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BSI Standards Publication

Stationary source emissions — Sampling and determination of hydrogen chloride content in ducts and stacks — Infrared analytical technique

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National foreword

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Émissions de sources fixes - Prélèvement et détermination du chlorure d'hydrogène dans les conduits et les cheminées - Technique analytique infrarouge

Emissionen aus stationären Quellen - Probenahme und Bestimmung von Chlorwasserstoff in Abgaskanälen und -kaminen - Infrarotverfahren

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Foreword

This document (CEN/TS 16429:2013) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

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1 Scope

This Technical Specification specifies an automatic method for determination of the mass concentration of hydrogen chloride (HCl) in ducts and stacks emitting to atmosphere. It describes the infrared analytical technique, including the sampling and gas conditioning system. The method should fulfil the performance characteristics requirements of this Technical Specification and the expanded uncertainty is less than 20 % relative at the daily Emission Limit Value (ELV).

In order to use an alternative method to this method, it is necessary to demonstrate equivalence according to the Technical Specification CEN/TS 14793. It is necessary that the capability to demonstrate equivalence is officially recognised by the national accreditation body or law.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN 15267-3:2007, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources*

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

3 Terms and definitions

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

3.1
adjustment of a measuring system
set of operations carried out on a measuring system so that it provides prescribed indications corresponding to given values of a quantity to be measured

[SOURCE: VIM 3.11]

3.2
ambient temperature
temperature of the air around the measuring system

3.3
drift
difference between two zero (zero drift) or span readings (span drift) at the beginning and at the end of a measuring period

3.4
emission limit value
ELV
emission limit value according to EU Directives on the basis of 30 min, one hour or one day

3.5
influence quantity
quantity that, in a direct measurement, does not affect the quantity that is actually measured, but affects the measurement result

[SOURCE: VIM 2.52, modified]

EXAMPLES

- Ambient temperature;
- atmospheric pressure;
- presence of interfering gases in the flue gas matrix;
- pressure of the gas sample.

3.6
interference

negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

3.7
lack of fit

systematic deviation within the range of application between the measurement result obtained by applying the calibration function to the observed response of the measuring system measuring test gases and the corresponding accepted value of such test gases

Note 1 to entry: Lack of fit may be a function of the measurement result.

Note 2 to entry: The expression “lack of fit” is often replaced in everyday language by “linearity” or “deviation from linearity”.

3.8
measurand

quantity intended to be measured

[SOURCE: VIM 2.3]

3.9
measuring system

complete set of measuring instruments and other equipment assembled to carry out specified measurements

[SOURCE: VIM 3.2, modified]

3.10
performance characteristic

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

3.11
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 to entry: Repeatability conditions include:

- the same measurement procedure;
- the same laboratory;
- the same measuring system, used under the same conditions;
- the same location;
- repetition over a short period of time.

Note 2 to entry: Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this Technical Specification, the repeatability is expressed as a value with a level of confidence of 95 %.

[SOURCE: VIM 2.20, modified]

3.12
residence time in the measuring system

time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.13
response time

duration between the instant when an input quantity value of a measuring instrument or measuring system is subjected to an abrupt change between two specified constant quantity values and the instant when a corresponding indication settles within specified limits around its final steady value

Note 1 to entry: By convention time taken for the output signal to pass from 0 % to 90 % of the final change.

[SOURCE: VIM 4.23, modified]

3.14
sampling plane

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

[SOURCE: EN 13284-1:2001, 3.8]

3.15
sampling point

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

[SOURCE: EN 13284-1:2001, 3.10]

3.16
span gas

test gas used to adjust and check a specific point on the response line of the measuring system

Note 1 to entry: This concentration is often chosen around 80 % of the upper limit of the range or around the emission limit value.

3.17
uncertainty

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

3.17.1
standard uncertainty u

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

3.17.2
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 1 to entry: In this Technical Specification, the expanded uncertainty is calculated with a coverage factor of k = 2n, and with a level of confidence of 95 %.

3.17.3
combined uncertainty u_c
standard uncertainty u_c attached to the measurement result calculated by combination of several standard uncertainties according to GUM

3.18
uncertainty budget
calculation table combining all the sources of uncertainty according to EN ISO 14956 or ENV 13005 in order to calculate the expanded uncertainty of the method at a specified value

4 Principle

4.1 General

This Technical Specification describes a method for the determination of the mass concentration of hydrogen chloride (HCl) in ducts and stacks emitting to atmosphere by means of an automatic analyser using the infrared absorption principle. The specific components and requirements for the sampling system and the infrared analyser are described in Clause 6. A number of performance characteristics with associated minimum performance criteria and an expanded uncertainty of the method are given. Requirements and recommendations for quality assurance and quality control are given for measurements in the field (see Table 1 in 7.3).

4.2 Measuring principle

The HCl concentration is measured with an infrared absorption method. The attenuation of infrared light passing through a sample cell is a measure of the concentration of HCl in the cell, according to the Lambert-Beer law. Not only HCl but also most hetero-atomic molecules absorb infrared light, in particular water and CO_2 have broad bands that can interfere with the measurement of HCl. Different technical solutions have been developed to suppress cross-sensitivity, instability and drift in order to design automatic monitoring systems with acceptable properties. For instance: Gas Filter Correlation, Tunable Diode Laser (TDL) and Fourier Transform Infrared Spectroscopy (FTIR).

Special attention is paid to infrared light absorbing gases such as water vapour, carbon dioxide, nitrous oxide, nitrogen dioxide and also hydrocarbons for some special applications.

Infrared analysers are part of extractive or in-situ systems. Most of them are combined with an extractive sampling system and a gas conditioning system. A representative sample of gas is taken from the stack with a sampling probe and conveyed to the analyser through the sampling line and gas conditioning system. The values from the analyser are recorded and/or stored by means of electronic data processing.

The concentration of HCl is measured in volume/volume units (if the analyser is calibrated using a volume/volume standard). The final results for reporting are expressed in milligrams per cubic meter using standard conversion factors (see Clause 10).

5 Sampling system

5.1 General

A representative volume (see 8.2.1) is extracted from the flue gas for a fixed period of time at a controlled flow rate. A filter removes the dust in the sampled volume before the sample is conditioned and passes to the analyser. Three different sampling and conditioning configurations can be used in order to avoid uncontrolled water vapour condensation in the measuring system. These configurations are:

- configuration 1: removal of water vapour through elimination using a permeation drier;
- configuration 2: maintaining the temperature of the sampling line up to the heated analyser;

- configuration 3: for in situ measurements.

Conditions and layout of the sampling equipment contribute to the expanded uncertainty. In order to minimise this contribution to the expanded uncertainty of the method, performance criteria for the sampling equipment and sampling conditions are given in 5.2 and 7.2.

5.2 Sampling probe

In order to access the representative sampling point(s) of the sampling plane, probes of different lengths and inner diameters may be used. The design and configuration of the probe used shall ensure the residence time of the sample gas within the probe is minimised in order to reduce the response time of the measuring system.

The procedure described in 8.1 shall be used when a lack of homogeneity in the flue gas is suspected.

5.3 Filter

The filter shall be made of an inert material (e.g. ceramic with an appropriate pore size). The particle filter shall be changed or cleaned periodically depending on the dust loading at the sampling site.

Overloading of the particle filter may increase the pressure drop in the sampling line.

5.4 Sampling line

The sampling line shall be heated up to the conditioning system, where required. It shall be made of a suitable corrosion resistant material (e.g. borosilicate glass, ceramic or titanium could be used; PTFE is suitable for flue gas temperatures lower than 200 °C).

5.5 Conditioning system

5.5.1 Permeation drier (configuration 1)

It is important that all parts of the sampling equipment upstream of the analyser are made of materials that do not react with or absorb HCl. The temperature of its components coming into contact with the gas shall be maintained, upstream the permeation system, at a sufficiently high temperature (between 180 °C and 200 °C) to prevent salt formation and condensation in the sampling equipment (in the presence of water vapour (beyond in 15 %) and ammonia (few ppm), risk occurs to have salt even at temperatures of 165 °C -170 °C).

The permeation drier is used before the gas enters the analyser in order to separate water vapour from the flue gas. A dew-point temperature below 4 °C is required at the outlet of the permeation drier.

The concentrations, provided by this sampling configuration, are considered to be given on dry basis. However, the results may be corrected for the remaining water vapour (refer to the table of Annex A in EN 14790:2005).

This configuration shall not be used if the flue gas has an ammonia concentration higher than 1 ppm.

5.5.2 Heated line and heated analyser (configuration 2)

It is important that all parts of the sampling equipment upstream of the analyser are made of materials that do not react with or absorb HCl. The temperature of its components coming into contact with the gas shall be maintained at a sufficiently high temperature (between 180 °C and 200 °C) to prevent salt formation and condensation in the sampling equipment (in the presence of water vapour (beyond in 15 %) and ammonia (few ppm), risk occurs to have salt even at temperatures of 165 °C -170 °C).

If the concentrations are given on wet basis, they shall be corrected so that they are expressed on dry basis. The correction shall be made from the water vapour concentration measured in the flue gas. The uncertainty attached to this correction shall be part of the uncertainty budget.

5.5.3 In situ analysers (configuration 3)

A calibration system, evaluated during the certification process shall be available to determine zero and span drift for the whole system.

5.6 Sample pump

The sample pump shall be capable of operating to the specified flow requirements of the manufacturer of the analyser and pressure conditions required for the sample cell. The pump shall be resistant to corrosion. If an external pump is used it shall be compatible with the requirements of the analyser to which it is connected.

5.7 Secondary filter

The secondary filter is used to separate fine dust, with a pore size less than 5 µm. For example it may be made of glass-fibre, sintered ceramic, stainless steel or PTFE-fibre.

5.8 Flow controller and flow meter

This apparatus sets the required flow. A corrosion resistant material shall be used. The sample flow rate into the analyser shall be maintained within the analyser manufacturer's requirements. A controlled pressure drop across restrictors is usually employed to maintain flow rate control into the infrared analyser.

NOTE No additional flow controller or flow meter is necessary when they are part of the analyser itself.

6 Analyser equipment

6.1 General

The main parts of the analyser are typically:

- source of infrared radiation;
- optics to focus the radiation through the measuring cell to the infrared detector;
- a way of modulating the infrared beam;
- means to select a suitable wavelength or wavelengths to measure the gas;
- a measuring cell that the sample gas enters. In some designs there may be a reference cell;
- an infrared detector; and
- an amplifier and signal processing system to give an electrical output proportional to the HCl concentration.

The standard of construction and vibration/corrosion resistance shall be suited to industrial environments and to the composition of the flue gas.

In Annex A, schematic diagrams are given of several different examples of infrared analysers.

6.2 Pressure and temperature effects

The output signal of the analyser is proportional to the number of HCl molecules present in the absorption cell and depends on the absolute pressure and temperature in the absorption cell. The effects of variations of pressure and temperature in the absorption cell should be taken into account by the manufacturer to give results in reference conditions of 273 K and 101,3 kPa.

6.3 Sampling pump for the analyser

The sampling pump can be separate or part of the analyser. It shall be capable of operating within:

- the manufacturer's specified flow requirements for the analyser; and
- the pressure conditions required for the infrared absorption cell.

6.4 Interferences due to infrared absorbing gases

As various gases absorb infrared radiation, interference from these gases can occur when their infrared absorption bands coincide or overlap the HCl infrared absorption bands. The degree of interference varies among individual infrared analysers.

The primary interferent is water vapour. However water vapour interference shall be minimised by using suitable techniques.

If the automated method has been certified the attention shall be focussed on specific interference gases (i.e. carbon dioxide, hydrocarbons, N_2O, NO_2) which have shown that they have influence on the result.

Knowledge of the gas composition and the cross sensitivity of the analyser is useful to ensure interference with the measurement is minimised.

7 Determination of the characteristics of the method: analyser, sampling and conditioning line

7.1 General

The user of this Technical Specification shall demonstrate that:

- the performance characteristics of the method shall be equal or better than the associated performance criteria given in Table 1 of EN 15267-3:2007; and
- the expanded uncertainty of the method calculated by combining values of standard uncertainties associated with the performance characteristics is less than 20 % at the daily emission limit value, on dry basis and before correction to the specified value of O_2.

The values of the performance characteristics shall be evaluated by means of a laboratory test and a field test. An experienced laboratory recognised by the competent authority shall perform the laboratory and field tests.

It is the responsibility of the user to check the performance characteristics with a periodicity given in Table 2 (Clause 9). These performance characteristics shall be determined using EN 15267-3.

7.2 Relevant performance characteristics of the method and performance criteria

The uncertainty of the measured values by the method is not only influenced by the performance characteristics of the analyser itself but also by:

- the sampling line and conditioning system;
- the site specific conditions;
- the certified reference material used (e.g. compressed gas in cylinders, certified gas generator).

The performance characteristics of the method shall be evaluated in accordance with EN 15267-3.

Table 1 of EN 15267-3:2007 gives an overview of the relevant performance characteristics and performance criteria, which shall be determined during laboratory and field tests according to the relevant CEN procedures, and indicates values included in the calculation of the expanded uncertainty of the method.

7.3 Establishment of the uncertainty budget

An uncertainty budget shall be established to determine if the analyser and its associated sampling system fulfil the requirements for a maximum allowable expanded uncertainty of the method.

The method shall have an expanded uncertainty lower than 20 % at the daily emission limit value. This expanded uncertainty of the method is calculated on a dry basis and before correction to the O_2 reference concentration. If the concentrations of the automated method are given on a wet basis, a correction to dry basis shall be carried out. The uncertainty attached to the correction of water vapour content shall be added to the uncertainty budget. An example of calculation is given in Annex B.

The principle of calculation of the expanded uncertainty of the method is based on the law on propagation of uncertainty laid down in EN ISO 14956:

- determine the standard uncertainties for each value included in the calculation of the budget uncertainty by means of laboratory and field tests, and according to EN ISO 14956;
- calculate the uncertainty budget by combining all the standard uncertainties according to EN ISO 14956. This shall include the uncertainty of the certified reference material. It shall also take variations in the range of influence quantities and interferents of the specific site conditions into account. If these conditions are unknown, default values defined in Table 1 shall be applied. When corrections for residual water content in the flue gas are applied, the uncertainty attached to this correction shall be added to the uncertainty budget;
- values of standard uncertainty that are less than 5 % of the maximum standard uncertainty can be ignored; and
- calculate the expanded uncertainty of the method at the daily emission limit value, on a dry basis.

Table 1 — Default variations ranges of influence quantities and interferents to be applied for the determination of the uncertainty budget

Performance characteristic or component	Default variations range on site
Atmospheric pressure	± 3 kPa
Sample volume flow variation	In accordance with the manufacturer's recommendations
Ambient temperature	between 5 °C and 40 °C[a]
Influence of voltage	at -15 % below and at +10 % above nominal supply voltage
O_2	3 % to 21 %
H_2O	1 % to 30 %
CO	0 mg/m³ to 300 mg/m³
CO_2	0 % to 15 %
CH_4	0 mg/m³ to 50 mg/m³
N_2O	0 mg/m³ to 20 mg/m³
N_2O fluidised bed combustion	0 mg/m³ to 100 mg/m³
NO	0 mg/m³ to 300 mg/m³
NO_2	0 mg/m³ to 30 mg/m³
NH_3	0 mg/m³ to 20 mg/m³
SO_2	0 mg/m³ to 200 mg/m³
SO_2 coal fired power plants (without desulphurisation)	0 mg/m³ to 1 000 mg/m³

[a] Bigger ranges can be specified by the manufacturer.

8 Field operation

8.1 Measurement plan and sampling strategy

The measurement plan and the sampling strategy shall be carried out in accordance with EN 15259 requirements.

The homogeneity can be demonstrated according to EN 15259.

To avoid long response times, the sample line shall be as short as possible. If necessary, a bypass pump shall be used. If necessary, a heated filter, appropriate to the dust loading, shall be used.

Typically, the following characteristics of flue gases should be considered before a field campaign:

- temperature of exhaust gases;
- flue gas moisture content and dew point;
- dust loading;

- expected concentration range of HCl and emission limit values;
- expected concentration of potentially interfering substances, including at least the components listed in Table 1; and
- flue gas cleaning system.

The full scale shall be chosen to be adapted to the measuring task.

8.2 Setting of the analyser on site

8.2.1 General

The complete measuring system, the sampling line including the conditioning unit, where required and the analyser, shall be connected according to the manufacturer's instructions. The probe is inserted so that its open end is at the representative sampling point(s) in the duct (see 8.1).

After pre-heating, the flow passing through the sampling system and the analyser shall be adjusted to the chosen flow rate to be used during measurement. This flow should be maintained at a constant level.

The conditioning unit, where required, sampling probe, filter, connection tube and analyser shall be stabilised with respect to temperature and humidity before adjustment of the analyser.

Time resolution of the data recording system shall be adapted to the measuring task and to the response time of the measuring system.

8.2.2 Preliminary zero and span check, and adjustments

8.2.2.1 Test gases

The zero gas shall be a gas containing no significant amount of hydrogen chloride (for example, nitrogen or purified air).

The span gases used to adjust the analyser shall have a certified concentration of HCl. Any other adjustment system (e.g. cuvette) may be applied, provided it has been tested for the specific instrument configuration used and validated. The uncertainty on the certified reference material shall be less than ± 2 % for HCl.

When the analyser is used for regulatory purposes, the span gas shall have a known concentration of approximately the half hourly ELV, or 50 % to 90 % of the selected range of the analyser.

8.2.2.2 Adjustment of the analyser

At the beginning of the measuring period, zero and span gases are supplied to the sampling port of the analyser. Adjustments are made until the correct zero and span gas values are given by the data sampling system:

- adjust the zero value;
- adjust the span; The regulator shall be resistant to corrosive gas (e.g. made of stainless steel). It shall be equipped with a double entry. To ensure no residual moisture remains in the regulator and line, they shall be rinsed by dry air or nitrogen prior to injection of the HCl. A long passivation time may occur before a stable reading is reached. The analyser shall not be adjusted until a stable reading is reached. After injection of the span gas the regulator and line need to be rinsed again with dry air or nitrogen; and
- finally, the zero value shall be checked again to ensure there have been no significant changes (i.e. zero deviation lower than two times the repeatability at zero). If there is a problem, the procedure shall be repeated until an acceptable zero reading is obtained.

8.2.2.3 Check of the sampling system including the leak test

The sampling line shall be checked for leakage according to the following procedure or any other relevant procedure.

Assemble the complete sampling system. Seal off the end of the probe and switch on the pump. After reaching minimum pressure, read or measure the flow rate with an appropriate measuring device. The leak flow rate shall not exceed 2 % of the expected sample gas flow rate used during measurement.

Zero and span gas are supplied to the analyser through the sampling system, as close as possible to the inlet of the line (in front of the filter if possible). Differences between the readings obtained during the adjustment of the analyser and during the check shall be lower than 2 % rel. A long passivation time may be required to reach a stable HCl reading.

The leak test can be performed with another gas, such as CO or nitrogen (measurement of O_2) if the analyser is a multi-component analyser.

8.2.3 Zero and span checks after measurement

At the end of the measuring period and at least once a day, zero and span checks shall be performed at the inlet of the sampling probe by supplying test gases. The results of these checks (i.e. deviations between checks before and after measurement) shall be documented and included in the measurement report.

If the span or zero drifts are higher than 2 % of the span value, it is necessary to correct both for zero and span drifts. The results shall be rejected if the drift in zero or span is higher than 5 % of the span value.

Annex C provides an example of drift calculation and determination of the formula to correct data.

9 Ongoing quality control

9.1 Introduction

Quality control is critically important in order to ensure the uncertainty of the measured values for HCl is kept within the stated limits during monitoring periods in the field. This means maintenance, as well as zero and span adjustment procedures shall be followed, as they are essential for obtaining accurate and traceable data.

9.2 Frequency of checks

Table 2 shows the minimum required frequency of checks which are carried out under the responsibility of the user and according to the relevant European Standards for determination of performance characteristics.

Table 2 — Frequency of checks

Checks	Frequency	Action criteria
Cleaning or changing of particulate filters[a] at the sampling inlet and at the monitor inlet	Every campaign if needed[a]	
Regular maintenance of several parts of the monitor	As required by manufacturer	As required
Lack of fit	At least every year and after repair of the analyser	As required and when lack of fit > ± 2 % of the range
Cross interferences: the effect of significant interferences [b] shall be checked. Carry out the test at HCl zero level.	At least every year	The total interference effects at zero shall be lower than 4 % of the upper limit of the certification range. [c]

[a] The particle filter shall be changed periodically depending on the dust loading at the sampling site. During this filter change the filter housing shall be cleaned. Overloading of the particle filter may increase the pressure drop in the sampling line.

[b] Significant interferences lead to an interference higher than 1% of the range.

[c] Calculate the sum of the interferents with a positive impact and with a negative impact (use data of certification and replace the result of the corresponding interferent obtained during the test).

10 Expression of results

The readings from the analyser are converted to concentrations using the appropriate calibration graph. The results are expressed in milligrams per cubic metre, or parts per million by volume, on a dry basis at 273 K and 101,3 kPa.

For HCl the conversion factors at 273 K and 101,3 kPa are:

— 1 mg/m^3 = 0,614 ppm.

— 1 ppm = 1,629 mg/m^3.

— When results are given on wet basis, the concentration on dry basis are calculated according to the following formula:

$$C_\mathrm{d} = \frac{100}{100 - \mathrm{H_2O}} C_\mathrm{w} \qquad (1)$$

where

C_d is the concentration of the measurand on a dry basis;

C_w is the measured concentration of the measurand on a wet basis;

$\mathrm{H_2O}$ is the water vapour content measured in gas, in percentage/volume.

Concentrations are generally expressed at a reference concentration of O_2 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; and
- 15 % for gas turbines.

The corrected concentration of measurand C_{corr} is calculated using the following formula:

$$C_{corr} = \frac{21 - 0_{2,ref}}{21 - 0_{2,mes}} C_{actual} \qquad (2)$$

where

C_{corr} is the corrected concentration of measurand;

C_{actual} is the measured concentration of measurand at actual O_2 concentration;

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

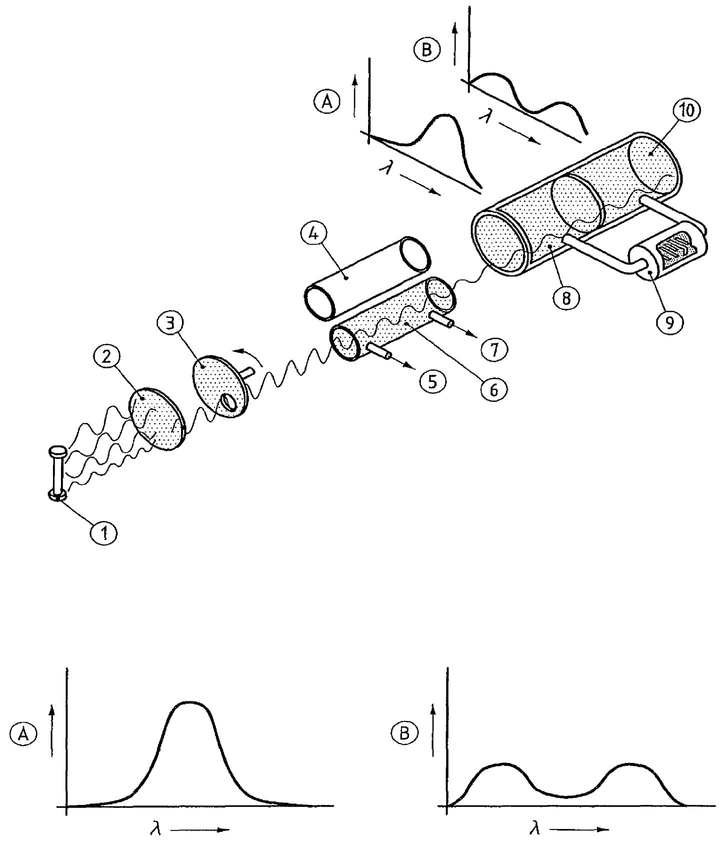
$O_{2,ref}$ is the oxygen reference concentration.

11 Measurement report

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

Annex A
(informative)

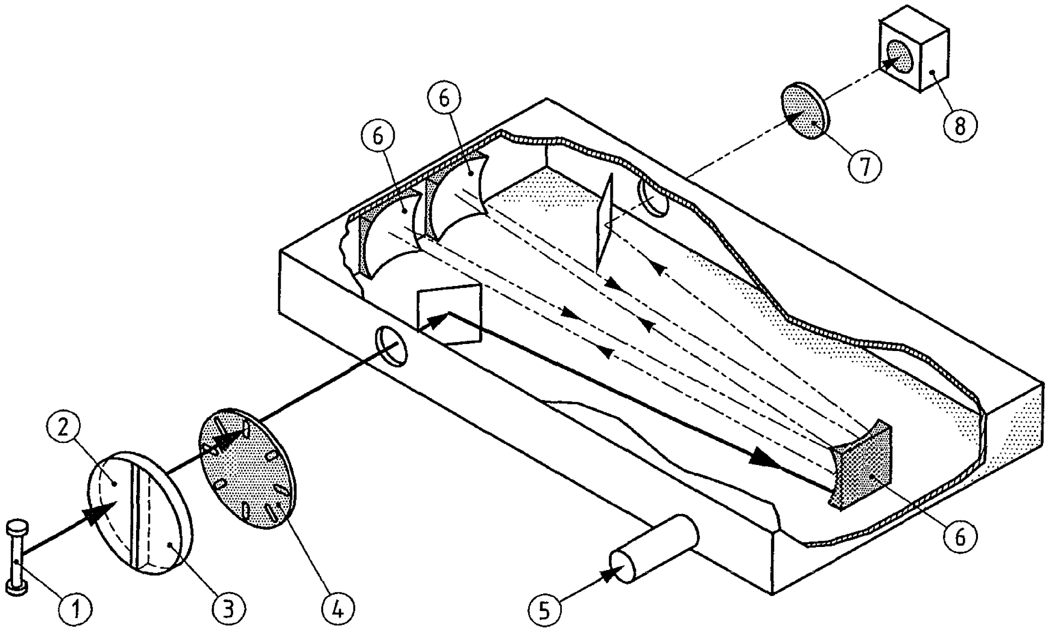
Examples of schematics of non-dispersive infrared spectrometer



Key

1	infrared lamp
2	light filter
3	chopper
4	reference cell
5	gas in
6	sample cell
7	gas out
8	first chamber
9	microflow sensor
10	second chamber
A	light absorption in first chamber
B	light absorption in second chamber
λ	wavelength

Figure A.1 — Example of a dual cell analyser



Key

1	infrared source
2	neutral filter (N_2)
3	gas filter cell (CO)
4	modulator
5	sample gas
6	mirror
7	filter
8	detector

Figure A.2 — Example of a gas filter correlation analyser

Annex B
(informative)

Example of assessment of compliance of non-dispersive infrared method for HCl with requirements on emission measurements

B.1 Process of uncertainty estimation

B.1.1 General

This informative annex gives an example of calculation of uncertainty budget established with configuration 1.

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

B.1.2 Determination of model function

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.

Establish the model function (i.e. the relationship between the measurand and the influence quantities) in mathematical equation form, if possible.

B.1.3 Quantification of uncertainty components

Each uncertainty source is estimated so that its contribution to the expanded uncertainty of the method is obtained.

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

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

B.1.4 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 with a concentration is expressed in expanded uncertainty form. The expanded uncertainty of the method 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 examples of:

- the specific conditions of the site (Table B.1) (i.e. the values and the variation range of the influence parameters);

- the performance characteristics of the method (Table B.2) related to the parameters which can have an influence on the response of the analyser, including the metrological performance of the analyser and the effect of influence parameters (i.e. environmental conditions like ambient temperature, voltage, pressure and chemical interferents).

B.2 Specific conditions in the site

Table B.1 — Site specific conditions, applied for the example

Specific conditions	Value/range
Range of analyser	15 mg/m^3
ELV	10 mg/m^3 (dry) at $O_{2,ref}$
H_2O concentration	10 %
Studied concentration of HCl (corresponds to the limit value of HCl for the site expressed on wet basis)	9 mg/m^3 (wet) at $O_{2,ref}$
Conditions on the field	
Sample volume flow	60 ± 5 l/h
Temperature during adjustment	285 K
Fluctuations of ambient temperature during the measurement period	283 to 308 K
Voltage variation	230 V ± 5 %
Atmospheric pressure during adjustment	99 kPa
Atmospheric pressure variation	99 – 100 kPa
O_2 reference concentration: $O_{2,ref}$	11 % volume
CO_2 concentration variations in the field	8 – 12 %
N_2O concentration variations in the field	negligible
CH_4 concentration variations in the field	0 – 10 mg/m^3
Calibration gas	8 ppm ± 2 %

B.3 Performance characteristics of the method

Table B.2 — Performance characteristics, applied for the example

Performance characteristic for infra-red method	Performance criteria	Example of results laboratory and field tests
Response time	≤ 200 s	120 s
Detection limit	≤ ± 2 % of the range	± 0,6 % of range
Lack of fit	≤ ± 2 % of the range	± 0,6 % of the range
Zero drift	≤ ± 2 % of the range/24 h	± 0,01 % of range/24 h
Span drift	≤ ± 2 % of the range/24 h	± 0,5 % of the range/24 h
Sensitivity to the sample volume flow	≤ 1 % of the range	0,2 % of the range/10 l/h
Sensitivity to atmospheric pressure	≤ 3 % of the range/2 kPa	0,4 % of the measured value/kPa
Sensitivity to ambient temperature	≤ 3 % of the range/10 K	0,5 %of range/10 K
Sensitivity to electric voltage at span level	≤ 2 % of the range/10 V	0,12 % of range/10 V
Interferents CO_2 (15 %) N_2O (20 mg/m^3) CH_4 (50 mg/m^3)	Total : ≤ ± 4 % of the range	 -0,98 mg/m^3 1,3 mg/m^3 2,61 mg/m^3
Standard deviation of repeatability in laboratory at zero	≤ 1 % of the range	0,3 % of range
Standard deviation of repeatability in laboratory at span level	≤ 2 % of the range	0,45 % of range

B.4 Calculation of standard uncertainty of concentration values given by the analyser

B.4.1 General

Model equations in this clause, as well as calculations of partial uncertainties are related to the values measured by the analyser and expressed in ppm.

Uncertainty associated to conversions in mg/m^3, expressed in reference conditions of pressure and temperature, is handled later in B.6.

Uncertainty associated to conversions in mg/m^3, expressed in dry basis, is handled later in B.7.

B.4.2 Model equation and application of rule of uncertainty propagation

The concentration in HCl is equal to the concentration given by the analyser plus corrections due to deviations associated to influence quantities and to the performance characteristics of the analyser.

$$C_{\mathrm{HCl,pp}m} = C_{\mathrm{HCl,read}} + Corr_{\mathrm{fit}} + Corr_{0,\mathrm{dr}} + Corr_{\mathrm{s,dr}} + Corr_{\mathrm{rep}} + Corr_{\mathrm{adj}} + \sum_{j=1}^{p} Corr_{\mathrm{inf}} + Corr_{\mathrm{int}} \tag{B.1}$$

where

$C_{\mathrm{HCl,ppm}}$	is the concentration of HCl in ppm;
$C_{\mathrm{HCl,read}}$	concentration of HCl given by the analyser;
$Corr_{\mathrm{fit}}$	correction of lack of fit;
$Corr_{0,\mathrm{dr}}$, $Corr_{\mathrm{s,dr}}$	corrections of zero drift and span drift;
$Corr_{\mathrm{rep}}$	correction of repeatability of the measurement;
$Corr_{\mathrm{adj}}$	correction of adjustment;
$\sum_{j=1}^{p} Corr_{\mathrm{inf}}$	correction of influence quantities (ambient temperature, atmospheric pressure, sample volume flow, voltage);
$Corr_{\mathrm{int}}$	correction of interferents.

The corrections are specific for each analyser. Sometimes, the value of correction is nil. For example, influence parameters (i.e. ambient temperature, atmospheric pressure and interferents) can increase or decrease during the measurement period and are generally not monitored; therefore, the best correction to apply is zero.

Whether the corrections are equal to zero or not, the uncertainties associated to these corrections shall be taken into account in the calculation of the global uncertainty. The combined standard uncertainty associated to HCl measurement is given by:

$$u^2(C_{\mathrm{HCl,ppm}}) = \sum_{i=1}^{N}\left[\left(\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Xi}\right)^2 u^2(Xi)\right] \tag{B.2}$$

where

$u(C_{\mathrm{HCl,ppm}})$	is the combined standard uncertainty associated to HCl measurement;
Xi, i=1 to N	are the influence quantities;
$\dfrac{\partial C_{\mathrm{HCl,ppm}}}{\partial Xi}$	is the sensitivity coefficient of $C_{\mathrm{HCl,ppm}}$, to X_{i};
$u(Xi)$	is the standard uncertainty associated to X_{i};
$\dfrac{\partial C_{\mathrm{HCl,ppm}}}{\partial Xi}u(Xi)$	is the partial uncertainty related to X_{i}.

The development of Formula (B.2) gives:

$$\begin{aligned}u^2(C_{\text{HCl,ppm}}) &= \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial C_{\text{HCl,read}}}\right)^2 u^2(C_{\text{HCl,read}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{fit}}}\right)^2 u^2(Corr_{\text{fit}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{0,dr}}}\right)^2 u^2(Corr_{\text{0,dr}}) \\ &+ \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{s,dr}}}\right)^2 u^2(Corr_{\text{s,dr}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{rep}}}\right)^2 u^2(Corr_{\text{rep}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{adj}}}\right)^2 u^2(Corr_{\text{adj}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{temp}}}\right)^2 u^2(Corr_{\text{temp}}) \\ &+ \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{a,press}}}\right)^2 u^2(Corr_{\text{a,press}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{s,vf}}}\right)^2 u^2(Corr_{\text{s,vf}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{V}}}\right)^2 u^2(Corr_{\text{V}}) + \left(\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{int}}}\right)^2 u^2(Corr_{\text{int}})\end{aligned} \quad \text{(B.3)}$$

B.4.3 Calculation of the partial uncertainties

— Sensitivity coefficients

$$\frac{\partial C_{\text{HCl,ppm}}}{\partial C_{\text{CO,read}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{fit}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{0,dr}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{s,dr}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{rep}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{adj}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{temp}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{a,press}}}$$
$$= \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{s,vf}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{V}}} = \frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{int}}} = 1$$

— $u(C_{\text{HCl,read}})$: the uncertainty related to the reading of the concentration is due to the resolution of the analyser and of the data acquisition. The uncertainty can be considered as negligible.

— $u(Corr_{\text{fit}})$: if $X_{\text{fit,max}}$ is the performance characteristic equal to the maximum deviation between the measured value and the value given through the linear regression achieved during the laboratory test, then, we can consider that the lack of fit has an equal probability to take any value included in the interval [-$X_{\text{fit,max}}$; + $X_{\text{fit,max}}$]. The standard uncertainty is calculated by application of a rectangular probability distribution.

If the performance characteristic is expressed in % of the range:

$$u(Corr_{\text{fit}}) = \frac{X_{\text{fit,max}} / 100 \times \text{range}}{\sqrt{3}}$$

$$\frac{\partial C_{\text{HCl,ppm}}}{\partial Corr_{\text{fit}}} u(Corr_{\text{fit}}) = \frac{X_{\text{fit,max}} / 100 \times \text{Range}}{\sqrt{3}}$$

— $u(Corr_{\text{0,dr}})$, $u(Corr_{\text{s,dr}})$: where $X_{\text{0,dr}}$ and $X_{\text{s,dr}}$ are the zero and the span drift, we can suppose that the drifts have the same probability to take any value included in the intervals [-$X_{\text{0,dr}}$;+ $X_{\text{0,dr}}$] and [-$X_{\text{s,dr}}$;+ $X_{\text{s,dr}}$]. The standard uncertainties are calculated by application of a rectangular probability distribution:

$u(Corr_{\text{0,dr}}) = \frac{X_{\text{0,dr}}}{\sqrt{3}}$ and $u(Corr_{\text{s,dr}}) = \frac{X_{\text{s,dr}}}{\sqrt{3}}$

Then $\frac{\partial C_{\text{CO,ppm}}}{\partial Corr_{\text{0,dr}}} u(Corr_{\text{0,dr}}) = \frac{X_{\text{0,dr}}}{\sqrt{3}}$ and $\frac{\partial C_{\text{CO,ppm}}}{\partial Corr_{\text{s,dr}}} u(Corr_{\text{s,dr}}) = \frac{X_{\text{s,dr}}}{\sqrt{3}}$

— $u(Corr_{\text{rep}})$: the standard uncertainty due to the repeatability is equal to the repeatability standard deviation calculated from the results of the repetitions of the measurements.

Several tests can be carried out at different concentrations (at least at zero and at one span level). But only one of the values shall be included in the calculation:

- choose the repeatability standard deviation corresponding to the closest concentration measured in stack (in the example, the emission limit value);
- or the highest repeatability (relative) standard deviation whatever is the concentration measured in stack.

In the example, the highest repeatability standard deviation has been chosen:

$$u(Corr_{\mathrm{rep}}) = \max(S_{0,\mathrm{rep}}\,;S_{\mathrm{s,rep}}) = S_{\mathrm{rep}}$$

where

$S_{0,\mathrm{rep}}$ is the standard uncertainty at level zero;

$S_{\mathrm{s,rep}}$ is the standard uncertainty at span level.

Then $\frac{\partial C_{\mathrm{CO,ppm}}}{\partial Corr_{\mathrm{rep}}} u(Corr_{\mathrm{rep}}) = S_{\mathrm{rep}}$

- Standard uncertainties associated to the influence quantities $u(Corr_{\mathrm{temp}})$, $u(Corr_{\mathrm{a,press}})$, $u(Corr_{\mathrm{s,vf}})$, $u(Corr_{\mathrm{V}})$: during laboratory test, the influence quantities are tested for one value of the parameter and the effects of the influence quantities are supposed to be proportional to the value of the parameter. The correction of the effect of an influence quantity is also proportional to its variation.

  If X_{j} is an influence quantity : $Corr_{\mathrm{Xj}} = c_{\mathrm{j}} \times \Delta X_{\mathrm{j}}$

where

c_{j} is a constant and ΔX_{j} is the variation of the influence quantity.

The uncertainty associated to the correction is given by:

$$u^2(Corr_{\mathrm{Xj}}) = \left(\frac{\partial Corr_{\mathrm{Xj}}}{\partial \Delta X_{\mathrm{j}}}\right)^2 u^2(\Delta X_{\mathrm{j}})$$

where

$\frac{\partial Corr_{\mathrm{Xj}}}{\partial \Delta X_{\mathrm{j}}} = c_{\mathrm{j}}$ is the sensitivity coefficient; the sensitivity factor corresponds to the effect of the variation ΔX_{j} of the influence quantity in the response of the analyser. Sensitivity coefficients are determined by laboratory tests;

$u(\Delta X_{\mathrm{j}})$ is the standard uncertainty associated to the variation of the influence quantity between the calibration period and the measuring period. We can suppose that the influence quantity has the same probability to take any value included in the interval ΔX_{j}.

In EN ISO 14956:2002, the calculation of the standard uncertainty associated to the variation of the influence quantity is given by the formula:

$$u(\Delta Xj)=\sqrt{\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,adj}})^2+(x_{\mathrm{j,min}}-x_{\mathrm{j,adj}})\times(x_{\mathrm{j,max}}-x_{\mathrm{j,adj}})+(x_{\mathrm{j,min}}-x_{\mathrm{j,adj}})^2}{3}}$$

where

$x_{\mathrm{j,min}}$ is the minimum value of the influence quantity X_{j} during the measuring period;

$x_{\mathrm{j,max}}$ is the maximum value of the influence quantity X_{j} during the measuring period;

$x_{\mathrm{j,adj}}$ is the value of the influence quantity X_{j} during the adjustment of the analyser.

Then $\frac{\partial C_{\mathrm{CO,ppm}}}{\partial Corr_{\mathrm{Xj}}}u(Corr_{\mathrm{Xj}})=\frac{\partial Corr_{\mathrm{Xj}}}{\partial X_{\mathrm{j}}}u(\Delta X_{\mathrm{j}})$

$$\frac{\partial C_{\mathrm{COppm}}}{\partial Corr_{\mathrm{Xj}}}u(Corr_{\mathrm{Xj}})=c_{\mathrm{j}}\sqrt{\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,adj}})^2+(x_{\mathrm{j,min}}-x_{\mathrm{j,adj}})\times(x_{\mathrm{j,max}}-x_{\mathrm{j,adj}})+(x_{\mathrm{j,min}}-x_{\mathrm{j,adj}})^2}{3}}$$

The calculation can be simplified in the two following cases:

- First case: if the value $X_{\mathrm{j,adj}}$ is at the centre of the interval $\lfloor X_{\mathrm{j,max}};X_{\mathrm{j,min}}\rfloor$:

$$u(\Delta X_{\mathrm{j}})=\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,min}})}{\sqrt{12}}$$

and $\frac{\partial C_{\mathrm{CO,ppm}}}{\partial Corr_{\mathrm{Xj}}}u(Corr_{\mathrm{Xj}})=c_{\mathrm{j}}\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,min}})}{\sqrt{12}}$

- Second case: if the value $X_{\mathrm{j,adj}}$ is equal to $X_{\mathrm{j,max}}$ or $X_{\mathrm{j,min}}$:

$$u(\Delta X_{\mathrm{j}})=\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,min}})}{\sqrt{3}}$$

and $\frac{\partial C_{\mathrm{CO,ppm}}}{\partial Corr_{\mathrm{Xj}}}u(Corr_{\mathrm{Xj}})=c_{\mathrm{j}}\frac{(x_{\mathrm{j,max}}-x_{\mathrm{j,min}})}{\sqrt{3}}$

- Standard uncertainties associated with the interferents (the case of the interferents is similar to the case of influence quantities). The effect of the interferents is tested for one concentration of interferent and is supposed to be proportional to the value of the parameter. The correction of the effect of an influence quantity is also proportional to its variation.

  If Int_{j} is an interferent for the measured compound, and ΔInt_{j} its variation interval during the measurement period, the standard uncertainty of the correction is given by:

$$u^2(Corr_{\mathrm{Intj}})=\left(\frac{\partial Corr_{\mathrm{Intj}}}{\partial \Delta Int_{\mathrm{j}}}\right)^2u^2(\Delta Int_{\mathrm{j}})$$

where

$\frac{\partial Corr_{\mathrm{Intj}}}{\partial \Delta Int_{\mathrm{j}}}$ is the sensitivity coefficient; sensitivity coefficients are determined by laboratory tests;

$u(\Delta Int_{\mathrm{j}})$ is the standard uncertainty associated to the variation of the concentration of the interferent $\mathrm{Int_j}$ during the measuring period. We can suppose that the influence quantity has the same probability to take any value included in the interval ΔInt_{j}.

In EN ISO 14956:2002, the calculation of the standard uncertainty associated to the variation of the influence quantity is given by the formula:

$$u(\Delta Int_{\mathrm{j}}) = \sqrt{\frac{(Int_{\mathrm{j,max}} - Int_{\mathrm{j,adj}})^2 + (Int_{\mathrm{j,min}} - Int_{\mathrm{j,adj}}) \times (Int_{\mathrm{j,max}} - Int_{\mathrm{j,adj}}) + (Int_{\mathrm{j,min}} - Int_{\mathrm{j,adj}})^2}{3}}$$

where

$Int_{\mathrm{j,min}}$ is the minimum concentration of the interferent Int_{j} during the measuring period;

$Int_{\mathrm{j,max}}$ is the maximum concentration of the interferent Int_{j} during the measuring period;

$Int_{\mathrm{j,adj}}$ is the concentration of the interferent Int_{j} in the calibration gas used to adjust the analyser.

Then $\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Intj}}} u(Corr_{\mathrm{Intj}}) = \left(\frac{\partial Corr_{\mathrm{Intj}}}{\partial \Delta Int_{\mathrm{j}}}\right) u(\Delta Int_{\mathrm{j}})$

$$\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Intj}}} u(Corr_{\mathrm{Intj}}) = \frac{c_{\mathrm{j}}}{Int_{\mathrm{j,test}}} \times \sqrt{\frac{(Int_{\mathrm{j,max}} - Int_{\mathrm{j,adj}})^2 + (Int_{\mathrm{j,min}} - Int_{\mathrm{j,adj}}) \times (Int_{\mathrm{j,max}} - Int_{\mathrm{j,adj}}) + (Int_{\mathrm{j,min}} - Int_{\mathrm{j,adj}})^2}{3}}$$

where

c_{j} is the sensitivity coefficient;

$Int_{\mathrm{j,test}}$ is the concentration of the interferent used to determine the sensitivity coefficient c_j during laboratory test;

$$\frac{c_{\mathrm{j}}}{Int_{\mathrm{j,test}}} = \frac{\partial Corr_{\mathrm{Intj}}}{\partial \Delta Int_{\mathrm{j}}}$$

The calculation can be simplified if the value $X_{\mathrm{j,adj}}$ is equal to zero, that is to say that the concentration of the interferent in the calibration gas is equal to zero, what is often the case. The standard uncertainty is given by:

$$u(\Delta Int_{\mathrm{j}}) = \sqrt{\frac{Int_{\mathrm{j,max}}{}^2 + Int_{\mathrm{j,min}} \times Int_{\mathrm{j,max}} + Int_{\mathrm{j,min}}{}^2}{3}}$$

$$\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Intj}}} u(Corr_{\mathrm{Intj}}) = \frac{c_{\mathrm{j}}}{Int_{\mathrm{j,test}}} \times \sqrt{\frac{Int_{\mathrm{j,max}}{}^2 + Int_{\mathrm{j,min}} \times Int_{\mathrm{j,max}} + Int_{\mathrm{j,min}}{}^2}{3}}$$

All interferents shall not be included in the calculation of the global uncertainty. In accordance with the standard EN ISO 14956, the calculation shall include the highest value between the sum $S_{\mathrm{int,p}}$ of the interferents with positive impact in the response of the analyser and the sum $S_{\mathrm{int,n}}$ of the interferents with negative impact.

$$S_{\mathrm{int,p}} = \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,p1}}} u(Corr_{\mathrm{int,p1}}) + \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,p2}}} u(Corr_{\mathrm{int,p2}}) + \ldots\ldots + \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,pk}}} u(Corr_{\mathrm{int,pk}})$$

$$S_{\mathrm{int,n}} = \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,n1}}} u(Corr_{\mathrm{int,n1}}) + \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,n2}}} u(Corr_{\mathrm{int,n2}}) + \ldots\ldots + \frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,nt}}} u(Corr_{\mathrm{int,nt}})$$

where

$S_{\mathrm{int,p}}$	is the sum of the interferents with positive impact;
$\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,p1}}} u(Corr_{\mathrm{int,p1}})$	is the partial uncertainty due to the 1st interferent with positive impact;
$\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,pk}}} u(Corr_{\mathrm{int,pk}})$	is the partial uncertainty due to the kth interferent with positive impact;
$S_{\mathrm{int,n}}$	is the sum of the interferents with negative impact;
$\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{Int,n1}}} u(Corr_{\mathrm{int,n1}})$	is the partial uncertainty due to the 1st interferent with negative impact;
$\frac{\partial C_{HCl,ppm}}{\partial Corr_{Int,nt}} u(Corr_{\mathrm{int,nt}})$	is the partial uncertainty due to the tth interferent with negative impact;

$$\left(\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{int}}}\right)^2 u^2(Corr_{\mathrm{int}}) = \max\left[S_{\mathrm{int,p}}{}^2; S_{\mathrm{int,n}}{}^2\right]$$

— $u(Corr_{\mathrm{adj}})$: the standard uncertainty $u(Corr_{\mathrm{adj}})$ is calculated from the uncertainty of the calibration gas. In general the uncertainty given by manufacturer is the expanded uncertainty; if X_{cal} is the expanded uncertainty of the calibration gas expressed in % relative, the standard uncertainty of the correction at ELV level is:

$$u(Corr_{\mathrm{adj}}) = \frac{X_{\mathrm{cal}} / 100 \times ELV}{2}$$

Then $\frac{\partial C_{\mathrm{HCl,ppm}}}{\partial Corr_{\mathrm{adj}}} u(Corr_{\mathrm{adj}}) = \frac{X_{\mathrm{cal}} / 100 \times ELV}{2}$

B.4.4 Result of combined uncertainty calculation

Table B.3 — Results of partial uncertainties calculation

Performance characteristic	Partial standard uncertainty	Value of partial standard uncertainty at limit value (in ppm)
Lack of fit	$u(Corr_{\text{fit}})$	$\frac{(0{,}6/100)\text{x}\,15}{\sqrt{3}} = 0{,}052$
Zero drift	$u(Corr_{\text{0,dr}})$	$\frac{(0{,}01/100)\text{x}\,15}{\sqrt{3}} = 0{,}0009$
Span drift	$u(Corr_{\text{s,dr}})$	$\frac{(0{,}5/100)\text{x}\,15}{\sqrt{3}} = 0{,}043$
Sensitivity to the sample volume flow	$u(Corr_{\text{s,vf}})$	$\frac{(0{,}2/100)}{10}\,\text{x}\,15\,\text{x}\,\frac{5\times 2}{\sqrt{3}} = 0{,}017$
Sensitivity to atmospheric pressure	$u(Corr_{\text{a,press}})$	$(0{,}4/100)\ \text{x}\ 9\times\frac{100-99}{\sqrt{3}} = 0{,}021$ for HCl
Sensitivity to ambient temperature	$u(Corr_{\text{temp}})$	$\frac{(0{,}5/100)}{10}\,\text{x}\,15\,\text{x}\sqrt{\frac{(308-285)^2+(308-285)(283-285)+(283-285)^2}{3}} = 0{,}096$
Sensitivity to electric voltage	$u(Corr_{\text{V}})$	$\frac{(0{,}12\,/100)}{10}\,\text{x}\,15\times\frac{2\times(230\times 5/100)}{\sqrt{12}} = 0{,}012$
Interferent: CH_4	$u(Corr_{\text{CH4}})$	$\frac{2{,}61}{50}\,\text{x}\sqrt{\frac{10^2}{3}} = 0{,}301$
Interferent: CO_2	$u(Corr_{\text{CO2}})$	$\frac{-0{,}98}{15}\,\text{x}\sqrt{\frac{12^2+12\times 8+8^2}{3}} = -0{,}41$
Repeatability in laboratory at span level	$u(Corr_{\text{rep}})$	$(0{,}45/100)\ \text{x}\ 15 = 0{,}0675$
Uncertainty of calibration gas	$u(Corr_{\text{adj}})$	$\frac{(2/100)\ \text{x}\ 9}{2} = 0{,}09$

B.4.5 Calculation of combined uncertainty

$S_{\text{int,n}} > S_{\text{int,p}}$

$$u(C_{\text{HCl,mg/m3}}) = \sqrt{\begin{aligned}&u^2(Corr_{\text{fit}}) + u^2(Corr_{\text{0,dr}}) + u^2(Corr_{\text{s,dr}}) + u^2(Corr_{\text{rep}}) + u^2(Corr_{\text{adj}}) + u^2(Corr_{\text{s,vf}})\\ &+ u^2(Corr_{\text{a,press}}) + u^2(Corr_{\text{temp}}) + u^2(Corr_{\text{volt}}) + S_{\text{int,n}}{}^2\end{aligned}}$$

$u(C_{\text{HCl,mg/m3}}) = 0{,}44$ mg/m^3 in wet and at pressure and temperature reference conditions

$U_{\text{c}}(C_{\text{HCl,mg/m}^3}) = \pm 0{,}88$ mg/m^3 (k=2) in wet and at pressure and temperature reference conditions

$U_{\mathrm{c,rel}}(C_{\mathrm{HCl,mg/m^3,rel}}) = \pm 9{,}8$ % relative (k=2) in wet and at pressure and temperature reference conditions

B.5 Uncertainty associated to the concentration on dry gas

The concentration expressed on dry gas is given by:

$$C_{dry} = C_{wet} \frac{100}{100 - H2O}$$

where:

C_{dry} is the concentration on dry gas;

C_{wet} is the concentration for the humid gas;

$H2O$ is the water vapour content of the gas.

The uncertainty associated to the concentration on dry gas is calculated using the following formula:

$$u^2(C_{dry}) = (C_{dry})^2 \times \left(\frac{u^2(C_{wet})}{(C_{wet})^2} + \frac{u^2(H2O)}{(100 - H2O)^2} \right)$$

where:

$u(C_{dry})$ is the standard uncertainty of the concentration on dry gas;

$u(C_{wet})$ is the standard uncertainty of the concentration on wet gas;

$u(H2O)$ is the standard uncertainty of water vapour content;

$u_{rel}(H2O)$ = 0,9 % (9 % of the measured value);

$u(C_{wet})$ = 0,44 mg/m^3 in wet and at pressure and temperature reference conditions;

C_{dry} = 10 mg/m^3 in dry and at pressure and temperature reference conditions;

C_{wet} = 9 mg/m^3 in wet and at pressure and temperature reference conditions;

➔ $u(C_{dry})$ = 0,158 mg/m^3 in dry and at pressure and temperature reference conditions;

$U_{\mathrm{c}}(C_{\mathrm{HCl,mg/m^3}}) = \pm 1{,}0$ mg/m^3 (k=2) in dry conditions;

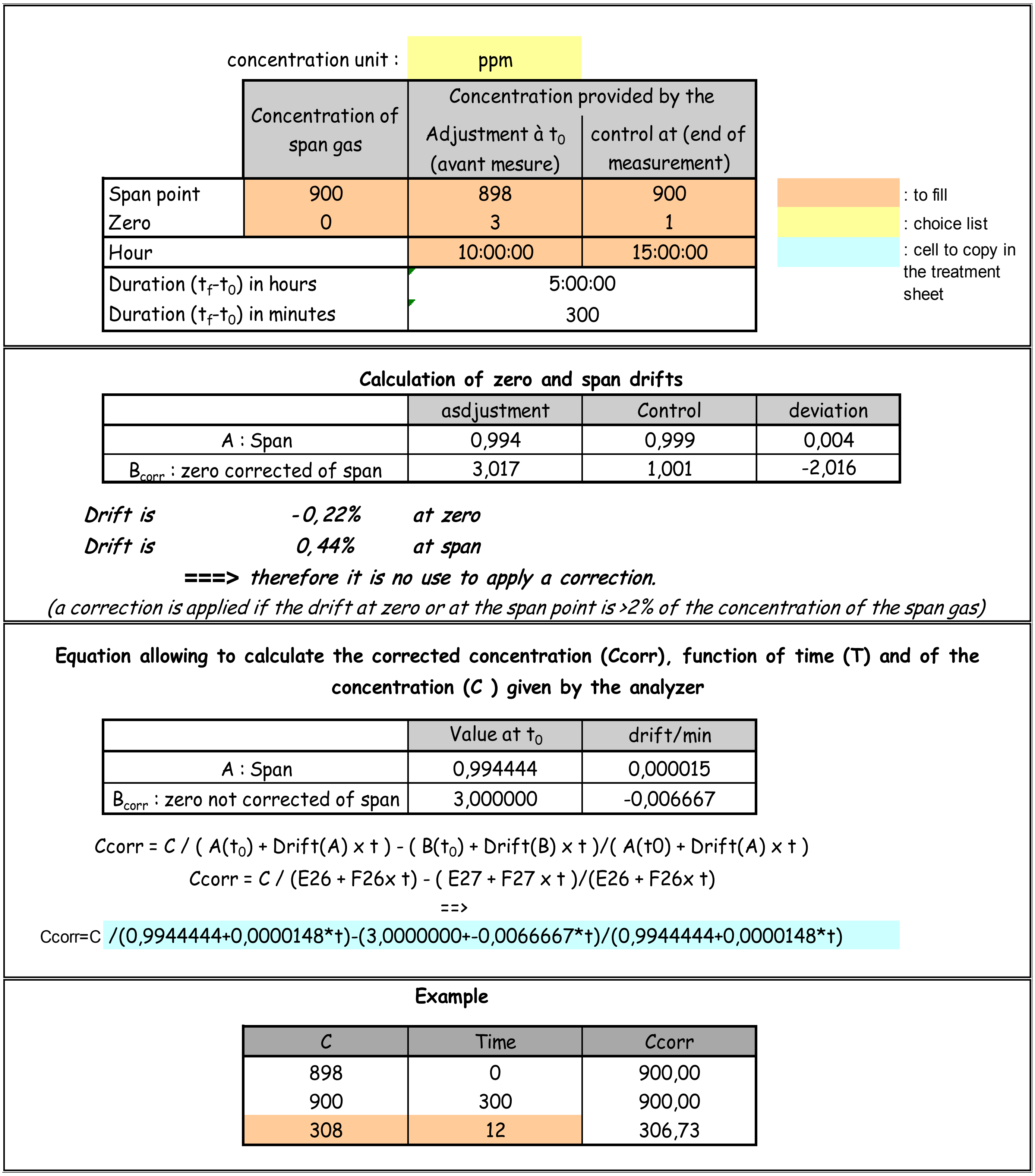
$U_{\mathrm{c,rel}}(C_{\mathrm{HCl,mg/m^3,rel}}) = \pm 10$ % relative (k=2) in dry conditions.

Conclusion: the measurement method fulfils the requirements.

Annex C
(informative)

Procedure for correction of data from drift effect

The drift is supposed to be proportional to the time:



concentration unit : ppm

	Concentration of span gas	Concentration provided by the	
		Adjustment à t_0 (avant mesure)	control at (end of measurement)
Span point	900	898	900
Zero	0	3	1
Hour		10:00:00	15:00:00
Duration (t_f-t_0) in hours		5:00:00	
Duration (t_f-t_0) in minutes		300	

🟧	: to fill
🟨	: choice list
🟦	: cell to copy in the treatment sheet

Calculation of zero and span drifts

	asdjustment	Control	deviation
A : Span	0,994	0,999	0,004
B_{corr} : zero corrected of span	3,017	1,001	-2,016

Drift is -0,22% at zero

Drift is 0,44% at span

===> therefore it is no use to apply a correction.

(a correction is applied if the drift at zero or at the span point is >2% of the concentration of the span gas)

Equation allowing to calculate the corrected concentration (Ccorr), function of time (T) and of the concentration (C) given by the analyzer

	Value at t_0	drift/min
A : Span	0,994444	0,000015
B_{corr} : zero not corrected of span	3,000000	-0,006667

Ccorr = C / (A(t_0) + Drift(A) x t) - (B(t_0) + Drift(B) x t)/(A(t0) + Drift(A) x t)

Ccorr = C / (E26 + F26x t) - (E27 + F27 x t)/(E26 + F26x t)

==>

Ccorr=C /(0,9944444+0,0000148*t)-(3,0000000+-0,0066667*t)/(0,9944444+0,0000148*t)

Example

C	Time	Ccorr
898	0	900,00
900	300	900,00
308	12	306,73

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