INTERNATIONAL STANDARD

ISO 21877

First edition
2019-08

Stationary source emissions — Determination of the mass concentration of ammonia — Manual method

Émissions de sources fixes — Détermination de la concentration en masse de l'ammoniac — Méthode manuelle

Reference number
ISO 21877:2019(E)

Contents

Page

Foreword .... **iv**

Introduction .... **v**

1 Scope **1**

2 Normative references **1**

3 Terms and definitions **1**

4 Symbols and abbreviated terms **3**

5 Principle of the method of measurement **5**

6 Sampling system **6**
- 6.1 General 6
- 6.2 Sampling equipment 6
  - 6.2.1 Non-isokinetic sampling 6
  - 6.2.2 Isokinetic sampling 7
- 6.3 Other equipment 9

7 Performance characteristics **9**
- 7.1 General 9
- 7.2 Performance characteristics of the sampling system 9
- 7.3 Performance characteristics of the analysis 10
  - 7.3.1 Sources of uncertainty 10
  - 7.3.2 Performance criterion of analysis 10
- 7.4 Establishment of the uncertainty budget 11

8 Field operation **11**
- 8.1 Measurement planning 11
- 8.2 Sampling strategy 11
- 8.3 Field blank 12
- 8.4 Leak test 12
- 8.5 Sampling 13
- 8.6 Sample transport and storage 13

9 Analytical determination **13**

10 Calculation of the results **14**

11 Measurement report **15**

Annex A (informative) **Validation of the method of measurement in the field** **16**

Annex B (informative) **Description of the analytical method — Spectrophotometry** **21**

Annex C (informative) **Description of the analytical method — Continuous flow analysis (CFA)** **25**

Annex D (informative) **Description of the analytical method — Ion chromatography** **28**

Annex E (informative) **Example of the calculation of the uncertainty budget** **32**

Annex F (informative) **Calculation of the uncertainty associated with a mass concentration expressed on dry gas and at an oxygen reference concentration** **40**

Bibliography **44**

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Ammonia emissions arise to a large extent from agriculture. Industries such as chemical production processes (e.g. fertilizer production plants) emit ammonia as well as power plants, cement factories and waste incineration plants with SCR and non-SCR reactors with ammonia slip. The ammonia emissions are measured and often controlled by legislation.

This document specifies an independent method of measurement for intermittent monitoring of ammonia emissions as well as for the calibration and validation of automated ammonia measuring systems.

This document can be used in conjunction with ISO 17179 which specifies performance characteristics of automated measuring systems (AMS) for the determination of the mass concentration of ammonia in waste gas. According to ISO 17179, permanently installed AMS for continuous monitoring of ammonia emissions are calibrated and validated by comparison with an independent method of measurement. The uncertainty of measured values obtained by permanently installed AMS for continuous monitoring are determined by comparison measurements with an independent method of measurement as part of the calibration and validation of the AMS. This ensures that the measurement uncertainty is representative of the emission at a specific plant.

Stationary source emissions — Determination of the mass concentration of ammonia — Manual method

1 Scope

This document specifies a manual method of measurement including sampling and different analytical methods for the determination of the mass concentration of ammonia (NH_3) in the waste gas of industrial plants, for example combustion plants or agricultural plants. All compounds which are volatile at the sampling temperature and produce ammonium ions upon dissociation during sampling in the absorption solution are measured by this method, which gives the volatile ammonia content of the waste gas.

This document specifies an independent method of measurement, which has been validated in field tests in a NH_3 concentration range of approximately 8 mg/m^3 to 65 mg/m^3 at standard conditions. The lower limit of the validation range was determined under operational conditions of a test plant. The measurement method can be used at lower values depending, for example, on the sampling duration, sampling volume and the limit of detection of the analytical method used.

NOTE 1 The plant, the conditions during field tests and the performance characteristics obtained in the field are given in Annex A.

This method of measurement can be used for intermittent monitoring of ammonia emissions as well as for the calibration and validation of permanently installed automated ammonia measuring systems.

NOTE 2 An independent method of measurement is called standard reference method (SRM) in EN 14181.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 7150-1, *Water quality — Determination of ammonium — Part 1: Manual spectrometric method*

ISO 11732, *Water quality — Determination of ammonium nitrogen — Method by flow analysis (CFA and FIA) and spectrometric detection*

ISO 14911, *Water quality — Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography — Method for water and waste water*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
mass concentration
mass of a substance in an emitted waste gas divided by the volume of the emitted waste gas

Note 1 to entry: Mass concentration is often expressed as milligrams per cubic metre (mg/m^3).

3.2
measurement site
place on the waste gas duct in the area of the *measurement plane(s)* (3.3) consisting of structures and technical equipment, for example working platforms, *measurement ports* (3.4), energy supply

Note 1 to entry: Measurement site is also known as sampling site.

3.3
measurement plane
plane normal to the centre line of the duct at the sampling position

Note 1 to entry: Measurement plane is also known as sampling plane.

3.4
measurement port
opening in the waste gas duct along the *measurement line* (3.5), through which access to the waste gas is gained

Note 1 to entry: Measurement port is also known as sampling port or access port.

3.5
measurement line
line in the *measurement plane* (3.3) along which the *measurement points* (3.6) are located, bounded by the inner duct wall

Note 1 to entry: Measurement line is also known as sampling line.

3.6
measurement point
position in the *measurement plane* (3.3) at which the sample stream is extracted, or the measurement data are obtained directly

Note 1 to entry: Measurement point is also known as sampling point.

3.7
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 *measurement point* (3.6)

3.8
field blank
test sample obtained according to the field blank procedure

3.9
field blank value
result of a measurement performed according to the field blank procedure at the plant site and in the laboratory

3.10
uncertainty of measurement
parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

3.11
standard uncertainty
u
uncertainty of the result of a measurement expressed as a standard deviation

3.12
combined uncertainty
u_c
standard uncertainty (3.11) attached to the measurement result calculated by combination of several standard uncertainties according to the principles laid down in ISO/IEC Guide 98-3 (GUM)

3.13
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

$$U = k \times u_c$$

Note 1 to entry: The value of the coverage factor k depends on the number of degrees of freedom and the level of confidence. In this document a level of confidence of 95 % is used.

Note 2 to entry: The expression overall uncertainty is sometimes used to express the expanded uncertainty.

3.14
uncertainty budget
calculation table combining all the sources of uncertainty according to ISO 14956 or ISO/IEC Guide 98-3 in order to calculate the combined uncertainty of the method at a specified value

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols apply.

a	intercept of the calibration function
A	peak area
b	slope of the calibration function
c	second order slope of the calibration function
c_m	NH_3 mass concentration at standard conditions
c_{corr}	NH_3 mass concentration corrected to oxygen reference volume concentration
c_{dry}	mass concentration expressed on dry basis
c_{wet}	mass concentration expressed on wet basis
E_λ	absorbance at wavelength λ
f	instrument specific factor for converting the result determined for NH_4^+ into a result for NH_3 and the unit mg/ml
f_N	factor for converting NH_4^+ to NH_3 (f_N = 0,944)

h_m volume fraction of the water vapour in the sample gas

k coverage factor

$k_{0,95}$ coverage factor for a coverage probability of 95 %

m_s NH_3 mass in the sample

o_m measured oxygen volume concentration in the duct

o_{ref} oxygen reference volume concentration

p_{atm} atmospheric pressure at the measurement site

p_m absolute pressure at the gas volume meter

p_{ref} standard pressure, 101,3 kPa

p_{rel} relative pressure measured at the gas volume meter

P coverage probability

$R_{2,1}$ peak resolution for the peak pair (2,1)

t_{R1} retention time for peak 1

t_{R2} retention time for peak 2

T_m temperature of the sample gas at the gas volume meter

T_{ref} standard temperature, 273 K

u standard uncertainty

u_c combined uncertainty

u_{cal} uncertainty contribution due to calibration

u_{dr} uncertainty contribution due to drift

u_{mean} uncertainty contribution due to calculation of the mean

u_{read} uncertainty contribution due to reading

u_{rel} relative standard uncertainty

u_{rep} uncertainty contribution due to repeatability standard deviation

u_{res} uncertainty contribution due to resolution

u_{tol} uncertainty contribution due to tolerance of the cylinder

U expanded uncertainty

$U_{0,95}$ expanded uncertainty for a coverage probability of 95 %

$U_{rel,0,95}$ relative expanded uncertainty for a coverage probability of 95 %

v_s volume of the sample absorption solution

V_m measured volume of the sample gas at operating conditions

$V_{m,ref}$	measured volume of the sample gas at standard conditions
w_1	peak width for peak 1
w_2	peak width for peak 2
y	measured value in units specific to the instrument
Z	dilution factor
$\beta\left(NH_4^+\right)$	NH_4^+ mass concentration in the calibration solution
$\beta_s\left(NH_4^+\right)$	NH_4^+ mass concentration in the sample absorption solution
λ	wavelength
ν	number of degrees of freedom

For the purposes of this document, the following abbreviated terms apply.

AMS	automated measuring system
DM water	demineralised water
PE	polyethylene
PP	polypropylene
SRM	standard reference method

5 Principle of the method of measurement

A representative sample is taken from the waste gas flow of the plant for a specified sampling duration and a specified sample gas flow. Isokinetic sampling is necessary if the waste gas contains droplets. The sampling probe is heated to a temperature that ensures evaporation of the droplets and avoids condensation of water vapour in the sample gas. Particles, which can be separated at this temperature, are deposited on a specified particle filter. For non-isokinetic sampling, the use of a particle filter inside the waste gas duct, is preferred since it does not require separate heating. If a particle filter outside the waste gas duct is used, then heating of the particle filter to a specified temperature is required to establish representative conditions and to avoid condensation of water vapour in the sample gas.

All compounds which are volatile at the sampling temperature and produce ammonium ions upon dissociation during sampling in the absorption solution are measured by this method, which therefore gives the volatile ammonia content of the waste gas.

NOTE 1 In the presence of semi-volatile ammonia salts, the choice of the sampling temperature can have influence on the gas/solid balance of the volatile ammonia content.

Ammonia (NH_3) in the sample gas passing through the filter is collected in an absorption system acidified with H_2SO_4. The mass of NH_4^+ is determined after sampling by using one of the analytical methods specified in Clause 9.

NOTE 2 For total ammonia determination, both particulate matter and gas are analysed. Analysis of particulate matter is not part of this document.

The volume of the sample gas is determined during sampling, for example by using a gas volume meter. The mass concentration is calculated as the quotient of the ammonia mass collected in the absorption solution in milligrams (mg) and the volume of the sample gas in cubic metres (m^3) and expressed as milligrams per cubic metre (mg/m^3) of ammonia (NH_3).

6 Sampling system

6.1 General

6.1.1 The sampling system shall allow for the extraction of the sample gas from the waste gas duct. It consists in principle of:

— sampling probe;

— particle filter;

— absorption unit consisting of two absorbers;

— suction unit.

The sampling system shall meet the following requirements:

— the sampling probe shall be a heated tube with an inlet made of titanium, quartz glass, borosilicate glass or PTFE;

— the particle filter shall be a quartz fibre plane filter, to be heated if used outside the waste gas duct;

— the absorbers shall be frit wash bottles (frit porosity: D1 or finer) for low flow sampling or impingers for high flow sampling;

— the suction unit shall be composed of a pump, volume flow controller, gas volume meter with thermometer and pressure gauge, and, if required, drying tower;

— all components of the sampling system coming in contact with the waste gas shall be made of corrosion-resistant material.

The sampling system shall be designed such that the residence time of the sample gas between the inlet of the sampling probe and the two absorbers is minimized.

The heating of the sample gas line down to the absorption unit shall be maintained at least 15 K above the dew-point of the waste gas to avoid any water vapour condensation.

6.1.2 The following absorption materials are required for sampling:

6.1.2.1 Absorption solution: 0,05 M H_2SO_4 solution (quality: analytical grade).

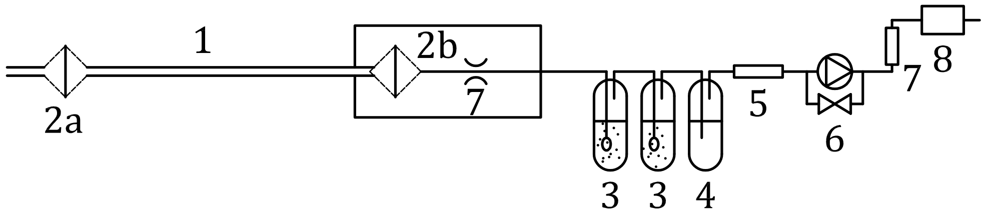
NOTE The concentration can be increased for high NH_3 concentrations to reach the minimum collection efficiency.

6.1.2.2 Demineralised water (DM water).

6.2 Sampling equipment

6.2.1 Non-isokinetic sampling

Non-isokinetic sampling may be carried out using a heated probe without nozzle. Figure 1 shows an example of a sampling system for non-isokinetic sampling. The use of a particle filter inside the waste gas duct, is preferred since it does not require separate heating. If a particle filter outside the waste gas duct is used, then heating of the particle filter to a specified temperature is required to establish representative conditions and to avoid condensation of water vapour in the sample gas and on the filter.



Key

1 heated sampling probe
2a in-stack particle filter or
2b heated particle filter
3 absorber(s)
4 guard bottle (optional)
5 drying tower (only for dry gas volume meter)
6 pump
7 flow meter behind the filter or before the gas volume meter
8 gas volume meter

Figure 1 — Example of non-isokinetic sampling system

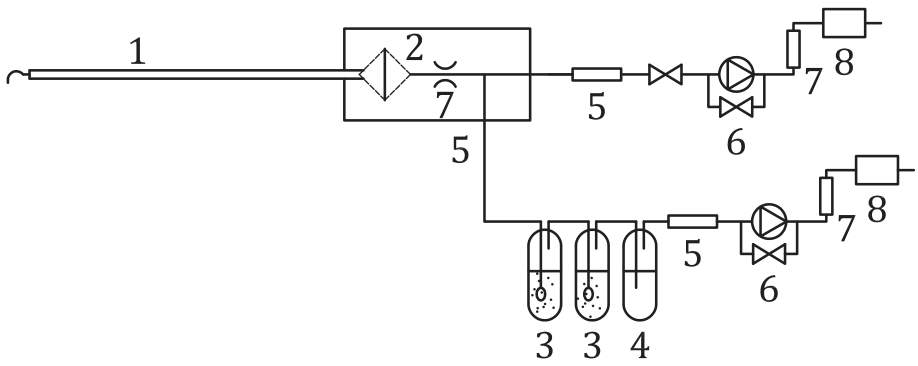
6.2.2 Isokinetic sampling

6.2.2.1 General

Isokinetic sampling is necessary if the waste gas contains droplets. The sampling probe shall be heated to a specified temperature that ensures evaporation of the droplets and avoids condensation of water vapour in the sample gas. The particle filter outside the waste gas duct shall be heated to the same temperature to establish representative conditions and to avoid condensation of water vapour on the filter.

6.2.2.2 Isokinetic sampling with side stream

Isokinetic sampling often requires volume flow rates much higher than those which can be tolerated by the absorbers used for gaseous compound 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 an orifice plate or any other appropriate device, placed behind the filter and before the T piece or before the gas volume meter (see Figure 2).



Key

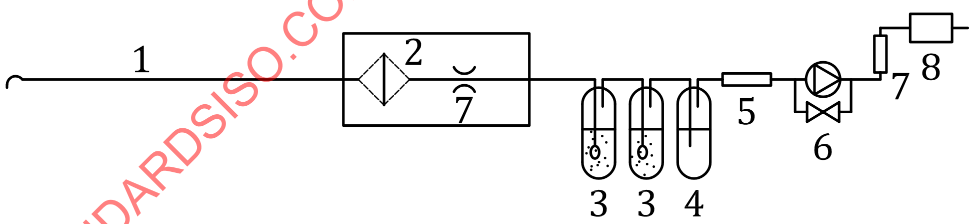
1 heated sampling probe with nozzle
2 heated particle filter
3 absorber(s)
4 guard bottle (optional)
5 drying tower (only for dry gas volume meter)
6 pump
7 flow meter behind the filter or before the gas volume meter
8 gas volume meter

Figure 2 — Example of isokinetic sampling system with side stream

6.2.2.3 Isokinetic sampling without side stream

A sampling system without secondary line (side stream) can be used for isokinetic sampling as shown in Figure 3.

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



Key

1 heated sampling probe with nozzle
2 heated particle filter
3 absorber(s)
4 guard bottle (optional)
5 drying tower (only for dry gas volume meter)
6 pump
7 flow meter behind the filter or before the gas volume meter
8 gas volume meter

Figure 3 — Example of isokinetic sampling system without a side stream

6.3 Other equipment

The following other equipment are required.

6.3.1 Equipment for the determination of isokinetic sampling such as pressure, temperature and gas composition measuring devices.

6.3.2 Containers for sample transport, such as bottles made of glass, PP, PE or other inert materials.

6.3.3 Pipettes, with suitable volumes.

6.3.4 Volumetric flasks, with nominal volumes of, for example, 50 ml, 100 ml and 1 000 ml.

7 Performance characteristics

7.1 General

Table 1 and Table 2 give an overview of the performance characteristics and the associated performance criteria of the method of measurement.

The test laboratory implementing the method of measurement shall demonstrate that:

— the performance characteristics of the sampling system used meet the performance criteria given in Table 1 and Table 2;

— the relative expanded uncertainty calculated by combining the values of selected performance characteristics by means of an uncertainty budget does not exceed 20 % of the applicable assessment standard, such as daily emission limit value or the lowest limit value specified for the plant by the local authorities. This expanded uncertainty is calculated on dry basis and before correction to the oxygen reference concentration.

The values of the selected performance characteristics shall be evaluated:

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

— for the analytical step by means of laboratory tests.

7.2 Performance characteristics of the sampling system

Table 1 shows the performance characteristics and performance criteria of the sampling system.

Table 1 — Performance characteristics of the sampling system to be determined in the laboratory (L) and in the field (F) and associated performance criteria

Performance characteristic	L	F	Performance criterion
Determination of the volume of the absorption solution		X	≤1,0 % of the volume of solution
Gas volume meter:			
— standard uncertainty of sample volume[b]	X[a]		≤2,5 % of the volume of gas sample[a]
— standard uncertainty of temperature[c]	X[a]		≤1,0 % of the absolute temperature[a]
— standard uncertainty of absolute pressure[c]	X[a]		≤1,0 % of the absolute pressure[a]
Absorption efficiency[d, e]		X	≥95 %
Leak in the sampling line		X	≤2,0 % of the nominal flow rate
Field blank value		X	≤10,0 % of assessment standard

[a] Performance criteria corresponding to the uncertainty of calibration.

[b] The uncertainty of the sampled volume is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations) and resolution or reading.

[c] The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations), resolution or reading, and standard deviation of the mean when several values are used to get the result.

[d] This characteristic is a quality assurance check to quantify the absorption efficiency in the first absorber; but it does not quantify a possible loss of absorption, and therefore it is not included in calculation of expanded uncertainty.

[e] If the criteria for the absorption efficiency for the first absorber cannot be met at very low concentrations, the concentration in the second absorber shall be below the analytical limit of quantification.

7.3 Performance characteristics of the analysis

7.3.1 Sources of uncertainty

Main possible sources of uncertainty associated with the analysis are:

— performance characteristics of the analytical equipment;

— preparation of calibration standards: purity of stock standard solution, and ratio of dilutions;

— linearity of the calibration curve depending on the extent of working range;

— measurement of volume of aliquot solution injected for analysis (ratio of the total absorption solution volume and the volume of the aliquot taken for injection);

— level of dilution, if a dilution of the absorption solution is necessary before analysis;

— interferences;

— repeatability.

7.3.2 Performance criterion of analysis

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

Table 2 — Performance characteristic of analytical procedure to be determined in the laboratory (L) and associated performance criterion

Performance characteristic	L	Performance criterion
Repeatability standard deviation	X	≤2,5 % of the measured value (value of quantity of NH_4^+ ions in the solution; in milligrams of NH_4^+ per litre of solution)

7.4 Establishment of the uncertainty budget

An uncertainty budget shall be established to evaluate whether the method fulfils the requirements for a maximum allowable expanded uncertainty.

The relative expanded uncertainty for this method of measurement shall not exceed 20 % of the applicable assessment standard, for example, daily emission limit value or of the lowest limit value fixed to the plant by the local authorities. This expanded uncertainty is calculated on dry basis and before correction to the oxygen reference concentration.

The principle of calculation of the combined uncertainty is based on the law on propagation of uncertainty laid down in ISO/IEC Guide 98-3 (GUM).

— Determine the standard uncertainties attached to the performance characteristics to be included in the calculation of the uncertainty budget according to ISO/IEC Guide 98-3.

— Calculate the uncertainty budget by combining all the standard uncertainties according to ISO/IEC Guide 98-3.

— Values of standard uncertainty that are less than 5 % of the maximum standard uncertainty may be neglected.

— Calculate the combined uncertainty at the measured value, reported as a dry gas value at actual concentration of oxygen.

Annex E shows an example of the calculation of an uncertainty budget.

NOTE When the concentration of a measured compound has to be expressed at an oxygen reference concentration (such as 3 % or 11 %), the correction of oxygen can bring an additional uncertainty which can be significant if the difference between the oxygen measured value and the oxygen reference value is too large. Annex F provides information on the contribution of oxygen correction to the uncertainty linked to the concentration.

8 Field operation

8.1 Measurement planning

Emission measurements at a plant shall be carried out such that the results are representative for the emissions from this plant and comparable with results obtained for other comparable plants. Therefore, measurements shall be planned in accordance with the applicable standards and requirements.

8.2 Sampling strategy

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. Measurements may be performed at one representative measurement point or at any measurement point, if the corresponding requirements on the homogeneity of the distribution of NH_3 or any other relevant component in the measurement plane are fulfilled. In all other cases the measurements shall be performed as grid measurements. In that case, the minimum number of measurement points to be used and the locations of the measurement points in the measurement plane for circular and rectangular ducts shall be selected in accordance with the applicable standards.

NOTE 1 Requirements for the minimum number of measurement points to be used and the locations of the measurement points in the measurement plane for circular and rectangular ducts are specified in, for example, ISO 9096 or EN 15259.

Measurement ports shall be provided for access to the measurement points selected.

Isokinetic sampling in combination with a grid measurement is only required if droplets are present in the sample gas, since these droplets can contain ammonia. In such cases, the sampling probe is to be equipped with a nozzle with a defined cross-section and the volume flow that is drawn off is to be controlled based on the gas velocity in the tip of the nozzle. Furthermore, the sample gas shall be heated just after the inlet such that all droplets including the ammonia are evaporated (sampling probe, filter, sample gas line) before reaching the absorber.

NOTE 2 Details on isokinetic sampling are given, for example, in ISO 9096 or EN 15259.

The flow rates in the main stream and in the side stream shall be proportional to the local velocity at each measurement point.

8.3 Field blank

To check the sampling procedure, a field blank shall be taken at least before each measurement series or at least once a day, following the whole measurement procedure specified in this document and including the assembly of the equipment described in Clause 6 without the suction step, i.e. without starting and operating the sample gas pump.

The average sample gas volume shall be used for calculation of the field blank value expressed in mg/m^3.

If the equipment in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken after the measurement series. If several measurements are performed at the same emission source, then one single field blank at the beginning and one at the end of the series shall be performed.

The field blank value shall be less than 10,0 % of the assessment standard. If the calculated result of measurement is less than the field blank value, the result of measurement shall be reported as less or equal to the field blank value.

The field blank value shall not be subtracted from the result of measurement. However, it is necessary to take into account the field blank value in the calculation of the uncertainty of the measured value (see Annex E).

8.4 Leak test

Before starting the measurement, check that there is no significant leakage in the sampling system by use of the following procedure or any other relevant procedure:

— assemble the complete sampling system, including charging the filter housing and absorbers;

— close the nozzle inlet;

— 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 2,0 % of the expected sample gas flow rate used during measurement.

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

In addition, the integrity of the sampling system can also be tested during sampling by continuously measuring the concentration of a suitable stack gas component (such as O_2) directly in the stack and downstream the sampling system. Any systematic difference between those concentrations indicates a leak in the sampling system (taking into account that the oxygen level measured at both locations is on the same basis, i.e. wet or dry gas).

8.5 Sampling

Ensure that the absorbers are filled with the required volume of absorbent. Insert the sampling probe into the waste gas duct.

The sampling probe and the filter shall be heated to the specified temperature which ensures that the droplets are evaporated, and condensation of water vapour is avoided.

At the start of sampling, the gas volume meter reading shall be taken and recorded together with the time. In addition, the barometer reading and the temperature at the gas volume meter shall be recorded.

After switching on the sample gas pump, the desired volume flow shall be set using the control valve.

The sample gas volume flow and temperature shall be controlled at regular intervals during sampling. The sample gas volume flow shall be regulated and recorded for each measurement point, if a grid measurement is carried out.

The sampling duration shall be at least 30 min and be sufficient to reach the measurement objective.

At the end of sampling, the gas volume meter reading and the temperature at the gas volume meter shall be taken and recorded.

The contents of the absorbers may be transferred into separate suitable bottles. In such cases, the absorbers shall be carefully rinsed with DM water or absorption solution. The rinsing solution of each absorber shall be combined with the absorption solution.

As an alternative, the absorbers may be sealed after removal from the sampling system and taken to sample transport.

The absorbers and bottles shall be labelled.

8.6 Sample transport and storage

The volume of the sample solutions shall be determined before the transport and storage.

The samples shall be transported and stored protected from light.

To avoid sample degradation in the event of potential biological activity, the samples shall be kept at a temperature below 5 °C and the analysis performed as soon as possible.

9 Analytical determination

The volume of the sample solutions shall be determined before the analysis.

The content of the two absorbers shall be analysed separately.

The absorption efficiency shall be at least 95 %.

NOTE The sample solutions of the two absorbers are analysed separately to determine the absorption efficiency and due to the low concentrations, i.e. to avoid dilution of the sample solutions of the first absorber.

The analytical determination shall be carried out based on one of the following analytical methods:

— spectrophotometry (indophenol method) according to ISO 7150-1 (see Annex B);

— flow analysis and spectrometric detection according to ISO 11732 (see Annex C);

— ion chromatography according to ISO 14911 (see Annex D).

10 Calculation of the results

The volume of the dry sample gas at standard conditions shall be calculated according to Formula (1) if the volume V_m of the sample gas is determined as dry gas:

$$V_{m,ref} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_m}{p_{ref}} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_{rel} + p_{atm}}{p_{ref}} \quad (1)$$

where

$V_{m,ref}$ is the volume of the dry sample gas at standard conditions, in m^3;

V_m is the measured volume of the sample gas at operating conditions, in m^3;

p_m is the absolute pressure at the gas volume meter, in kPa;

p_{rel} is the relative pressure measured at the gas volume meter, in kPa;

p_{ref} is the standard pressure, 101,3 kPa;

p_{atm} is the atmospheric pressure at the measurement site, in kPa;

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

T_m is the temperature of the sample gas at the gas volume meter, in K.

The volume of the dry sample gas at standard conditions shall be calculated according to Formula (2) if the volume V_m of the sample gas is determined as wet gas:

$$V_{m,ref} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_m}{p_{ref}} \times \frac{100\% - h_m}{100\%} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_{rel} + p_{atm}}{p_{ref}} \times \frac{100\% - h_m}{100\%} \quad (2)$$

where h_m is the volume fraction of the water vapour in the sample gas, in percent.

The NH_3 mass concentration c_m shall be calculated on the basis of the result of the analytical determination provided for each sample as a mass m_s in milligrams (mg) and the volume $V_{m,ref}$ of the sample gas at standard conditions in cubic metres (m^3) according to Formula (3):

$$c_m = \frac{m_s}{V_{m,ref}} \quad (3)$$

where

c_m is the NH_3 mass concentration at standard conditions, in mg/m^3;

m_s is the NH_3 mass in the sample, in mg;

$V_{m,ref}$ is the measured volume of the sample gas at standard conditions, in m^3.

The mean sample gas volume of each measurement series shall be used for the calculation of the field blank value. The field blank value shall be assessed in case of significant values, such as field blank values above 10,0 % of the assessment threshold (e.g. emission limit value).

The result of field blank shall not be subtracted from the result of measured value. However, it is necessary to take into account the value of the field blank in the calculation of the uncertainty of the measured value (see Annex E).

11 Measurement report

The measurement report shall include at least the following information:

a) a reference to this document, i.e. ISO 21877:2019;

b) description of the measurement objective;

c) description of the whole sampling system and the analytical system;

d) description of plant and process;

e) identification of the measurement plane;

f) description of the location of the measurement points in the measurement plane;

g) description of the operating conditions of the plant process;

h) changes in the plant operations during sampling, for example burner load changes;

i) sampling date, time and duration;

j) measured values;

k) measurement uncertainty;

l) results of any checks (such as field blank value, absorption efficiency);

m) any deviations from this document.

Annex A
(informative)

Validation of the method of measurement in the field

The method of measurement has been validated by comparative measurements, which were carried out on the waste gas of a cement plant, with eight test laboratories (teams) participating. These measurements took place in two campaigns (campaign 1 in winter 2013, campaign 2 in autumn 2014), with four participants each. The measurements were carried out as point measurements after a homogeneity test according to EN 15259. Two different operational conditions were measured at the cement plant at both campaigns to cover a greater range of concentrations.

Sampling was carried out according to EN 15259. Identical devices were used for the sampling. All the analytical methods specified in Clause 9 were used during subsequent analysis.

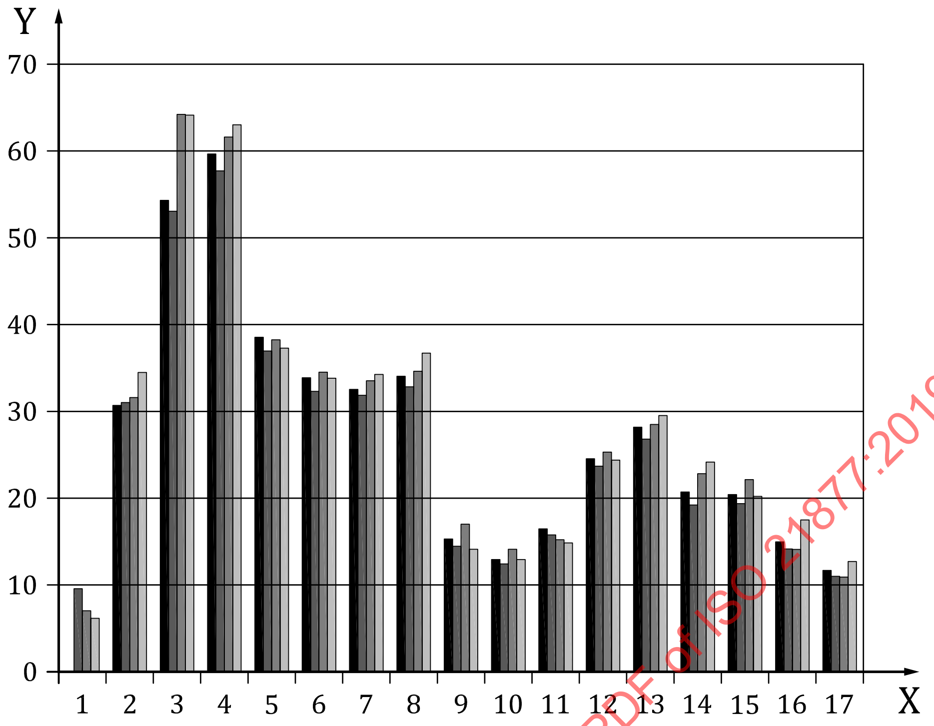
The results of one test laboratory were not included in the analysis based on the results of a Grubbs outlier test and the plausibility assessment of the data. There were thus 165 individual results available for the determination of the performance characteristics.

The measurements cover a concentration range from 7,6 mg/m^3 to 60,5 mg/m^3 (mean value for the individual measurements). Figure A.1 and Figure A.2 show the graphical illustration of the results.

The measurement uncertainty was determined on the basis of the results of the comparative measurements according to ISO 20988 (Experimental design A8 “Parallel measurements with identical measuring systems”). The expanded measurement uncertainty was calculated for a coverage probability of P = 95 %. The results of the comparative measurements are given in Table A.1 and Table A.2.

Based on the results of the measurements of the first campaign, a combined standard uncertainty of 1,6 mg/m^3, an expanded uncertainty of 3,2 mg/m^3 and a relative expanded uncertainty of 12 % have been calculated (see Table A.3).

Based on the results of the measurements of the second campaign, a combined standard uncertainty of 0,8 mg/m^3, an expanded uncertainty of 1,6 mg/m^3 and a relative expanded uncertainty of 11 % have been calculated (see Table A.3).



Key

X measurement number

Y NH_3 concentration in mg/m³

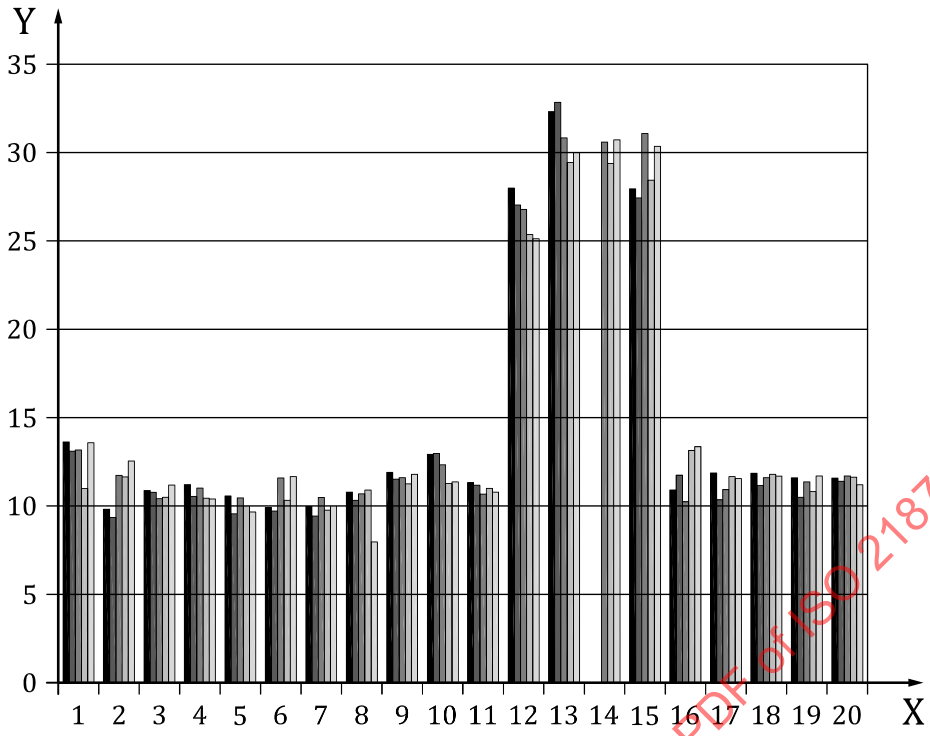
■ Team 1/1

■ Team 1/2

■ Team 2

□ Team 3

Figure A.1 — Graphical illustration of the results of the comparative measurements (campaign 1)



Key

X measurement number

Y NH_3 concentration in mg/m^3

■ Team 4/1

■ Team 4/2

■ Team 5

■ Team 6

□ Team 7

Figure A.2 — Graphical illustration of the results of the comparative measurements (campaign 2)

Table A.1 — Results of the comparative measurements conducted on the waste gas of a cement plant (campaign 1)

Measurement number	Number of parallel measurements	Mean value of the ammonia concentration in mg/m^3	Standard deviation in mg/m^3
1	3	7,6	1,8
2	4	31,9	1,8
3	4	58,9	6,1
4	4	60,5	2,3
5	4	37,7	0,8
6	4	33,6	0,9
7	4	33,0	1,1
8	4	34,5	1,6
9	4	15,2	1,3
10	4	13,1	0,7
11	4	15,6	0,7
12	4	24,5	0,7
13	4	28,2	1,1
14	4	21,7	2,2
15	4	20,5	1,1
16	4	15,2	1,6
17	4	11,6	0,8
Mean value:		27,5	1,6
Bias:		0,9	—

Table A.2 — Results of the comparative measurements conducted on the waste gas of a cement plant (campaign 2)

Measurement number	Number of parallel measurements	Mean value of the ammonia concentration in mg/m³	Standard deviation in mg/m³
1	5	12,9	1,1
2	5	11,0	1,4
3	5	10,8	0,3
4	5	10,7	0,4
5	5	10,0	0,5
6	5	10,6	0,9
7	5	9,9	0,4
8	5	10,1	1,2
9	5	11,6	0,2
10	5	12,2	0,8
11	5	11,0	0,3
12	5	26,5	1,2
13	5	31,1	1,5
14	3	30,2	0,7
15	5	29,1	1,6
16	5	11,9	1,4
17	5	11,3	0,6
18	5	11,6	0,3
19	5	11,2	0,5
20	5	11,5	0,2
Mean value:		14,4	0,8
Bias:		0,5	—

Table A.3 — Results of the uncertainty evaluation

	Campaign 1	Campaign 2
Number of degrees of freedom, v:	51	80
Standard uncertainty, u:	1,6 mg/m³	0,8 mg/m³
Coverage factor, $k_{0,95}$:	2,0	2,0
Expanded uncertainty, $U_{0,95}$:	3,2 mg/m³	1,6 mg/m³
Relative expanded uncertainty, $U_{rel,0,95}$:	12 %	11 %

Annex B
(informative)

Description of the analytical method — Spectrophotometry

B.1 General

The photometric method is based on the principle that ammonium ions react at $pH \approx 12{,}6$ with hypochlorite and salicylate ions in the presence of sodium nitroprusside as a catalyst to produce a blue-green indophenol dye. An overview of the analytical method and the calculation of the NH_3 mass in the sample is given in the following. A detailed description of the analytical method is given in ISO 7150-1.

B.2 Reagents

B.2.1 General

All reagents that are used shall be of analytical grade purity.

B.2.2 Calibration solutions

The following calibration solutions are required.

B.2.1.1 Ammonium stock solution, with a mass concentration $\beta\left(NH_4^+\right)$ = 1 000 mg/l.

The solution can be obtained ready-to-use or can be made as follows: 2,965 g NH_4Cl (dried at 105 °C) is dissolved in water in a 1 000 ml volumetric flask.

B.2.2.2 Ammonium standard solution I, with a mass concentration of $\beta\left(NH_4^+\right)$ = 100 mg/l.

5 ml ammonium stock solution is pipetted into a 50 ml volumetric flask. The flask is then filled-up to the mark with water and the contents mixed thoroughly.

B.2.2.3 Ammonium standard solution II, with a mass concentration $\beta\left(NH_4^+\right)$ = 10 mg/l.

500 µl ammonium stock solution is pipetted into a 50 ml volumetric flask. The flask is then filled-up to the mark with water and the contents mixed thoroughly.

B.2.3 Reagents for analysis

The following reagents for analysis are required.

B.2.3.1 Sodium pentacyanonitrosylferrate(III): $Na_2[Fe(CN)_5NO]\cdot 2\ H_2O$, for the salicylate-citrate solution.

B.2.3.2 Sodium dichloroisocyanurate: $C_3Cl_2N_3O_3Na\cdot 2\ H_2O$, for the reagent solution.

B.2.3.3 Sodium hydroxide: NaOH, for the reagent solution.

B.2.3.4 Sodium salicylate: $C_7H_5O_3Na$, for the salicylate-citrate solution.

B.2.3.5 Trisodium citrate: $C_6H_5O_7Na_3 \cdot 2\ H_2O$, for the salicylate-citrate solution.

B.2.3.6 Salicylate-citrate solution.

Dissolve 130 g sodium salicylate and 130 g trisodium citrate in 800 ml water. Then 0,970 g sodium nitroprusside is added. After being shaken thoroughly in the volumetric flask, the solution is filled-up to 1 l with water. The shelf life is at least two weeks, provided it is kept in the dark.

B.2.3.7 Reagent solution.

Dissolve 3,2 g NaOH in 50 ml water.Once the solution has cooled to room temperature, 0,2 g sodium dichloroisocyanurate is added. After the chemicals have fully dissolved, the solution is poured into a 100 ml volumetric flask and filled-up to the mark with water. The solution is to be freshly made on the same the day which it is to be used.

B.3 Analytical equipment

The following analytical equipment is required.

B.3.1 UV/VIS spectrophotometer, suitable for detection at a wavelength of λ = 655 nm.

B.4 Analysis

Absorbers filled with absorption solution are used in the same way for the field blank value determination (see 8.3).

Depending on the expected concentration, an appropriate aliquot of the absorption solution is taken and then first mixed with 20 ml water in a 50 ml volumetric flask. The pH should be between 5 and 8 and if it is not, it is adjusted to within this range. Following this, 4 ml salicylate-citrate solution is added while shaking the flask.

While the solution is being shaken thoroughly, 4 ml of the reagent solution is added. After this, the pH of the solution should be 12,6.

The sample is then filled-up to the mark with water, once again mixed thoroughly, and then kept for 1 h to 3 h at 25 °C. The absorbance is measured at λ = (655 ± 2) nm in a cuvette with a coating thickness of 1 cm or 5 cm against water in the comparison cuvette after 1 h at the earliest, but no later than after 3 h.

The analysis can also be carried out in a 25 ml volumetric flask to save on reagents and waste. To this end, the sample and reagent solution volumes given in B.4 are halved.

B.5 Calibration

At least three calibration solutions should be made for the calibration procedure. Suitable volumes of the NH_4^+ standard solutions (see B.2.2) are transferred into 50 ml volumetric flasks. The concentrations of the calibration solutions should cover the concentration range up to 1,0 mg/l (in the case of 1 cm cuvettes) or 0,2 mg/l (in the case of 5 cm cuvettes). Sufficient water should be added to each of these volumes to result in a total volume of 40 ml. Each sample is then treated as specified in B.4.

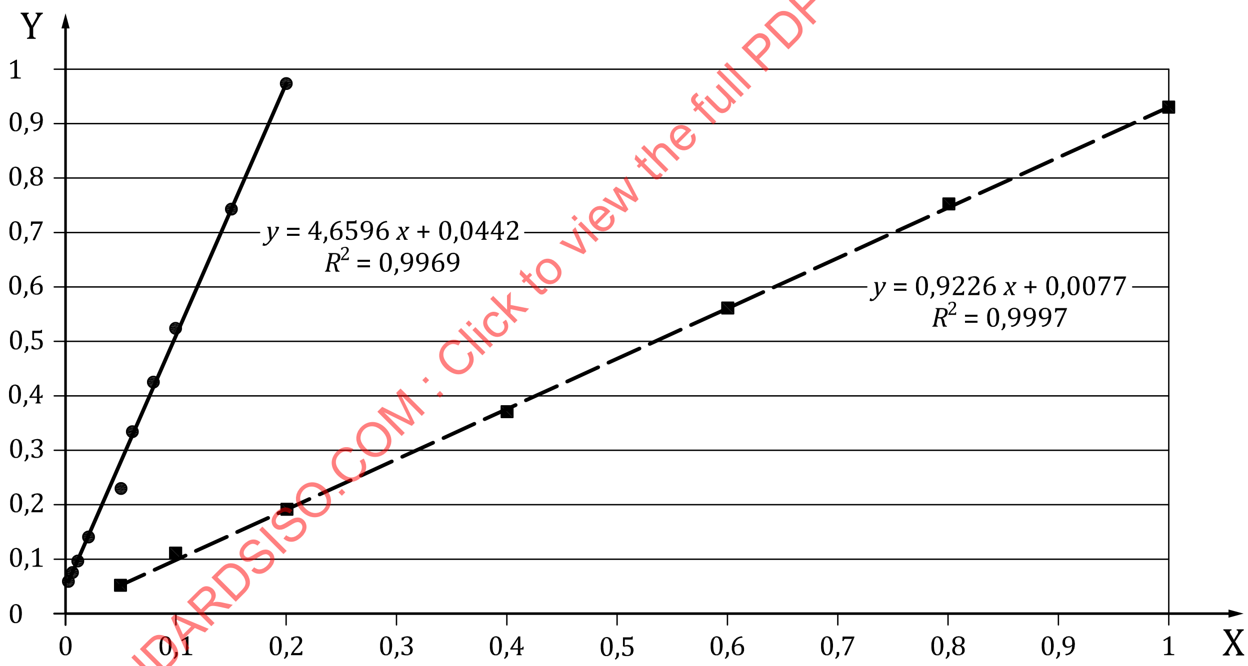
On a coordinate system, the NH_4^+ mass concentration $\beta\left(NH_4^+\right)$ in the calibration samples are plotted on the absissa (x axis) and the corresponding absorbance values E_λ on the ordinate (y axis) as shown in Figure B.1. The calibration line is determined using Formula (B.1) for the series of values thus obtained:

$$E_\lambda = a + b \times \beta\left(NH_4^+\right) \tag{B.1}$$

where

E_λ	is the absorbance at wavelength λ;
$\beta\left(NH_4^+\right)$	is the NH_4^+ mass concentration in the calibration solution, in mg/l;
a	is the intercept of the calibration function;
b	is the slope of the calibration function.

The concentrations of the standard solutions shall cover the expected concentration range. It can be necessary to use 5 cm cuvettes in cases of very low concentrations of NH_3.



Key

X mass concentration in mg/l

Y absorbance

● 5 cm cuvette

■ 1 cm cuvette

Figure B.1 — Examples of calibration lines from a basic calibration

B.6 Calculation

The NH_4^+ mass concentration $\beta_s\left(NH_4^+\right)$ in the sample solution is calculated using Formula (B.2), based on the calibration line that is described by Formula (B.1):

$$\beta_s\left(NH_4^+\right)=\frac{E_\lambda - a}{b} \tag{B.2}$$

Taking into consideration the dilution factor, Z, the sample volume, v_s, and the conversion factor, f_N, for the conversion of NH_4^+ to NH_3, the ammonia mass, m_s, in the sample is then determined using Formula (B.3):

$$m_s=\beta_s\left(NH_4^+\right)\times Z\times v_s\times f_N \tag{B.3}$$

where

m_s	is the NH_3 mass in the sample, in mg;
$\beta_s\left(NH_4^+\right)$	is the NH_4^+ mass concentration in the sample absorption solution, in mg/l;
Z	is the dilution factor;
v_s	is the volume of the sample absorption solution;
f_N	is the factor for converting NH_4^+ to NH_3 (f_N = 0,944).

The value that is obtained is used for the calculation of the measurement result, as specified in Clause 10.

Annex C
(informative)

Description of the analytical method — Continuous flow analysis (CFA)

C.1 General

In a continuously flowing, gas-segmented carrier stream, the ammonium in the sample reacts in alkaline solution with hypochlorite, which is released from dichloroisocyanurate as an intermediate. The chloramine that is produced is converted into a blue-green indophenol dye under catalysis at temperatures of 37 °C to 50 °C, which is quantified in a continuous flow photometer at 640 nm to 660 nm. An overview of the analytical method and the calculation of the NH_3 mass in the sample is given in this annex. A detailed description of the analytical method is given in ISO 11732.

C.2 Reagents

C.2.1 General

All reagents that are used shall be of analytical grade purity.

C.2.2 Calibration solutions

The calibration solutions are specified in B.2.2.

C.2.3 Reagents for analysis

All reagents that are used shall be of analytical grade purity.

The following reagents for analysis are required.

C.2.3.1 Trisodium citrate dihydrate: $Na_3C_6H_5O_7 \cdot 2H_2O$.

C.2.3.2 Polyethylene glycol dodecyl ether, with a melting range of 33 °C to 41 °C; solution (30 %). The solution has a shelf life of four weeks.

C.2.3.3 Sodium salicylate: $C_7H_5O_3Na$.

C.2.3.4 Sodium dichloroisocyanurate dehydrate: $NaC_3Cl_2N_3O_3 \cdot 2H_2O$.

C.2.3.5 Sodium nitroprusside dehydrate: $Na_2[Fe(CN)_5NO)] \cdot 2H_2O$.

C.2.3.6 Sodium hydroxide: NaOH.

C.2.3.7 Citrate buffer solution.

Dissolve 40 g trisodium citrate dihydrate and 1 ml polyethylene glycol dodecyl ether solution in water in a 1 000 ml volumetric flask and fill-up to the mark with water. The solution has a shelf life of one week when stored in a brown glass bottle and refrigerated.

C.2.3.8 Dilution solution.

A buffer solution is required when working with a dialyser, such as a citrate buffer solution. A buffer solution or water can also be used for the online dilution.

C.2.3.9 Sodium salicylate solution.

Dissolve 34 g sodium salicylate, 0,4 g sodium nitroprusside dihydrate and 1 ml polyethylene glycol dodecyl ether in water in a 1 000 ml volumetric flask and then fill-up to the mark with water. The solution has a shelf life of one week when stored in a brown glass bottle and refrigerated.

C.2.3.10 Sodium dichloroisocyanurate solution.

Dissolve 0,8 g sodium dichloroisocyanurate dihydrate and 10 ml sodium hydroxide pellets in water in a 1 000 ml volumetric flask and then fill-up to the mark with water. The solution shall be freshly made before use.

C.3 Analytical equipment

The following analytical equipment is required.

C.3.1 Autosampler, composed of a sample holder, sampler and flushing unit.

C.3.2 Low-pulsation pump, with chemically inert tubes.

C.3.3 Manifold, for dosing the reagents and buffer solutions, with a highly reproducible gas bubble feed.

C.3.4 Dialysis cell.

C.3.5 Photometric detector, with flow-through cuvette, wavelength range of 640 nm to 660 nm.

C.3.6 Recording and analysis unit.

C.4 Sample preparation

Samples with suspended particulate matter are filtered using a membrane filter with a pore size of 0,45 µm. In addition, dialysis is integrated into the instrument for each parameter, to eliminate any interferences.

C.5 Calibration

The instrument is calibrated with 10 standards (see C.2.2) before each sample series. In addition, two control standards are also run for each parameter after 10 to 20 measurements, of which one is in the lower and one in the upper third of the working range. Baseline drift and chemical drift are corrected by the analytical software.

C.6 Calculation

The calculation is carried out based on the calibration function, using Formula (C.1):

$$m_s = \left(\frac{y-a}{b}\right) \times v_s \times f \qquad (C.1)$$

where

m_s is the NH_3 mass in the sample, in mg;

y is the measured value in units specific to the instrument;

a is the intercept of the calibration function in units specific to the instrument;

b is the slope of the calibration function in units specific to the instrument;

v_s is the volume of the sample absorption solution;

f is the instrument specific factor for converting the result determined for NH_4^+ into a result for NH_3 and the unit mg/ml.

Annex D
(informative)

Description of the analytical method — Ion chromatography

D.1 General

The ion chromatography method is based on the separation of NH_4^+ from other ions by means of a separator column and subsequent detection by conductivity. An overview of the analytical method and the calculation of the NH_3 mass in the sample is given in the following. A detailed description of the analytical method is given in ISO 14911.

D.2 Reagents

D.2.1 General

All reagents that are used shall be of analytical grade purity.

D.2.2 Calibration solutions

The calibration solutions are specified in B.2.2.

D.2.3 Reagents for analysis

The following reagents for analysis are required.

D.2.3.1 DL-2,3-diaminopropionic acid monohydrochloride: $C_3H_8N_2O_2 \cdot HCl$, for the eluent when using the suppressor method.

D.2.3.2 Methane sulphonic acid: CH_3SO_3H, for the eluent when using the suppressor method.

D.2.3.3 Sodium hydroxide solution: aqueous solution of sodium hydroxide in water, $c(NaOH) = 0,2$ mol/l.

D.2.3.4 Pyridine-2,6-dicarboxylic acid: $C_7H_5NO_4$.

D.2.3.5 Nitric acid: HNO_3, $c(HNO_3) = 1$ mol/l.

D.2.3.6 Hydrochloric acid: HCl, $c(HCl) = 7,7$ mol/l.

D.2.3.7 Tartaric acid: 2,3-dihydroxybutanedioic acid, $C_4H_6O_6$.

D.2.3.8 Eluent.

Various mixtures of reagents have proven suitable as an eluent, depending on the type of separation column and detector. All eluents shall be degassed or made using degassed water.

D.3 Analytical equipment

The following analytical equipment are required.

D.3.1 Ion chromatography system, composed of an eluent pump, pre-column, separation column, with the option of degassing the eluent and temperature adjustment for the columns.

D.3.2 Autosampler, to inject sample solution onto the separation column.

D.3.3 Separation column, suitable for separation of ammonium.

D.3.4 Detector, with conductivity cell or UV detector.

D.4 Preparations

Prior to the start of measurement, the ion chromatography system is put into operation in accordance with the manufacturer's instructions. The instrument is ready once the baseline is stable.

The peak resolution $R_{2,1}$ for the peak pair (2,1) (see Figure D.1), calculated using Formula (D.1), shall not be less than R = 1,3 in the chromatograms for the samples and standard solutions:

$$R_{2,1} = \frac{t_{R2} - t_{R1}}{0{,}5(w_2 + w_1)} \qquad \text{(D.1)}$$

or for equal peak widths at half peak height:

$$R_{2,1} = \frac{t_{R2} - t_{R1}}{w} \qquad \text{(D.2)}$$

where

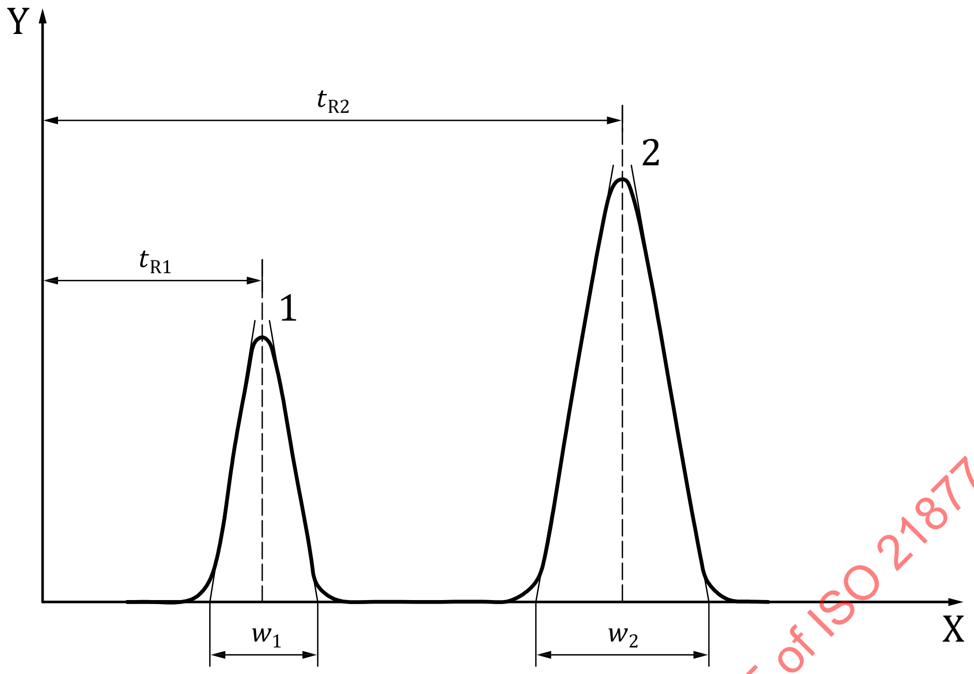
$R_{2,1}$ is the peak resolution for the peak pair (2,1);

t_{R2} is the retention time for peak 2, in s;

t_{R1} is the retention time for peak 1, in s;

w_2 is the peak width for peak 2, in s;

w_1 is the peak width for peak 1, in s.



Key

X time

Y signal

1 component 1

2 component 2

Figure D.1 — Parameters for calculating the peak resolution *R*

D.5 Measurement

There is a relationship between peak area A that is dependent on conductivity and the NH_4^+ mass concentration $\beta\left(NH_4^+\right)$ in the solution in conductometric measurements. As a rule, this is a linear relationship based on Formula (D.3):

$$A = a + b \times \beta\left(NH_4^+\right) \tag{D.3}$$

where

A is the peak area;

a is the intercept of the calibration function;

b is the slope of the calibration function;

$\beta\left(NH_4^+\right)$ is the NH_4^+ mass concentration in the calibration solution;

It can be necessary to carry out a quadratic regression according to Formula (D.4) if the suppressor method is used.

$$A = a + b \times \beta\left(NH_4^+\right) + c \times \beta^2\left(NH_4^+\right) \quad (D.4)$$

where c is the second order slope of the calibration function.

The ammonium content in the sample should not lie outside the calibration range. If necessary, the sample shall be diluted with water.

The sample should be analysed as soon as possible after elution.

D.6 Calibration and checks on the calibration

At least three calibration solutions should be made for the calibration procedure. To this end, specific quantities of the NH_4^+ standard solutions (see D.2.2) are suitably diluted. The NH_4^+ masses in the calibration samples are plotted on the abscissa (x axis) on a coordinate system. The corresponding peak areas are plotted on the ordinate (y axis). The calibration function (regression line) is determined using Formula (D.3) for the series of values thus obtained.

D.7 Calculation

The NH_4^+ mass concentration in the injected sample is calculated from the calibration function given in Formula (D.4):

$$\beta_s\left(NH_4^+\right) = \frac{A - a}{b} \quad (D.5)$$

Taking into consideration the dilution factor Z, the volume of the sample absorption solution v_s and the conversion factor f_N for converting NH_4^+ to NH_3, the mass m_s of the ammonia that has been absorbed is then determined using Formula (D.5):

$$m_s = \beta_s\left(NH_4^+\right) \times Z \times v_s \times f_N \quad (D.6)$$

where

m_s	is the NH_3 mass in the sample, in mg;
$\beta_s\left(NH_4^+\right)$	is the NH_4^+ mass concentration in the sample absorption solution, in mg/l;
Z	is the dilution factor;
v_s	is the volume of the sample absorption solution;
f_N	is the factor for converting NH_4^+ to NH_3 (F_N = 0,944).

The value that is thus obtained is used for the calculation of the result, as specified in Clause 10.

Annex E
(informative)

Example of the calculation of the uncertainty budget

E.1 General

This annex gives an example of the calculation of the uncertainty budget established to demonstrate compliance with given uncertainty requirements.

The following procedure for calculating the measurement uncertainty is based on the law of propagation of uncertainty as described in ISO 14956 or ISO/IEC Guide 98-3 (GUM). The individual standard uncertainties, the combined standard uncertainty and the expanded uncertainty are determined according to the requirements of ISO 14956 or ISO/IEC Guide 98-3.

E.2 Elements required for the uncertainty determinations

In the first step, the model equation is established. The model equation describes the mathematical relationship between the measurand and all the parameters that influence the result of measurement. These parameters are called input quantities. It is necessary to clearly define the measurand and the input quantities.

The model function is used to calculate the result of measurement on the basis of the values assigned to the input quantities and to obtain the combined uncertainty of the result of measurement by application of the law of propagation of uncertainty.

The expanded uncertainty, U, is obtained by multiplying a coverage factor, k, with the combined uncertainty, 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 %.

E.3 Example of an uncertainty calculation

E.3.1 Specific conditions in the field

Table E.1 gives one example of the specific conditions of the site, that is to say the values and the variation range of the influence parameters.

The mass flow is homogenous.

Table E.1 — Example of measurement conditions

Specific conditions	Value
Studied concentration (limit value of NH_3 for the site) at standard conditions of temperature (273 K) and pressure (101,3 kPa), and at 11 % oxygen reference concentration	50 mg/m^3
Oxygen reference volume concentration, o_{ref}	11 %
Measured oxygen volume concentration, o_m	12,3 %
Relative expanded uncertainty of o_m for k = 2	6 %
Volume of solution, v_s, used for measurement (total volume in two absorbers)	200 ml
Volume, V_m, of the sample gas at operating conditions	0,049 m^3
Mean temperature at the gas volume meter[a]	296,2 K
Mean absolute pressure at the gas volume meter[b]	100,3 kPa
Analysis	Ion chromatography

[a] Mean temperature is calculated from data recording of continuous temperature measurement (one measurement per 30 s leads to 60 measurements in 30 min). The standard deviation of the mean of measurements calculated is equal to 0,231 K.

[b] Mean absolute pressure is calculated from five measurements of relative pressure at the gas volume meter and one measurement of atmospheric pressure during the sampling period.

Table E.2 gives one example of the measured values of relative pressure.

Table E.2 — Measured values of relative pressure

Measurement	Relative pressure p_{rel} at gas volume meter Pa
1	70,0
2	68,7
3	69,0
4	68,6
5	69,8
Mean	69,2
Standard deviation	0,287
Barometric pressure: 100 235 Pa	
Mean absolute pressure: 100 304 Pa	

E.3.2 Performance characteristics

Table E.3 shows the performance characteristics of the method related to the parameters which can have an influence.

Table E.3 — Example of performance characteristics

Performance characteristics	Performance criterion	Results obtained in laboratory or field
Volume of absorption solution:	≤1,0 % of the volume of solution	
Expanded uncertainty		
The total volume of solution is determined with a graduated measuring cylinder:		
— tolerance of the cylinder		±1,4 ml
— reading		2 ml
— repeatability standard deviation		0,5 ml
Gas volume sampled:	≤2,5 % of the measured value	
Expanded uncertainty		
— expanded uncertainty of calibration		1,5 % of the measured value
— repeatability standard deviation		0,3 % of the measured value
— drift between two calibrations		1,0 % of the measured value
— reading		0,002 m^3
Temperature at the gas volume meter:	≤1,0 % of the absolute temperature	
Expanded uncertainty		
— expanded uncertainty of calibration		1,0 K
— drift between two adjustments		0,2 K
— resolution		0,1 K
— standard deviation (average value)		0,231 K
Absolute pressure at gas volume meter:	≤1,0 % of the measured value	
Expanded uncertainty		
Relative pressure at the gas volume meter; scale of the manometer: 0 Pa to −200 Pa		
— expanded uncertainty of calibration		0,6 Pa
— resolution		0,01 Pa
— lack of fit		1,4 % of measuring range
— drift between two calibrations		1,0 % of measuring range
Atmospheric pressure		
— expanded uncertainty of calibration		300 Pa
— reading		20 Pa
Absorption efficiency of the first absorber	>95,0 %	98 %
Concentration β_s in the absorption solution: — repeatability standard deviation of analysis	≤5,0 % of the measured value	5,0 % of the measured value

E.3.3 Model equation and application of rule of uncertainty propagation

E.3.3.1 Concentration of NH_3

The measured NH_3 mass concentration c_m is calculated by Formula (E.1):

$$c_m = \frac{\beta_s \times v_s \times \frac{17}{18}}{V_{m,ref}} \quad \text{(E.1)}$$

where the volume $V_{m,ref}$ is given by Formula (E.2):

$$V_{m,ref} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_m}{p_{ref}} = V_m \times \frac{T_{ref}}{T_m} \times \frac{p_{rel} + p_{atm}}{p_{ref}} \quad \text{(E.2)}$$

and

β_s is the NH_4^+ mass concentration in the sample absorption solution, in mg/l;

v_s is the volume of sample absorption solution, in l;

$V_{m,ref}$ is the measured volume of the sample gas at standard conditions, in m^3;

V_m is the measured volume of the sample gas at operating conditions, calculated by difference between the gas volume at the end and at the beginning of the sampling period, in m^3 (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 the reading of a measured value);

T_m is the temperature of the sample gas at the gas volume meter, in K;

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

p_m is the absolute pressure at the gas volume meter (which is equal to the sum of relative pressure measured at the gas volume meter and the atmospheric pressure), in kPa;

p_{rel} is the relative pressure measured at the gas volume meter, in kPa;

p_{atm} is the atmospheric pressure at the measurement site, in kPa;

p_{ref} is the standard pressure, 101,3 kPa.

Conversion of the NH_3 mass concentration at oxygen reference concentration is performed according to Formula (E.3):

$$c_{corr} = \frac{21\% - o_{ref}}{21\% - o_m} \times c_m \quad \text{(E.3)}$$

where

c_{corr} is the NH_3 mass concentration corrected to oxygen reference volume concentration, in mg/m^3;

c_m is the NH_3 mass concentration at standard conditions (at measured oxygen volume concentration in the duct), in mg/m^3;

o_{ref} is the oxygen reference volume concentration, in %;

o_m is the measured oxygen volume concentration in the duct, in %.