# Monitoring Quick Guide 5

**version 1.0**

## SM-QG-05 - Monitoring oxides of Nitrogen

## 1. Scope

This note describes the techniques and standards required to monitor oxides of nitrogen, covering (i) definitions and sources of oxides of nitrogen, (ii) common techniques, (iii) applicable standards, (iv) reporting emissions of oxides of nitrogen, and (v) calibration functions for NOx when applying EN 14181.

## 2. Practical Guidance

### 2.1 Definition of sources of oxides of nitrogen

Oxides of nitrogen ($NO_x$) can theoretically include any gaseous compounds that consist of oxygen and nitrogen. However, this guidance note focuses on the commonest compounds in $NO_x$, which are:

- Nitric oxide (NO)
- Nitrogen dioxide ($NO_2$)

The dominant source of $NO_x$ is combustion and within the emissions from combustion plant the total $NO_x$ is typically dominated by NO. In most installations, the concentration of NO in total $NO_x$ is typically greater than 95% with $NO_2$ concentration less than 5%. In combined-cycle gas turbines (CCGTs) and some types of chemical process, emissions of $NO_2$ can be much higher than 5%.

Some types of combustion plant emit relatively smaller proportions of nitrous oxide ($N_2O$), whilst a small number of other types of installation are also known to emit $N_2O$.

### 2.2 Legal requirements for reporting $NO_x$

Although most of the $NO_x$ that installations emit consists of mainly NO, permits typically require operators to report emissions of $NO_x$ as “Oxides of Nitrogen (as $NO_2$)” and additionally comply with emission limit values (ELVs) as $NO_2$ (see Example 1). This is because once NO enters the atmosphere, it is rapidly oxidised to $NO_2$ ($2NO + O_2 \rightarrow 2NO_2$).

Operators with $NO_x$ emissions dominated by NO may monitor NO alone, subject to the following caveat:

- The operators must verify that the $NO_x$ emissions are dominated by NO, and then apply a conversion factor to compensate for the $NO_2$ in the $NO_x$ which NO monitors cannot detect. This verification can be performed through regular compliance monitoring, e.g. when UKAS accredited test-laboratories measure total $NO_x$ by applying the Standard Reference Method (SRM) for $NO_x$, BS EN 14792.

- Alternatively, operators may: (i) use a $NO_x$ converter to convert any $NO_2$ to NO. The operator must then report the NO emissions as $NO_2$, or (ii) measure $NO_2$ separately within a Continuous Emission Monitoring system (CEM), in addition to the CEM measuring NO, and then report the total $NO_x$ as $NO_2$.

It should be noted that the exhaust gases from CCGTs typically include higher proportions of $NO_2$ than other types of combustion process. Therefore the CEMs used on CCGTs must be able to measure total $NO_x$.

Example 1: Converting NO to $NO_2$. One mol of NO yields one mol of $NO_2$ upon oxidation. One mol of NO at STP weighs 30g whilst one mol of $NO_2$ at STP weighs 46g. Therefore to calculate the amount of $NO_2$ produced when 302 mg.m$^{-3}$ is oxidised, the following calculation is used:

Emissions as $NO_2$ = $\frac{46}{30} \times 302$ mg.m$^{-3}$ = 463 mg.m$^{-3}$

Example 2: An operator measures NO alone. The proportion of NO in the $NO_x$ is 95%. The measured value of NO is 302 mg.m$^{-3}$.

Step 1: convert the NO to $NO_2$ using the equation above, which gives 463 mg.m$^{-3}$ of NO

Step 2: To calculate the total $NO_x$, divide the NO readings by 0.95, = $\frac{463}{0.95}$ = 487 mg.m$^{-3}$

## 2.3 Techniques for monitoring $NO_x$

There are several instrumental techniques for measuring $NO_x$. These include:

- **Chemiluminescence (CLS) analysers:** These exploit a chemiluminescent reaction which occurs between NO and ozone. IR analysers for NO may also measure $NO_2$ if they are equipped with a $NO_2$-to-NO converter.
- **Infrared spectroscopic analysers (IR):** These include gas-filter correlation (GFC-IR) and fourier-transform (FTIR) analysers. NO, $N_2O$ and $NO_2$ all have strong IR spectra, so this technique is useful for measuring $NO_x$.
- **Ultraviolet (UV) spectroscopic analysers:** NO and $NO_2$ also absorb electromagnetic radiation in the UV region of the electromagnetic spectrum.
- **Electrochemical cells:** There are analysers using electrochemical cells, available for NO and $NO_2$.

## 2.4 Converter efficiencies

If the proportion of $NO_2$ in the total $NO_x$ is more than 5%, then the converter efficiency needs to be at least 95%, as specified by BS EN 14972.

## 2.5 Applicable standards

The European Union BREF on the General Principles of Monitoring specifies the standards and methods which the Scottish Environment Protection Agency requires for monitoring $NO_x$. This states that a hierarchy of standards should be used with European (CEN) Standard Reference Methods (SRM) recommended as being the most suitable. The Waste Incineration Directive (WID) and Large Combustion Plant Directive (LCPD) state that CEN SRMs are mandatory where available and must be used for monitoring emissions. In the UK CEN SRMs are transposed as BS EN SRMs.

Current available SRMs are summarised in The Environment Agency Technical Guidance Note (TGN) M2. For $NO_x$ CEMs TGN M2 specifies BS EN 15267-3, which is a performance-based standard, this means that the CEM can apply any technique as stated in section 2.3 as long as the CEM meets the performance requirements in BS EN 15267-3.

For periodic monitoring TGN M2 specifies BS EN 14792, as the SRM for measuring $NO_x$. It is based on a CLS technique, although other techniques may be used provided they are proven alternative methods and meet the performance standards specified in BS EN 14792. In order to carry out UKAS accredited monitoring of $NO_x$, it is necessary for a monitoring organisation to be accredited to use this SRM.

A summary of available methods available for NO, $NO_2$ and $N_2O$ are given in the table below:

**Table 1 Standards which apply to monitoring NO, $NO_2$ and $N_2O$**

| Standard Reference Number | Notes |
|---|---|
| BS EN 14792 | This is the CEN standard and SRM for monitoring $NO_x$. It is based on the CLS technique. CEN standards are mandatory when monitoring WID and LCPD sites and are recommended for all other sites covered by the IPPC directive. |
| BS EN 15267-3 | This standard specifies performance specifications and test procedures for CEMs measuring gases and particulates. The scope of the standard includes $NO_x$ monitoring CEMs, and therefore it will supersede ISO 10849. |
| BS EN 21258 | This is a new CEN/ISO standard and SRM for monitoring $N_2O$ using NDIR. It has replaced VDI 2469-1 and VDI 2469-2. |
| TGN M22 | This is an Environment Agency alternative method for monitoring a variety of determinands using FTIR. The scope of the standard can include NO, $NO_2$ and $N_2O$. It has replaced the US ASTM D6348-3. If companies can show that they have demonstrated equivalence to the SRM then this method can be accepted. Accreditation (e.g. UKAS) can generally be used to show this. |

## 2.6 $NO_x$ calibration functions

The three ways in which installations measure $NO_x$ are:

- Measuring NO alone and then applying a conversion factor to account for $NO_2$ in the stack gases, i.e. inferring the $NO_2$ concentrations.
- Measuring NO and $NO_2$ separately and combining the measurements.
- Using a $NO_x$ converter to measure both NO and $NO_2$.

This can create challenges when performing a QAL2 or AST, especially if the standard reference method (SRM) uses a different technique to the CEMs. Furthermore, in the case of separate calibration functions for NO and $NO_2$, the NO can be oxidised in sampling lines, there can be different rates of oxidation in the SRM and CEM sampling lines, or not at all with in situ CEMs. This would mean that SRMs and CEMs both measuring NO and $NO_2$ separately are not always comparable.

Expressing NO as $NO_2$, on the other hand, and adding the two $NO_2$ concentrations, would eliminate this problem. Therefore we recommend the following approaches when performing QAL2 and AST exercises.

<table>
<tr><th>CEMs</th><th>SRMs</th><th>Approach</th></tr>
<tr><td>NO</td><td>NO</td><td>Generate a calibration function for NO</td></tr>
<tr><td>NO</td><td>Total - $NO_x$</td><td>Generate a calibration function for NO using the measurements for total-$NO_x$, bearing in mind that the calibration function should implicitly include the proportion of $NO_2$ in the stack gas.</td></tr>
<tr><td>$NO+NO_2$</td><td>Total -$NO_x$</td><td rowspan="3">Convert the $NO+NO_2$ to total $NO_x$.<br>Generate calibration function.</td></tr>
<tr><td>Total -$NO_x$</td><td>$NO+NO_2$</td></tr>
<tr><td>$NO+NO_2$</td><td>$NO+NO_2$</td></tr>
</table>

## 2.7 Treatment of $NO_x$ calibration functions during ASTs

Where there are existing NO and $NO_2$ calibration functions from the previous QAL2, and where the $NO_2$ data is below 20% of the $NO_x$ ELV, carry out the following:

Check the current NO function against a total $NO_x$ figure. If it passes the variability and acceptance tests, then no further action is needed, beyond reporting.

If the AST tests result in a failure, then regenerate the function for total $NO_x$ from the original QAL2 data and check the AST using total $NO_x$.

If this new function passes, state this in the report and advise the site that the calibration function has changed.

If the new calibration function and AST data results in a failure of the variability and/or acceptance tests, then a new QAL2 will be required.

# 3. Further information

## 3.1 Quick Guides

- SM-QG-01 Selecting continuous emission monitoring systems (CEMs)

## 3.2 Environment Agency Technical Guidance Notes

- TGN M2 – Monitoring of stack emissions to air
- TGN M20 – Quality assurance of continuous emissions monitoring systems

# 4. Feedback

Any comments or suggested improvements to this note should be e-mailed to Duncan Stewart at duncan.stewart@sepa.org.uk.

# 5. Acknowledgments

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