NOx measurement in combustion processes

NOx is a generic term for the oxides of nitrogen that have significant effects on the environment and human health. These include nitric oxide (NO) and nitrogen dioxide (NO2), which are mostly produced by the combustion of fossil fuels such as in vehicles and engines, as well as industrial processes such as power generation and cement manufacture. Consequently, NOx measurements are vital to minimise emissions and demonstrate compliance in applications such as engine development, combustion control, emissions abatement, stack testing, and in the development of any products or processes that burn hydrocarbon fuels. Examples include process boilers, gas turbines, stationary diesel engines, domestic boilers and wood burners.

Why are NOx emissions a problem?

Globally, a wide variety of organisations have published reports linking serious health effects with short- and long-term exposure to NO2. For example, in 2015, the UK's Committee on the Medical Effects of Air Pollutants (COMEAP) reviewed the available evidence and concluded: Studies have shown associations of NO2 in outdoor air with adverse effects on health, including reduced life expectancy. It has been unclear whether these effects are caused by NO2 itself or by other pollutants emitted by the same sources (such as traffic). Evidence associating NO2 with health effects has strengthened substantially in recent years and we now think that, on the balance of probability, NO2 itself is responsible for some of the health impact found to be associated with it in epidemiological studies.

From an environmental perspective, NOx gases contribute to the formation of smog and acid rain, and NOx in the atmosphere contributes to nutrient pollution in coastal waters. Globally, emission limits for NOx are becoming more stringent as governments seek to address these concerns.

NOx measurement in product development

The designers of engines, boilers, turbines and incinerators seek to optimise combustion efficiency whilst minimising the harmful emissions of gases such as NOx. In many cases, this means that products have to be designed to comply with the local emission regulations, wherever they are sold.

Organisations conducting combustion research have a different monitoring requirement to plant operators and stack testers. This is because stack testers simply require analysers that comply with certain performance requirements, whereas those in R&D require highly accurate, definitive measurements of NO, NO2 and NOx in order to fine-tune their designs and optimise the performance of their products. In addition, it will frequently be necessary for them to provide defensible measurement data in order to secure formal approvals in local markets. This is extremely important because the untimely discovery of any NOx measurement errors, interferences or excessive levels of uncertainty could prove costly.

Reference Method – chemiluminescence (CLD)

The European Standard EN 14792 specifies chemiluminescence as the standard reference method (SRM) for the measurement of NOx in stationary source emissions. However, the method cites several alternative CLD configurations but it only stipulates Chemiluminescence as the method of detection. The Standard does not specify whether the analyser should be heated or unheated, or whether the detector should be vacuum based or atmospheric. In addition, it does not specify whether the NO2 component should be converted to NO prior to any water in the sample being condensed for removal. The EN standard reference method EN 14792 is intended for stack testing laboratories, to verify the installation of a Continuous Emissions Monitor on an industrial chimney stack.

Designing a true reference analyser - key considerations

1. Chemiluminescent photon detector

The chemiluminescence reaction of Ozone and Nitric Oxide causes the oxidation of Nitric Oxide (NO) to Nitrogen Dioxide (NO2) which generates photons that are measured using a photomultiplier tube. To obtain maximum sensitivity from the photomultiplier tube it must be cooled so that its 'dark current' can be reduced (dark current is a small electric current that flows even when no photons are entering the device).

It would be possible to increase the sample flow to the detector to increase its sensitivity, but it is necessary to keep the sample flow as low as practicable to achieve the quenching target. Typically, at Signal Group, the flows of Ozone and sample are set in a ratio of 10:1. Signal's CLD instruments employ two detectors for continuous measurements of NO and NO2. The sample is passed directly to one of the detectors, and via the NO2 converter for the other. The NO2 value is derived by continuously subtracting the NO-only detector signal from the other detector's signal. The reaction chamber design is particularly important with a vacuum based analyser because the reaction gases pass very quickly to the vacuum pump.

2. Advantages of a vacuum CLD

Water vapour and Carbon Dioxide within a sample will reduce, or quench, the reading of NO, and combustion exhausts usually contain high levels of both. Signal Group has therefore developed a CLD with a vacuum in the reaction chamber, which eliminates the quenching effect, and increases the signal to noise ratio considerably. An additional advantage of the vacuum is that it allows for the delivery of a hot wet sample gas to the reaction chamber without the threat of condensation.

3. Ozonator design

Ozone is necessary for the oxidation of NO, but a number of potential pitfalls exist in the choice of ozone generation technology. For example, high-voltage corona discharge lamps would oxidise any Nitrogen in the

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air feed to NO and NO2; artificially raising the readings and presenting a threat of corrosive Nitric Acid formation. This could be resolved by using pure Oxygen as the feed gas, but that would be prohibitively expensive. Signal Group therefore employs a soft-discharge neon lamp in its ozonator, which does not oxidise Nitrogen.

4. NO2 Converter

The choice of NO2 converter material is an important consideration because at high temperatures stainless steel would oxidise any Ammonia in the sample to NO. Furthermore, if there is insufficient oxygen in the sample, it will be 'robbed' from NO2, so an oxygen bleed to the sample would be necessary. To avoid this unnecessary complication, the Signal Group CLD analysers use a vitrified type of carbon in a heated quartz vessel which has none of these characteristics, and lasts for at least two years of operation.

5. Vacuum pump

Traditional oil filled rotary vane pumps are prone to problems caused by Ozone contaminating the oil. Signal Group therefore employs membrane pumps with a catalyst for removing Ozone.

With over 30 years of experience in the design and manufacture of reference CLD analysers, Signal Group has continually refined its product offering to ensure the highest levels of accuracy, sensitivity and repeatability. Recognising Signal's experience and expertise in NOx analysis, James Clements, Signal Group MD, is now a member of the SAE E-31 Aircraft Exhaust Emissions Measurement committee.

In addition to the advantages of Signal's core CLD technology, recent developments have included functionality enhancements such as compatibility with 3G, 4G, GPRS, Bluetooth, Wifi and satellite communications. Each instrument now has its own IP address and runs on Windows software; providing users with simple, secure access to their analysers at any time, from anywhere.

The most recent development is an option for a detachable screen. Customers will find this useful when it is necessary to install the analyser in a location with difficult access – such as: in an ATEX enclosure; in vehicle exhaust gas test cells; with a raised gantry on a stack; in a combustion test rig, or on any site where the location of analysis is not an ideal or safe working space.

Further details on Signal Group's gas analysis technologies are available at [www.signal-group.com.](http://www.signal-group.com)

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