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Factsheet L40-1P AIR

Nitrogen oxides NO_x

Periodic measurement

This factsheet is part of the L40 series "Measurement of air emissions". L40 consists of a manual that deals with the background of the measurement of air emissions and a series of factsheets that per component consider the specific quality-determining aspects of the measurement in question. These main quality aspects can be found in the checklist on page 4.

The factsheets and the manual serve to support the competent authority. You can use them in the assessment of the quality of air measurements.

The right factsheet?

In the factsheets a distinction is made between periodic measurements and continuous measurements with automated measuring systems. This factsheet focuses on the assessment of periodic NO_x emission measurements that are performed by a measurement body. This can also involve parallel measurements for the calibration and validation of automated measuring systems for NO_x.

If you have any questions concerning this factsheet, please surf to website www.infomil.nl. You can also contact the helpdesk, telephone +31 (0)70 373 55 75, e-mail helpdesk@infomil.nl. You can find the opening hours on the website.

Background

Standard NEN-ISO 10849

Stationary source emissions – Determination of the mass concentration of nitrogen oxides – Performance characteristics of automated measuring systems.

NEN-ISO 10849 is focused on automated measuring systems (AMS). The standard does not prescribe a specific measurement principle, but does set requirements on the performance characteristics and provides procedures for determining them. The described methods can also be applied for performing periodic measurements of nitrogen oxides (NO_x). When draft standard NEN-EN 14792 becomes definite it will be the standard reference method for periodic NO_x emission measurements. NEN-EN 14792 is focused on chemoluminescence. In future, other measurement principles will no longer be allowed as a reference method.

Sampling

Periodic measurements by a measurement body are performed with an extractive system. This means that a representative sample is drawn from the stack* with a sampling probe and transported via a transport and conditioning system to the analyser. Extractive systems can be divided into:

- systems that measure in wet flue gas;
- systems that measure in dry flue gas.

In the first case, the condensation of water vapour in the sample gas is prevented through heating or dilution. In the second case, the water vapour is removed through cooling or drying, during which process the loss of flue gas components needs to prevented.

Measurement principles

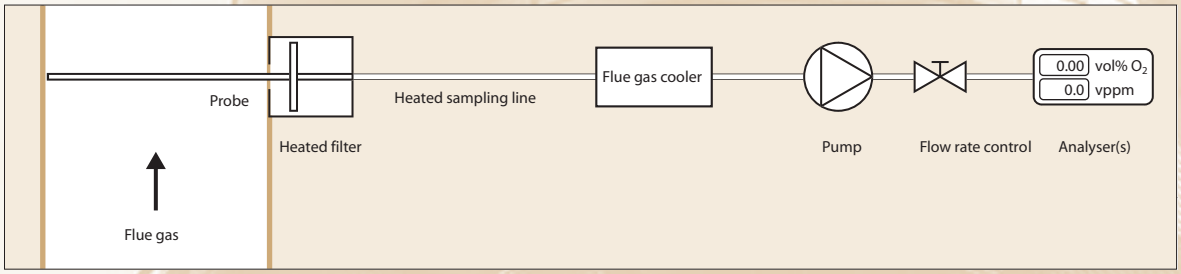
Different measurement principles can be applied. In the chemoluminescence method, nitrogen monoxide (NO) reacts with ozone (O_3) to form nitrogen dioxide (NO_2), part of which is in an "excited state". Upon decay to the "basic state", these NO_2 molecules emit light with a characteristic wave length. This is called chemoluminescence. The intensity of the light is dependent on the quantity of NO in the sample and is therefore a measure for it. The presence of carbon dioxide (CO_2) or water vapour can interfere with this measurement principle.

Non-dispersive infrared spectroscopy (NDIR) is another principle that is applied. Gasses that consist of molecules with different atoms (such as NO) absorb light with a characteristic wave length in the infrared spectrum. The NDIR method uses the fact that this absorption is a measure for the quantity of NO in the sample. Interference by water vapour is possible. Non-dispersive ultraviolet spectroscopy (NDUV) is based on the principle that NO molecules in a specific way absorb light in the ultraviolet spectrum. The degree of absorption is again a measure for the quantity of NO. Interference can, for example, occur due to the presence of sulphur dioxide (SO_2).

Most of the principles described above are specific for the determination of the quantity of NO. If the quantity of NO_2 or the combination of both (NO + NO_2 = NO_x) also needs to be determined, use is made of a converter, which reduces the NO_2 that is present to NO. The analysis of a sample after it has flowed through the converter provides the total quantity of NO_x. The analysis of a sample that flows past the converter only provides the amount of NO. The quantity of NO_2 is then the difference between the quantity of NO_X and NO.

* For the sake of readability, this factsheet uses the term "flue gas" for all canalised emissions to the air.

Diagrammatic representation of an extractive NO_X system with sample gas cooling



Main quality aspects

1 The law and regulations can specify that a measurement body must be accredited on the basis of NEN-EN-ISO/IEC 17025 or 17020 or that it must apply these standards in a demonstrable way. The standards contain the requirements that a measurement body must meet when it wants to demonstrate that it works in accordance with a quality system, is technically competent and is able to provide technically-valid results. In the Netherlands, accreditation takes place by the Council for Accreditation (Raad voor Accreditatie, RvA). Accreditation by comparable foreign agencies is also recognised. Please note, the accreditation is related to a scope. The scope states for which type of measurement the accreditation is valid. Certification is not the same as accreditation; certified measurement bodies must also demonstrate that they properly apply NEN-EN-ISO/IEC 17025 or 17020.

2 It is important that the measurements are performed under representative operating conditions and that they are aligned to the character of the process for which the measurements are taken. For cyclical (batch) processes, the sampling time must, for example, be aligned to the duration of the cycle. When it concerns a continuous process, a constant operation (fixed load) must be guaranteed over the duration of the measurements.

3 For extractive sampling, the concentration in the sample gas must be representative for the concentration in the flue gas. Knowledge of any concentration differences in the stack is therefore necessary. In accordance with NEN-ISO 10396 this must be checked by performing a concentration measurement at several points in the cross-section of the stack. The sampling points for these measurements are determined in accordance with NEN-ISO 9096. When substantial concentration differences are observed and no alternative sampling location is available, multiple point sampling or network sampling is prescribed.

4 If the space between the sampling probe and the entry opening in the stack is too large, outside air can flow in when there is under-pressure and this can influence the NO_x concentration. Conversely it must be prevented that the persons who perform the measurements are exposed to noxious gasses. The space between the probe and the entry opening must therefore be reduced with suitable materials.

5 Outside air leaking into the sample transport and conditioning system can lead to unintended flue gas dilution and this can result in wrong measurement values. The set-up must therefore be tested for leak-tightness and any leakages must be corrected.

6 The sampling probe must be made of corrosion-resistant material. Polytetrafluorethene (PTFE) is suitable for temperatures up to 220°C. Stainless steel can cause a change in the ratio NO: NO_2 at temperatures above 250°C. When this ratio is relevant, ceramic materials or glass is recommended. The system must be provided with a heated filter.

7 Systems that measure in dry flue gas can use sample gas cooling to separate the water vapour from the flue gas. A cooling temperature of 2 to 5°C is recommended. When setting up the measuring system, care must be taken against NO_2 loss due to absorption of this compound in the condensate. That is why the sample gas cooler, must at any rate be placed in front of the sample pump, as shown in the figure opposite. The use of permeation drying also restricts the risk of NO_2 loss.

8 Systems that measure in wet flue gas can use heating to prevent condensation in the system. Special care must be taken against cold spots where unwanted condensation, and hence NO_2 loss, can occur. By heating and good insulation, the temperature of both the sample transport system and the analyser must be kept above the condensation point of water.

9 When measurements are taken with a NO analyser, while the flue gas contains a ratio of more than 10% NO_2, a converter should be used. This must have a yield of at least 95% for the conversion of NO_2 to NO. A method for determining the converter yield is described in standard NEN-ISO 7996.

10 When a method on the basis of chemoluminescence is used, the measurement can be interfered with by the presence of CO_2 and water vapour; this can cause the chemoluminescence signal to "fade" (known as quenching). The extent of fading under the prevailing conditions must be known (by the manufacturer's specification or by self-performed tests) and for this the measurement result must be corrected.

11 Before and after each measurement, the sensitivity of the measuring system must be checked by providing a zero gas (without NO_x) and a control gas (with known NO_x concentration). The reading of the analyser is then compared with the provided concentration. This procedure is known as zero and span check. The concentration of the control gas should be around 70–80% of the measuring range. Each control gas bottle must be provided with an analysis certificate with the concentration and must be traceable to an (inter)national standard. The observed differences between the zero and span value before and after a measurement is called the zero and span drift. The measurement body must have criteria for dealing with drift. From a specific minimum drift, the analyser must be adjusted and the measurement values corrected. From a specific maximum drift, the measurement values must be rejected (rejection criterion).

12 It is important to adjust the measuring range to the highest occurring concentrations, so that these values can also be integrated correctly in the average values.

13 When the NO concentration must be reported at a specific standard oxygen content, the actual oxygen concentration must be determined, at the same time as the NO_x measurement, in the vicinity of the measuring plane. This must be used to convert the measured NO_x concentrations. When measurements are taken in wet flue gas and must be reported in dry flue gas, the moisture content must also be corrected.

More information	
Quality assurance of measurement body / laboratory	NEN-EN-ISO/IEC 17025 or 17020
Sampling	NEN-ISO 10396; NEN-ISO 9096
Determination of yield of converter	NEN-ISO 7996
Determination of oxygen content	Factsheet on Oxygen
Determination of moisture content	Factsheet on Moisture
Background information	InfoMil publication "Measurement of air emissions"(L40)

Checklist for NO_x periodic measurement

When one of the questions in the checklist is answered negatively and no satisfactory reasons are given for the deviation, then corrective measures are necessary for obtaining a reliable measurement result.

			yes	no	n/a
1	**Accreditation of measurement body**	Does the measurement body meet the quality requirements for accreditation in accordance with the permit or the law and regulations in question?	☐	☐	☐
2	**Operating conditions**	Is the measurement performed under representative operating conditions?	☐	☐	☐
3	**Sampling**	Does sampling occur in a demonstrably representative way (report)?	☐	☐	☐
4	**Leak-tightness of entry opening**	Has the space between the sampling probe and the entry opening to the stack been reduced?	☐	☐	☐
5	**Leak-tightness of sampling system**	Has a leakage test been performed in a demonstrable way and have any leaks been corrected (log)?	☐	☐	☐
6a	**Sampling probe**	Is the sampling probe made of a suitable material?	☐	☐	☐
6b	**Filter**	Is the sampling system provided with a heated filter?	☐	☐	☐
7	**Determination in dry flue gas**	Is the sample gas cooler placed in front of the pump or is permeation drying applied?	☐	☐	☐
8a	**Determination in wet flue gas**	Is the entire sampling system kept at a sufficiently high temperature to prevent condensation?	☐	☐	☐
9	**Converter**	Has the yield of the converter been determined and is it above 95%?	☐	☐	☐
10	**Quenching of chemoluminescence**	Is the extent of the quenching effect by CO_2 and water vapour on the chemoluminescence reaction known and are the measurement values corrected for this?	☐	☐	☐
11a	**Zero and span check**	Is the system checked demonstrably before and after each measurements with zero and control gas?	☐	☐	☐
11b	**Zero and span check – quality of control gas**	Does the control gas have a valid analysis certificate and is it traceable to an (inter)national standard?	☐	☐	☐
11c	**Zero and span check – concentration of control gas**	Does the control gas concentration correspond with 70–80% of the measuring range?	☐	☐	☐
11d	**Zero and span check – criteria**	Does the measurement body have criteria for dealing with the measurement values in relation to drift and does it act accordingly?	☐	☐	☐
12	**Measuring range**	Do all measurement values fall within the measuring range?	☐	☐	☐
13	**Measurements for conversion**	Are the actual oxygen content and moisture content determined at the same time as the measurement and are the NO_x concentrations converted with it?	☐	☐	☐

InfoMil, a link between environmental policy and implementation.
InfoMil is an initiative of the Ministry for the Environment and the Ministry of Economic Affairs in co-operation with the Association of Provinces (IPO), the Association of Dutch Municipalities (VNG) and the Union of Water Boards.

in charge of

VROM

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