1,42 \text{ g}\cdot\text{cm}^{-3}$) in water to 1 000 ml.

6.4.3.3 Nitric acid approximately 1 mol·l⁻¹.

Dilute 70 ml of nitric acid ($\rho = 1,42 \text{ g}\cdot\text{cm}^{-3}$) in water to 1 000 ml.

6.4.3.4 Solution of ferric ammonium sulphate.

Dissolve 8 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 100 ml of $6\text{ mol}\cdot\text{l}^{-1}$ nitric acid.

6.4.4 Procedure

6.4.4.1 Establishing the reference straight-line plot

Pipette 2 ml, 5 ml, 10 ml and 15 ml respectively of the reference NaCl solution (see 6.2.1) into 50 ml flasks. Have an empty flask ready for the chemical blank determination.

To each flask add the following reagents, in the order of:

- 0,1 ml of nitric acid $1\text{ mol}\cdot\text{l}^{-1}$ (see 6.4.3.3);
- 8 ml of the ferric ammonium sulphate solution (see 6.4.3.4);
- 4 ml of mercuric thiocyanate solution (see 6.4.3.1).

Make up to volume with water and mix. Allow the coloration to develop for 20 min at $20\text{ }^\circ\text{C}$. The coloration then remains stable for approximately 3 h.

Measure the absorbance of the reference solutions and of the chemical blank at 460 nm. The length of the measurement cells shall be so chosen that absorbance values are lower than 1,0 and absorbance response f (mg HCl) is linear. Use a linear regression to establish the equation for the straight line.

NOTE The reference straight line should be checked each time the reagent is renewed.

6.4.4.2 Analysis of the sample

Pipette an aliquot of solution S_s (see 6.2.2.1) into a 50 ml flask and then add in the following order:

- 0,1 ml of nitric acid at $1\text{ mol}\cdot\text{l}^{-1}$ (see 6.4.3.3);
- 8 ml of ferric ammonium sulphate solution (see 6.4.3.4);
- 4 ml of mercuric thiocyanate solution (see 6.4.3.1).

Make up to volume with water and homogenise the content of the flask. Allow the coloration to develop for 20 min at $20\text{ }^\circ\text{C}$.

Measure the absorbance of the above solutions at 460 nm.

Use the equation for reference straight line to determine the quantity of gaseous chlorides present in the test specimen.

6.4.5 Interferences

Ions such as Br^- , I^- and CN^- can react with the mercuric-thiocyanate and cause interferences. Oxidising agents such as nitrites, hydrogen peroxide and chlorine also cause interferences, as do ions that form complexes with mercuric chlorides.

If these ions are suspected to be present, use one of the other methods (e.g. ion chromatographic which can indicate their presence).

6.4.6 Calculations

The gaseous chlorides mass in the absorption solution is calculated using the following formula:

$$m_{\text{chlorides}} = \frac{V_s}{V_{s,a}} \times m \quad (4)$$

where

$m_{\text{chlorides}}$ is the quantity of gaseous chlorides collected;

m is the quantity of gaseous chlorides present in the aliquot test sample of solution S_e (see 6.2.2.1);

V_s is the volume of absorption solution S_e (see 6.2.2.1), in millilitres (ml);

$V_{s,a}$ is the aliquot portion of S_e (see 6.2.2.1) used for analysis, in millilitres (ml).

6.5 Ion-exchange chromatography

This analytical method is described in EN ISO 10304-1. Therefore, the following is only a recall of the procedure.

The reference solutions shall be made from the reference NaCl solution (see 6.2.1). Make up to volume by water or by chromatographic eluent (see below).

Ensure that the baseline is stable, and that the system is free of chloride, by injecting water.

Inject the reference solutions and a chemical blank to cover the expected concentration range of the samples, while remaining within the linear response range of the apparatus. Using linear regression, establish the equation of the reference straight line.

Inject samples S_e , and calculate their gaseous chlorides concentrations. Periodically, and at the end of analysis, inject a reference solution in order to allow for possible drift of reference straight line.

Check for possible carbonate interference, which depends upon the column and eluent used.

With some chromatographic systems water distorts the base line at the elution volume for the chloride peak. This disturbance can be attenuated or removed altogether by using chromatographic eluent to make up to volume and to perform dilutions.

The gaseous chlorides quantity in the absorption solution is calculated using the following formula:

$$m_{\text{chlorides}} = V_s \times C \quad (5)$$

where

$m_{\text{chlorides}}$ is the mass of chlorides collected;

C is the concentration of chlorides of the solution S_e (see 6.2.2.1);

V_s is the volume of absorption solution S_e (see 6.2.2.1), in millilitres (ml).

7 Expression of results

The following is related to the whole measurement method, as described in the standard.

For each test, calculate the concentration of chlorides on a dry basis and under normal temperature and pressure, using the following equation:

$$C_{chlorides(Cl)} = m_{chlorides} / V_{std} \quad (6)$$

When the concentration of gaseous chloride shall be expressed as HCl, it is advisable to apply the following equation:

$$C_{chlorides(HCl)} = C_{chlorides(Cl)} \times \frac{M_{HCl}}{M_{Cl}} \quad (7)$$

where

$C_{chlorides(Cl)}$ is the chlorides content at standard conditions of pressure and temperature and dry basis, expressed in milligrams Cl⁻ per cubic metre;

$m_{chlorides}$ is the quantity of gaseous chlorides collected in the sampling device, determined in accordance with 6.3.4.2, 6.4.6 or 6.5, in milligrams Cl⁻;

V_{std} is the volume of gas sampled under standard conditions and dry basis, in cubic metres (m³);

M_{Cl} is the molar mass of chloride;

M_{HCl} is the molar mass of hydrogen chloride.

Concentrations are generally expressed at a reference concentration of O₂ defined in the European Directives:

- 11 % for incineration of waste in waste incinerators;
- 10 % for co-incineration of waste in cement kilns;
- 3 % for combustion of gas or liquid fuels;
- 6 % for combustion of solid fuels;
- 15 % for gas turbines.

The corrected concentration of measurand C_{corr} is calculated using the followed equation:

$$C_{corr} = \frac{21 - O_{2,ref}}{21 - O_{2,meas}} \times C_{actual} \quad (8)$$

where

C_{corr} is the corrected concentration of measurand;

C_{actual} is the measured concentration of measurand at actual O₂ concentration;

$O_{2,meas}$ is the measured mean dry oxygen content during the sampling time;

$O_{2,ref}$ is the oxygen reference concentration.

8 Determination of the characteristics of the method: sampling and analysis

8.1 General

When this European Standard is used as the SRM, the user shall demonstrate that:

- performance characteristics of the method given in Table 1 are better than the minimum performance criteria; and
- the overall uncertainty calculated by combining values of selected performance characteristics by means of an uncertainty budget is less than 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.

NOTE The required uncertainty results from the capacity of the method tested in the field (Annex D) and in the laboratory (see performance characteristics in Tables 1 and 2 and Annex C).

The values of the selected performance characteristics shall be evaluated:

- for sampling step: by means of laboratory tests in order to determine uncertainty of the calibration of the equipment and by means of field tests in order to determine other parameters;
- for analytical step: by means of laboratory tests.

8.2 Relevant performance characteristics of the method and performance criteria

8.2.1 General

The uncertainty of the measured values is influenced by:

- the sampling line and conditioning system;
- the sampling procedure;
- the analysis;
- the site specific conditions.

The uncertainty budget is drawn up according to 8.3.

8.2.2 Sampling procedure

Table 1 gives an overview of the relevant performance characteristics and performance criteria.

Table 1 — Performance characteristics and minimum performance criteria of the sampling system

Performance characteristic for sampling	Performance criterion
Determination of the volume of the absorption solution	$\leq 1,0$ % of the volume of solution
Volume gas meter: — uncertainty of sample volume ^b — uncertainty of temperature ^b — uncertainty of absolute pressure ^b	$\leq 2,0$ % of the volume of gas sampling ^a $\leq 2,5$ K ^a $\leq 1,0$ % of the absolute pressure ^a
Absorption efficiency ^c	> 95 %
Leak in the sampling line ^c	$\leq 2,0$ % of the nominal flow rate
Value of the field blank ^c	$\leq 10,0$ % of ELV
<p>^a Performance criteria corresponding to the uncertainty of calibration.</p> <p>^b The uncertainty of the sampled volume is a combination of uncertainties due to: calibration, drift (random drift, drift between two calibrations), reading and repeatability. The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties related to: calibration, drift (random drift, drift between two calibrations), reading.</p> <p>^c These characteristics correspond to assurance quality checks which are not included in the calculation of overall uncertainty.</p>	

8.2.3 Analyse procedure

8.2.3.1 Sources of uncertainty

Main possibly sources of uncertainty associated to analysis are:

a) for analysis by ion chromatography:

- 1) performance characteristics of the analysis equipment;
- 2) preparation of calibration standards: purity of stock standard solution, and ratio of dilutions;
- 3) linearity of calibration curve depending on the extend of working range;
- 4) measurement of volume of aliquot solution injected for analyse (ratio of the total absorption solution volume and the volume of the aliquot taken for injection);
- 5) if a dilution of the absorption solution is necessary before analyse: ratio of dilution;
- 6) interferences;
- 7) drift of retention time;
- 8) analytical repeatability;

b) for analysis by titration:

- 1) performance characteristics of analytical equipment;

- 2) preparation of standard volumetric solution used for titration;
 - 3) adjustment of pH of absorption solution;
 - 4) measurement of volumes of aliquots of titrated solutions (ratio of the volume of the sample solution to be titrated and the volume of the aliquot taken): for the absorption solution and chemical blank;
 - 5) detection of the colour change;
 - 6) measurement of volume of standard volumetric solution used for titration;
 - 7) interferences;
 - 8) analytical repeatability;
- c) for analysis by mercuric-thiocyanate spectrophotometry:
- 1) performance characteristics of the analysis equipment;
 - 2) preparation of calibration standards: purity of stock standard solution, and ratio of dilutions;
 - 3) linearity of the calibration curve;
 - 4) if a dilution of the absorption solution is necessary before analysis: ratio of dilution;
 - 5) interferences;
 - 6) repeatability.

8.2.3.2 Performance criterion of analysis

Because all the components of uncertainty attached to the analysis are difficult to identify and to estimate, the laboratory can determine the overall uncertainty due to analysis by taking the standard deviation of analytical repeatability calculated during an interlaboratory comparison. A maximum performance criterion is given in the following Table 2.

Table 2 — Performance characteristics of analytical procedure

Performance characteristic	Performance criterion
Standard deviation of analytical repeatability of chloride ions analysis for concentrations > 10 D _L ^a	≤ 2,5 % of the measured value (value of quantity of chloride ions in the solution; in mg HCl/l of solution)
^a Analytical detection limit (see 3.1.3 and D.1).	

8.3 Establishment of the uncertainty budget

An uncertainty budget shall be established to evaluate whether or not the method fulfils the requirements for a maximum allowable overall uncertainty. An uncertainty budget is a 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.

The overall uncertainty for this method used as a reference shall be lower than 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.

This overall uncertainty is calculated on dry basis and before correction to the O₂ reference concentration.

The principle of calculation of the overall uncertainty is based on the law on propagation of uncertainty laid down in ENV 13005:

- Determine the standard uncertainties attached to the performance characteristics to be included in the calculation of the budget uncertainty by means of laboratory and field tests, and according to ENV 13005.
- Calculate the uncertainty budget by combining all the standard uncertainties according to ENV 13005.
- Values of standard uncertainty that are less than 5 % of the maximum standard uncertainty can be neglected.
- Calculate the overall uncertainty at the daily emission limit value, on dry basis.

An example of the evaluation of overall uncertainty is given in Annex C.

9 Measurement report

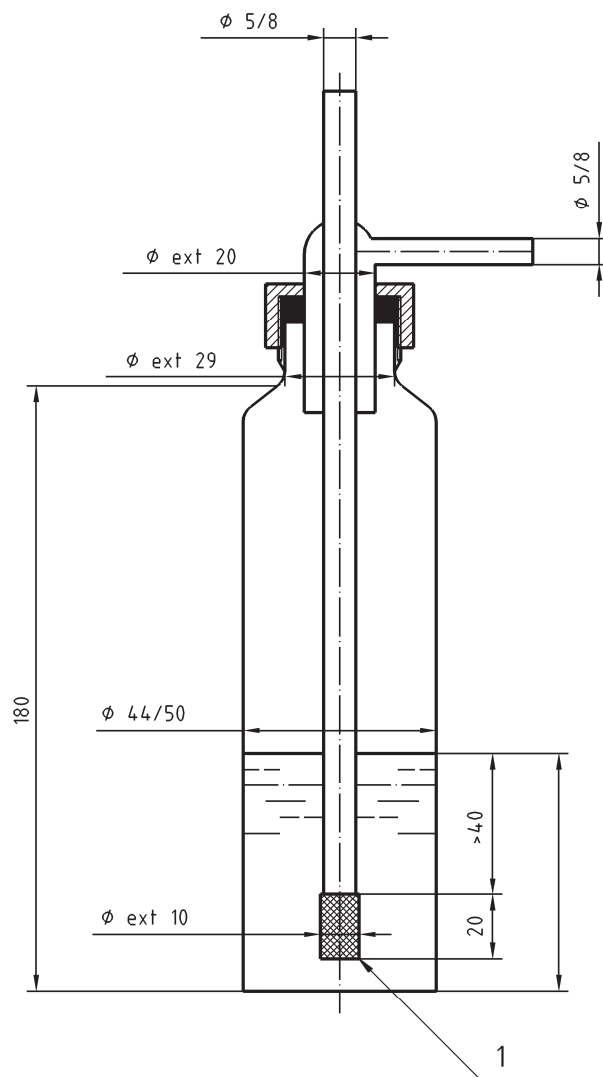
The measurement report shall provide a comprehensive account of the measurements, a description of the measurement objectives and the measurement plan. It shall provide sufficient details to enable the results to be traced back through the calculations to the collected basic data and process operating conditions. The measurement report shall comply with EN 15259:2007, Clause 9.

Annex A (informative)

Examples of absorbers

As an example, an absorber assembled as showing in Figure A.1 allows an absorption efficiency greater than 95 % to be achieved at the sampling volume flow rate, of $2 \text{ l}\cdot\text{min}^{-1}$ to $3 \text{ l}\cdot\text{min}^{-1}$ with the bottle filled to an initial volume of 100 ml.

Dimensions in millimetres



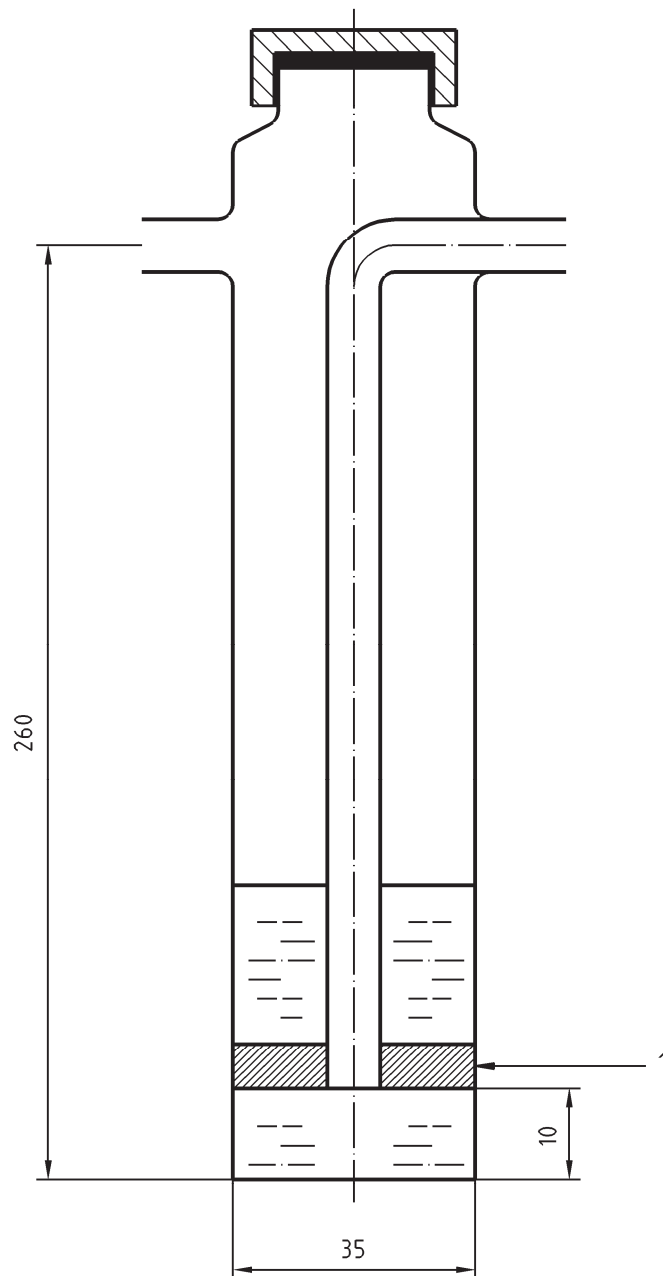
Key

- 1 Sintered frit

Figure A.1 — Example of a suitable washing bottle

The absorber shown in Figure A.2 allows an absorption efficiency greater than 95 %, which can be achieved at the sampling volume flow rate of $2 \text{ l}\cdot\text{min}^{-1}$ to $3 \text{ l}\cdot\text{min}^{-1}$ with the bottle filled to an initial volume of 40 ml.

Dimensions in millimetres



Key

- 1 Sintered frit

Figure A.2 — Alternative design of a suitable washing bottle

Annex B (informative)

Comparison between mercuric-thiocyanate spectrophotometry and ion exchange chromatography method (methods B and C)

After sampling of gases emitted by a municipal refuse incinerator (range of HCl concentration $5 \text{ mg}\cdot\text{m}^{-3}$ to $15 \text{ mg}\cdot\text{m}^{-3}$), 26 absorption solution samples were analysed by two different laboratories, the first one by method B, the second by method C, without comparing reference chloride solutions used by both laboratories.

In the tested range of chlorides concentrations in the absorption solutions ($0,2 \text{ mg}\cdot\text{l}^{-1}$ to $25 \text{ mg}\cdot\text{l}^{-1}$), Student and Wilcoxon tests were applied concluding that both methods may be considered as giving equivalent results.

Annex C (informative)

Example of assessment of compliance of the reference method for chlorides

C.1 General

This informative annex gives an example of calculation of the overall uncertainty.

C.2 Process of uncertainty estimation

C.2.1 General

The procedure for calculating measurement uncertainty as follows is based on the law on propagation of uncertainty laid down in EN ISO 14956 or ENV 13005. The calculation procedure presents different steps:

C.2.2 Determination of the model equation

Define the measurand and all the parameters that influence the result of the measurement. These parameters, called "input quantities" shall be clearly defined.

Identify all sources of uncertainty contributing to any of the input quantities or to the measurand directly.

Then the model equation, that is to say the relationship between the measurand and the influence quantities, shall be established, if possible in mathematical equation form.

C.2.3 Quantification of uncertainty components

Each uncertainty source is estimated to obtain its contribution to the overall uncertainty.

Use available performance characteristics of the measurement system, data from the dispersion of repeated measurements, data provided in calibration certificates.

Convert all uncertainty components (e.g. performance characteristics) to standard uncertainties of input and influence quantities.

C.2.4 Calculation of the combined uncertainty

Then the combined uncertainty u_c is calculated by combining standard uncertainties, by applying the "law of propagation of uncertainty".

In general, the uncertainty associated to a concentration is expressed in overall uncertainty form. The overall uncertainty U_c corresponds to the expanded combined uncertainty, obtained by multiplying by a coverage factor k : $U_c = k \times u_c$. The value of the coverage factor k is chosen on the basis of the level of confidence required. In most cases, k is taken equal to 2, for a level of confidence of approximately 95 %.

The following tables give one example of:

- the specific conditions of the site (Table C.1);
- the performance characteristics of the method (Table C.2) related to the parameters which can have an influence on the results.

C.3 Specific conditions in the field

Table C.1 — Example of measurement conditions

Specific conditions	Value/range
Studied concentration of gaseous chlorides (limit value of HCl for the site, at $O_{2,ref}$)	10 mg/m ³ ^a at standard conditions of temperature and pressure, and at 11 % O ₂ concentration corresponding to: $m_{chlorides}=1,02$ mg Cl ⁻ trapped in absorption solution
O ₂ reference concentration for the site: $O_{2,ref}$	11 % volume
O ₂ measured concentration: $O_{2,mes}$	12,3 % volume ± 6 % relative ($k = 2$)
Volume of gas sampled	0,132 m ³
Mean temperature (in Kelvins (K)) at the gas meter ^b	296,2 K
Mean absolute pressure at the gas meter ^c	100 281 Pa
Analyse	Ion chromatography
<p>^a m³: cubic meter at standard conditions of temperature (273 K) and pressure (101,325 kPa).</p> <p>^b Mean temperature is calculated from data recording of continuous temperature measurement (1 measurement / 30 s = 60 measurements in 30 min). The standard deviation of the mean $\sigma_{mean,T}$ of measurements calculated is equal to 0,854 K.</p> <p>^c Mean absolute pressure is calculated from five measurements of relative pressure at the gas meter and one measurement of atmospheric pressure during the sampling period (100,212 kPa).</p>	

Table C.2 — Example of measured values of relative pressure

Full scale of the pressure device: 0-200 Pa

Measurement	1	2	3	4	5	Mean	Standard deviation of the mean $\sigma_{mean,PreI}$ of measured values Pa
Relative pressure at the gas meter (Pa)	70,0	68,7	69,0	68,6	69,8	69,2	0,287

Mean absolute pressure: P = 100,281 kPa

C.4 Performance characteristics of the method

Table C.3 — Example of performance characteristics

Performance characteristics for the reference method	Performance criteria	Laboratory or field tests results
<u>Gas volume sampled V_{std} :</u> — Overall uncertainty of calibration — Standard deviation of repeatability of measurement — Drift between two adjustments — Reading	Expanded uncertainty of calibration $\leq 2,0$ % of the measured value	1,4 % of the measured value 0,3 % of the measured value 1,0 % of the measured value 0,000 2 m ³
<u>Temperature at the gas volume meter</u> — Overall uncertainty of calibration — Drift between two adjustments — Resolution	Expanded uncertainty of calibration $\leq 2,5$ K	1,0 K 1,0 K 0,1 K
<u>Absolute pressure at gas volume meter</u> Relative pressure at the gas volume meter; scale of the manometer: 0-200Pa — Overall uncertainty of calibration — Resolution — Lack of fit — Drift between two adjustments — Atmospheric pressure — Maximum permissible error — Reading	Expanded uncertainty of calibration $\leq 1,0$ % of the meas. value	$\pm 0,6$ Pa 0,01 Pa 1,4 % FS (full scale) 1,0 % FS ± 300 Pa 20 Pa
Absorption efficiency of the first absorber	$> 95,0$ %	98 %
<u>Gaseous chlorides quantity in the absorption solution $m_{\text{chlorides(Cl)}}$</u> — Standard deviation of analytical repeatability	$\leq 2,5$ % of the measured value	2,1 % of the measured value

C.5 Calculation of standard uncertainty of concentration measured

C.5.1 Model equation and application of rule of uncertainty propagation

$$C_{\text{chlorides}(HCl)} = C_{\text{chlorides}(Cl)} \times \frac{M_{HCl}}{M_{Cl}} = \frac{m_{\text{chlorides}}}{V_{std}} \times \frac{M_{HCl}}{M_{Cl}} \quad (\text{C.1})$$

$$\text{with } V_{std} = V_{T,P} \frac{T_{std}}{T} \times \frac{P}{P_{std}} \quad (\text{C.2})$$

where

$C_{\text{chlorides}(HCl)}$ is the mass concentration of gaseous chlorides at standard conditions of temperature and pressure, expressed as HCl (in mg HCl/m³);

$C_{\text{chlorides}(Cl)}$ is the mass concentration of gaseous chlorides at standard conditions of temperature and pressure, expressed as chlorides (in mg Cl/m³);

$m_{\text{chlorides}}$ is the mass concentration of gaseous chlorides (in milligrams (mg)) collected in the sample absorption solution;

V_{std} is the gas volume sampled from the gas meter, dry and at standard conditions, in cubic metres (m³);

T is the mean temperature (in Kelvins (K)) of the sampled gas at the gas-meter;

T_{std} is the standard temperature, 273 K;

$P = P_{rel} + P_{atm}$ is the absolute pressure (in kilopascals (kPa)) at the gas volume meter; P is equal to the sum of relative pressure measured at the gas volume meter P_{rel} plus atmospheric pressure P_{atm} ;

P_{std} is the standard pressure, 101,325 kPa;

$V_{T,P}$ is the gas volume sampled (in cubic metres (m³)) achieved by difference between values given by the gas volume meter at the end and at the beginning of the sampling period. The value at the beginning of the sampling period corresponds to a reading of an indicator; the value at the end of the sampling period corresponds to a reading of a measured value.

Calculation of the concentration:

$$V_{std} = 0,132 \times \frac{273}{296,2} \times \frac{100,281}{101,325} = 0,120 \text{ m}^3$$

The mass concentration at standard conditions of temperature and pressure, and at O₂ concentration measure, is equal to:

$$C_{\text{chlorides}(HCl)} = \frac{m_{\text{chlorides}}}{V_{\text{std}}} \times \frac{M_{HCl}}{M_{Cl}} = \frac{1,020}{0,120} \times \frac{36,5}{35,5} = 8,71 \text{ mg HCl/m}^3$$

Expression for the calculation of the combined uncertainty of $C_{\text{chlorides}(HCl)}$:

$$\frac{u^2(C_{\text{chlorides}(HCl)})}{(C_{\text{chlorides}(HCl)})^2} = \frac{u^2(m_{\text{chlorides}})}{(m_{\text{chlorides}})^2} + \frac{u^2(V_{\text{std}})}{(V_{\text{std}})^2} + \frac{u^2(M_{HCl})}{(M_{HCl})^2} + \frac{u^2(M_{Cl})}{(M_{Cl})^2} \quad (\text{C.3})$$

Uncertainty associated to the molar mass can be neglected:

$$\frac{u^2(C_{\text{chlorides}(HCl)})}{(C_{\text{chlorides}(HCl)})^2} = \frac{u^2(m_{\text{chlorides}})}{(m_{\text{chlorides}})^2} + \frac{u^2(V_{\text{std}})}{(V_{\text{std}})^2} \quad (\text{C.4})$$

Calculation of the combined uncertainty of V_{std} :

$$V_{\text{std}} = V_{T,P} \frac{T_{\text{std}}}{T} \times \frac{P}{P_{\text{std}}} = V_{T,P} \frac{T_{\text{std}}}{T} \times \frac{P_{\text{rel}} + P_{\text{atm}}}{P_{\text{std}}} \quad (\text{C.5})$$

Hypothesis: we consider that uncertainties of T_{std} and P_{std} are negligible.

$$u^2(V_{\text{std}}) = \left(\frac{\partial V_{\text{std}}}{\partial V_{T,P}} \right)^2 \times u^2(V_{T,P}) + \left(\frac{\partial V_{\text{std}}}{\partial T} \right)^2 \times u^2(T) + \left(\frac{\partial V_{\text{std}}}{\partial P_{\text{rel}}} \right)^2 \times u^2(P_{\text{rel}}) + \left(\frac{\partial V_{\text{std}}}{\partial P_{\text{atm}}} \right)^2 \times u^2(P_{\text{atm}}) \quad (\text{C.6})$$

Calculation of sensitivity coefficients:

$$\frac{\partial V_{\text{std}}}{\partial V_{T,P}} = \frac{T_{\text{std}}}{T} \times \frac{P_{\text{rel}} + P_{\text{atm}}}{P_{\text{std}}} = \frac{V_{\text{std}}}{V_{T,P}} \quad (\text{C.7})$$

$$\frac{\partial V_{\text{std}}}{\partial T} = -V_{T,P} \times T_{\text{std}} \times \frac{P_{\text{rel}} + P_{\text{atm}}}{P_{\text{std}}} \times \frac{1}{T^2} = -\frac{V_{\text{std}}}{T} \quad (\text{C.8})$$

$$\frac{\partial V_{\text{std}}}{\partial P_{\text{rel}}} = V_{T,P} \times \frac{T_{\text{std}}}{T} \times \frac{1}{P_{\text{std}}} = \frac{V_{\text{std}}}{P_{\text{rel}} + P_{\text{atm}}} = \frac{V_{\text{std}}}{P} \quad (\text{C.9})$$

$$\frac{\partial V_{\text{std}}}{\partial P_{\text{atm}}} = V_{T,P} \times \frac{T_{\text{std}}}{T} \times \frac{1}{P_{\text{std}}} = \frac{V_{\text{std}}}{P_{\text{rel}} + P_{\text{atm}}} = \frac{V_{\text{std}}}{P} \quad (\text{C.10})$$

Equation (C.6) is equivalent to:

$$u^2(V_{\text{std}}) = \left(\frac{V_{\text{std}}}{V_{T,P}} \right)^2 \times u^2(V_{T,P}) + \left(-\frac{V_{\text{std}}}{T} \right)^2 \times u^2(T) + \left(\frac{V_{\text{std}}}{P} \right)^2 \times u^2(P_{\text{rel}}) + \left(\frac{V_{\text{std}}}{P} \right)^2 \times u^2(P_{\text{atm}}) \quad (\text{C.11})$$

Equation (C.4) is equivalent to:

$$\frac{u^2(C_{\text{chlorides}(HCl)})}{(C_{\text{chlorides}(HCl)})^2} = \frac{u^2(m_{\text{chlorides}})}{(m_{\text{chlorides}})^2} + \frac{u^2(V_{T,P})}{(V_{T,P})^2} + \frac{u^2(T)}{(T)^2} + \frac{u^2(P_{\text{rel}})}{(P_{\text{rel}})^2} + \frac{u^2(P_{\text{atm}})}{(P_{\text{atm}})^2} \quad (\text{C.12})$$

C.5.2 Results of the standard uncertainties calculations

Table C.4 — Results of the standard uncertainty calculations

Performance characteristic	Value of standard uncertainty at limit value	Relative standard uncertainty
Determination of the quantity of gaseous chlorides $m_{chlorides}$ in the absorption solution	$u(m_{chlorides}) = \frac{2,10}{100} \times 1,02 = 0,0214$ mg Cl ⁻	$\frac{u(m_{chlorides})}{(m_{chlorides})} = 0,021$
Volume of sampled gas	$u^2(V_{T,P}) = u^2(cal, V_{T,P}) + u^2(rep, V_{T,P})$ $+ u^2(drift, V_{T,P}) + u^2(resol, V_{T,P})$ $u(V_{T,P}) = \sqrt{\left(\frac{1,4 \times 0,132}{2 \times 100}\right)^2 + \left(\frac{0,3 \times 0,132}{100}\right)^2 + \left(\frac{1/100 \times 0,132}{\sqrt{3}}\right)^2 + 2\left(\frac{0,0002}{2\sqrt{3}}\right)^2} = 0,0013 \text{ m}^3$	$\frac{u(V_{T,P})}{(V_{T,P})} = 0,0096$
Temperature at the gas volume meter	$u^2(T) = u^2(cal, T) + u^2(resol, T)$ $+ u^2(drift, T) + (\sigma_{mean,T})^2$ $u(T) = \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{0,1}{2\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2 + 0,854^2} = 1,146 \text{ K}$	$\frac{u(T)}{(T)} = 0,0039$
Relative pressure at the gas meter	$u^2(P_{rel}) = u^2(cal, P_{rel}) + u^2(resol, P_{rel})$ $+ u^2(lfit, P_{rel}) + u^2(drift, P_{rel}) + (\sigma_{mean,P_{rel}})^2$ $u(P_{rel}) = \sqrt{\left(\frac{0,6}{2}\right)^2 + \left(\frac{0,01}{2\sqrt{3}}\right)^2 + \left(\frac{1,4/100 \times 200}{\sqrt{3}}\right)^2 + \left(\frac{1/100 \times 200}{\sqrt{3}}\right)^2 + 0,287^2} = 2,030 \text{ Pa}$	$\frac{u(P_{rel})}{P} = 2,1 \cdot 10^{-5}$
Atmospheric pressure	$u^2(P_{atm}) = u^2(MPE, P_{atm}) + u^2(resol, P_{atm})$ $u(P_{atm}) = \sqrt{\left(\frac{300}{\sqrt{3}}\right)^2 + \left(\frac{20}{2\sqrt{3}}\right)^2} = 173,3 \text{ Pa}$	$\frac{u(P_{atm})}{P} = 0,00173$

C.5.3 Estimation of the combined uncertainty

Uncertainty associated to $C_{chlorides(HCl)}$ ·

The result of the calculation of the combined uncertainty according to Equation (C.12) is:

Standard uncertainty: $u(C_{chlorides(HCl)}) = 0,21 \text{ mg HCl/m}^3$

C.6 Calculation of the overall (or expanded) uncertainty

Overall uncertainty: $U(C_{\text{chlorides(HCl)}}) = \pm 0,41 \text{ mg HCl/m}^3 (k = 2)$;

$$U_{\text{rel}}(C_{\text{chlorides(HCl)}}) = \pm 4,7 \% (k = 2).$$

C.7 Uncertainty associated to the mass concentration of gaseous chlorides at O₂ reference concentration

The mass concentration of gaseous chloride at O₂ reference concentration is calculated as follows:

$$C_{\text{chlorides(HCl)},O_{2,\text{ref}}} = C_{\text{chlorides(HCl)}} \times \frac{21 - O_{2,\text{ref}}}{21 - O_{2,\text{meas}}} \quad (\text{C.13})$$

where

$C_{\text{chlorides(HCl)},O_{2,\text{ref}}}$ is the mass concentration at O₂ reference concentration (mg/m³);

$C_{\text{chlorides(HCl)}}$ is the mass concentration at O₂ measured concentration in the duct (mg/m³);

$O_{2,\text{ref}}$ is O₂ reference concentration (in % volume);

$O_{2,\text{meas}}$ is O₂ measured concentration in the duct (in % volume).

The uncertainty associated to this concentration is calculated by applying Equation (C.14):

$$u^2(C_{\text{chlorides(HCl)},O_{2,\text{ref}}}) = (C_{\text{chlorides(HCl)},O_{2,\text{ref}}})^2 \times \left(\frac{u^2(C_{\text{chlorides(HCl)}})}{(C_{\text{chlorides(HCl)}})^2} + \frac{u^2((O_{2,\text{meas}})_{\text{dry}})}{(21 - (O_{2,\text{meas}})_{\text{dry}})^2} \right) \quad (\text{C.14})$$

where

$u(C_{\text{chlorides(HCl)},O_{2,\text{ref}}})$ is the uncertainty associated the mass concentration at O₂ reference concentration;

$u((O_{2,\text{meas}})_{\text{dry}})$ is the uncertainty associated to the measured O₂ concentration.

The mass concentration at standard conditions of temperature and pressure, and at O₂ reference concentration, is equal to:

$$C_{\text{chlorides(HCl)},O_{2,\text{ref}}} = 8,71 \times \frac{21 - 11}{21 - 12,3} = 10,01 \text{ mg HCl/m}^3$$

The combined standard uncertainty is equal to:

$$u(C_{\text{chlorides}(HCl)O_{2,ref}}) = \sqrt{10,01^2 \times \left(\frac{0,204^2}{8,71^2} + \frac{\left(\frac{6}{2 \times 100} \times 12,3 \right)^2}{(21 - 12,3)^2} \right)} = 0,485 \text{ mg HCl/m}^3$$

Overall uncertainty: $U(C_{\text{chlorides}(HCl)O_{2,ref}}) = \pm 0,97 \text{ mg HCl/m}^3 (k = 2)$;

$$U_{rel}(C_{\text{chlorides}(HCl)O_{2,ref}}) = \pm 9,7 \% (k = 2).$$

Annex D (informative)

Performance characteristics of the whole measurement method

D.1 Analytical detection limit of the method

Based on measurements achieved at very low HCl concentration (less than $0,2 \text{ mg}\cdot\text{m}^{-3}$), the standard deviation of results is $0,07 \text{ mg}\cdot\text{m}^{-3}$. This leads to an estimation of the analytical detection limit (three times the standard deviation) which is about $0,2 \text{ mg}\cdot\text{m}^{-3}$. However, it has to be noted that these results were achieved by sampling during 2 h (sampled gas volumes 400 l to 500 l); by sampling only 30 min, the analytical detection limit would be higher.

D.2 Repeatability and reproducibility of the method in the field

Repeatability standard deviation s_r and reproducibility standard deviation s_R are determined by performing inter-laboratory tests.

Repeatability standard deviation s_r , repeatability confidence interval (CI_r) are calculated according to ISO 5725-2 and ISO 5725-6, from the results of the double measurements implemented by the same laboratory.

$$CI_r = t_{0,95;n-1} \times s_r \text{ and } r = \sqrt{2} \times t_{0,95;n-1} \times s_r$$

where

CI_r is the repeatability confidence interval;

s_r is the repeatability standard deviation;

$t_{0,95;n-1}$ is the Student factor for a level of confidence of 95 % and a degree of freedom of $n-1$ (n : number of double measurements).

Available data concerning the repeatability confidence interval are listed in Table D.1, which distinguishes between wet gases (water saturated) and dry gases (temperature in the duct much higher than the dew point).

In the range of $0 \text{ mg}\cdot\text{m}^{-3}$ to $230 \text{ mg}\cdot\text{m}^{-3}$, Table D.1 gives values of repeatability confidence interval.

Reproducibility standard deviation s_R , reproducibility confidence interval (CI_r) are calculated according to ISO 5725-2, from the results of parallel measurements performed simultaneously by several laboratories.

$$CI_R = t_{0,95;np-1} \times s_R$$

where

CI_r is the reproducibility confidence interval;

s_R is the reproducibility standard deviation;

$t_{0,95,np-1}$ is the Student factor for a level of confidence of 95 % and a degree of freedom of np-1 (n: number of measurements; p: number of laboratories).

Because most of the tests were performed in order to compare different sampling protocol results, only few data are available in order to estimate the reproducibility confidence interval.

Table D.1

Plant	Concentration mean value (extreme values) mg·m ⁻³	Number of double determinations	Reproducibility Standard deviation s_R mg·m ⁻³	Reproducibility confidence interval CI_R %
Wet gases	0,08 (0,02 to 0,2)	9	0,07	200
	5 (3 to 8)	15	0,7	30
	40 (35 to 45)	10	0,8	5
Dry gases	5 (1 to 15)	18	0,4	17
	4 (less than 10)	19	1,05	26
	14 (10 to 20)	14	0,8	6
	27 (20 to 40)	6	0,7	3
	215 (190 to 230)	9	6	7
Plant A:	Industrial waste incinerator, equipped with an electrostatic precipitator (ESP) and wet scrubber.			
Plants B and C:	Municipal refuse incinerator equipped with an ESP and wet scrubber.			
Plants D and E:	Municipal refuse incinerator equipped with and ESP and semi dry process (gas temperature: 140 °C).			
Plant F:	Coal boiler equipped with an ESP (gas temperature: 130 °C).			

Annex E (informative)

Significant technical changes

Details of significant technical changes between this European Standard and the previous edition are:

- This European Standard, EN 1911, is now a single document (instead of three) for the sampling and analysis dealing with chloride concentration determination expressed as HCl.
- Requirements of EN 15259 are integrated.
- A procedure for carrying out isokinetic sampling without a side stream is included.
- The temperature of filtration has undergone lengthy discussions and divergent opinions that have ultimately led to not set any value, but to establish the requirement that the filtration temperature shall be at least 20 °C above the dew point.
- Performance criteria and a maximum uncertainty are fixed (Clause 8).
- An example of uncertainty calculation is given in Annex C.

Bibliography

- [1] CEN/TS 14793, *Stationary source emission — Intralaboratory validation procedure for an alternative method compared to a reference method*
- [2] 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] ISO 5725-6, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*
- [4] ISO/IEC Guide 99:2007, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*
- [5] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste

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