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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

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Foreword

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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).

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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

$V_{\mathrm{m,ref}}$	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
$\beta\left(\mathrm{NH}_4^+\right)$	NH_4^+ mass concentration in the calibration solution
$\beta_{\mathrm{s}}\left(\mathrm{NH}_4^+\right)$	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 $\mathrm{H}_2\mathrm{SO}_4$. 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).

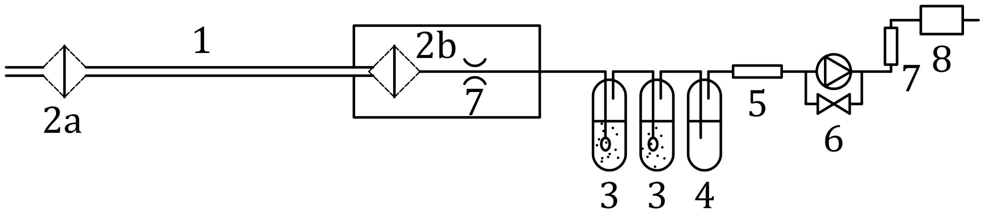
NOTE The concentration can be increased for high NH_3 concentrations to reach the minimum collection efficiency.

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

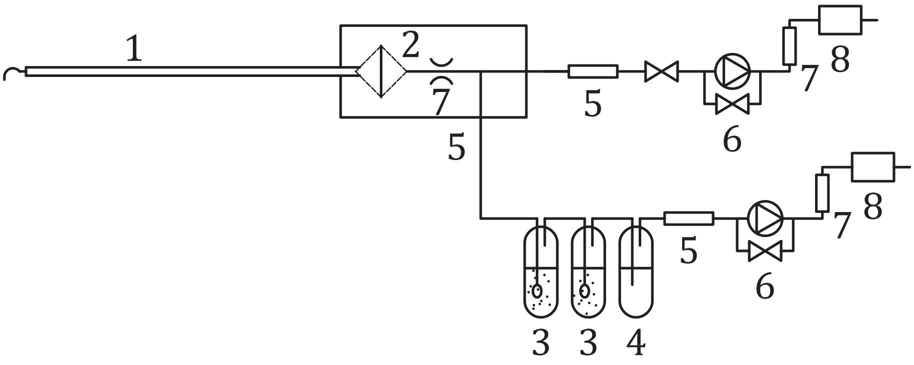
6.2.2 Isokinetic sampling

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

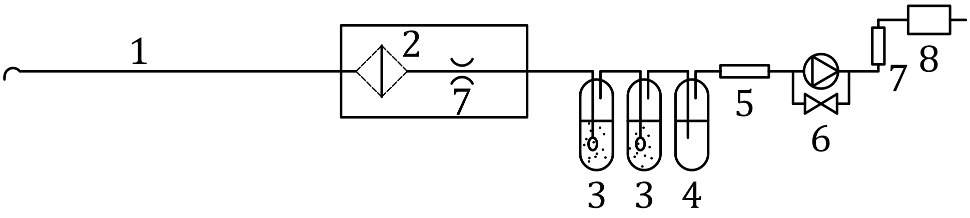
1	heated sampling probe with nozzle
2	heated particle filter
3	absorber(s)
4	guard bottle (optional)
5	drying tower (only for dry gas volume meter)
6	pump
7	flow meter behind the filter or before the gas volume meter
8	gas volume meter

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.