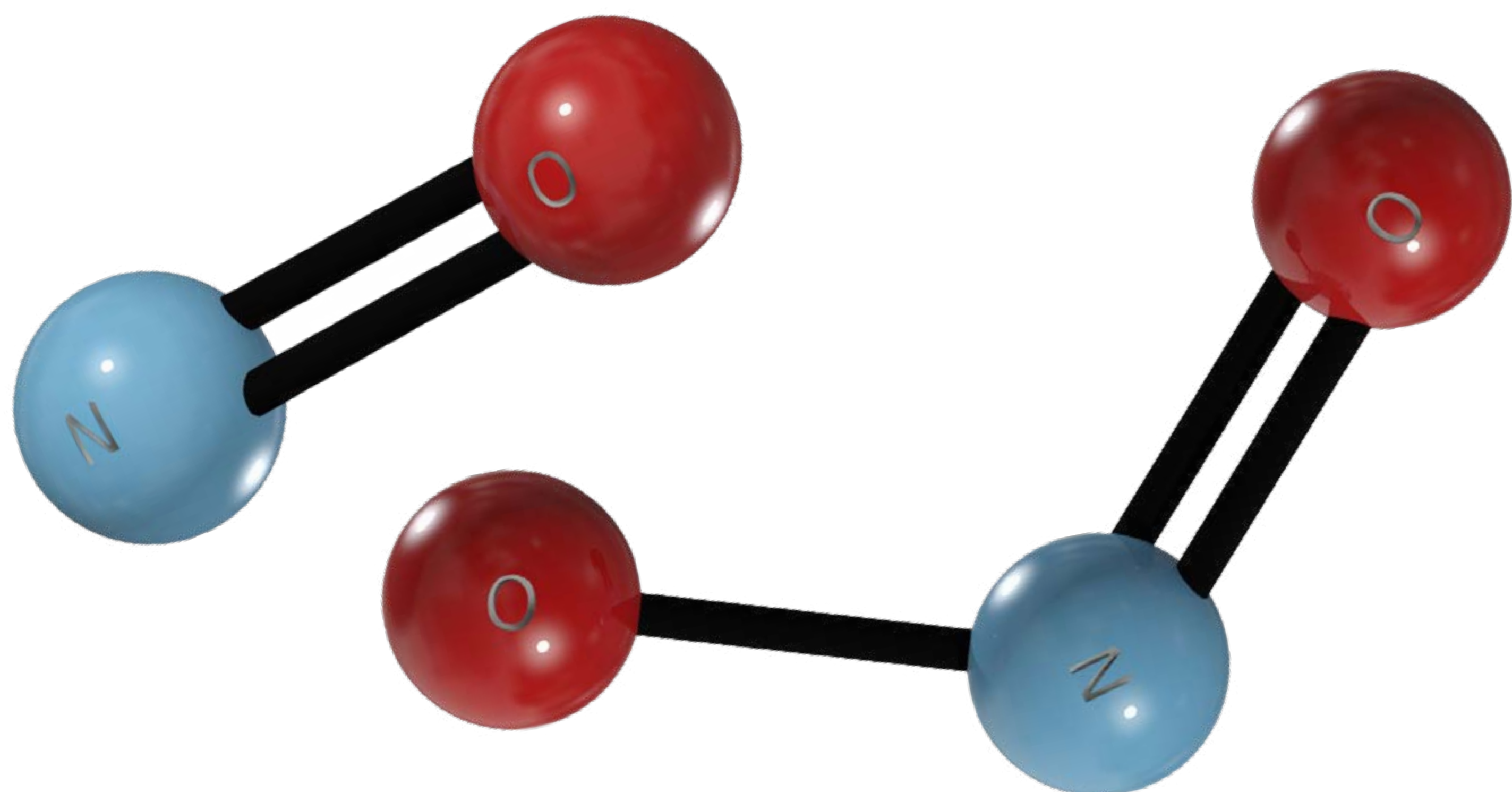# Oxides of Nitrogen and Smoking machines
Cerulean, Milton Keynes, UK

Introduction

Smoking cigarettes, cigars and even heated tobacco products (HTP) produces oxides of nitrogen but what are these?

NOx – A mixture of NO and NO_2. There is a conversion between NO and NO_2 in the gas phase which is time based. NO_2 is an important air pollutant associated with respiratory symptoms in humans and emphysema development in animal models.

Gas phase chemistry of NO/NO_2 mixtures needs to be recognised. There is a conversion with a mixture of NO to NO_2 with time as the NO is oxidised to NO_2

$$NO + \tfrac{1}{2}\,O_2 \longrightarrow NO_2$$

This is a time-based phenomenon so the longer the nitric oxide is present in air the more this reaction moves to the right. This is accelerated by temperature and by the concentration of gasses involved but for our purposes we can state that this is something that occurs in seconds and has significant measurable effects in a matter of one or two minutes. This concern drives the demand for puff by puff analysis when analysts want to determine the ratio of NO_2 to NO when the gases are first formed.

There is a further confusing factor in that there are other reactions happening in the smoke matrix between NO and other gas phase molecules such as CO_2 and HCN. This can be supressed by highly diluting gas which "quenches" some of these reactions.

The selection of an appropriate analyser for the industry has been driven by capability. Analysis of oxides of nitrogen started back in the 1950's/1960's [6] and it was recognised that NDIR was not capable to distinguishing low concentrations of gas and was not as selective as required (there are spectroscopic interferences to consider in the complex matrix). An alternative analyser was sought and a chemiluminescence analyser, which was commercially available, selected. Today a different selection may have been made as infra-red analysers using FTIR and laser diode spectroscopy would be much more selective and capable [1], however the cigarette industry is committed to chemiluminescence AND because of the driver for HTP testing comes from the same industry it is highly probable that the same methods will be adopted for HTP despite any technical short comings[2].

Chemiluminescence analysers work in this way:

Chemiluminescence operates on the principle that Nitric Oxide (NO) and Ozone (O_3) react and create a molecule with excess energy that luminesces. The resulting light can be measured and correlated to a concentration of NO using a photomultiplier tube.

$$NO + O_3 \longrightarrow NO_2{}^* + O$$
$$NO_2{}^* \longrightarrow NO_2 + \gamma$$
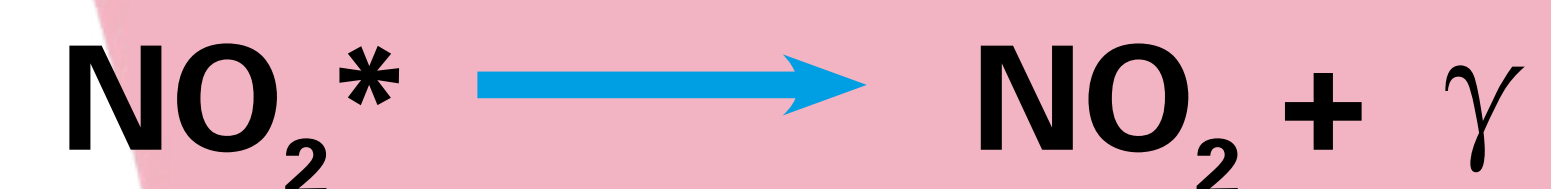
Where:

NO_2 - NO_2 molecule in an electronically excited state
γ – photon emitted when excited NO_2 molecule returns to ground state

The chemiluminescence procedure was found to be very selective for NO with no known interference from tobacco smoke.

Ozone is generated by the unit itself and is mixed in excess with the gas to be analysed and the NO is raised to an excited state. The $NO_2{}^*$ is allowed to relax and this involves the loss of energy in the form of a photon, the number of photons emitted being directly proportional to the amount of NO originally in the target gas.

This measures only one part of the mixture and as we have seen NO is converted to NO_2 with time so this alone would underestimate the amount of NO present and not measure the NO_2 at all. This is overcome by a neat trick.

NO_x is equal to NO + NO_2. Since the chemiluminescence reaction only works with NO, Nitrogen dioxide (NO_2) needs to be converted into NO in order to be measured. NO_2 is converted to NO (reduced) using a molybdenum or stainless-steel converter/catalyst. Stainless steel is the most popular choice for converter material for stack monitoring as it is robust and does not easily poison.

The stainless-steel converter is typically heated to 625 °C which can be a problem because it also converts other gases such as ammonia (NH_3) to NO causing a falsely high reading. Hence the molybdenum converter that is heated to 325 °C is used in preference for our application but with the caveat that it has a finite lifetime for use.

The molybdenum "strips" one of the oxygen atoms off the NO_2 leaving NO which then reacts in the ozone chamber and the excited NO is measured along with the NO originally in the sample.

If a measurement is made on a sample without catalysis and then with the catalyst it is possible to determine the NO concentration, the NOx concentration and by difference the NO_2 concentration.

The measurement at the analyser is made in parts per million (ppm) and then this is converted into micrograms per cigarette using some simple mathematics and application of gas laws.

The range of measurement for a combustible cigarette would be in the region of 500 to 700ppm of total NO_x which equates to about 350 to 500µg of NO_x per cigarette. Of this we would expect to have from fresh gas 50 to 70ppm of NO_2 within this sample which is about 30 to 50µg per cigarette.

If the analyst accepts that the ratio of NO to NO_2 is constant when produced by smoking, then the total NO_x of a smoke sample suitably filtered of particulates is valuable provided that the sample does not sit around too long and allow reactions in the gas phase with the rest of the smoke matrix resulting in low estimates of NO_x.

There are still some caveats that need to be understood, the first is that the NO and NO_2 tend to "coat" pipework and it may be necessary to discard, or be wary of, early measurements as these can be up to 4% lower than subsequent measurements [3].

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If the limitations described in the preceding two paragraphs are accepted it is possible to capture the gas phase from cigarettes in a bag much as we do with CO (in fact the same bag could be used, the Tedlar version being recommended) and then analysis can be performed on this gas much in the same way as we would for CO but using the chemiluminescence analyser rather than an NDIR CO analyser.

Here we would only measure the NOx (total oxides) value as we would recognise that the NO content would be supressed by the reaction detailed at the start of this document.

With the advent of HTP oxides of nitrogen have become of renewed interest.

Firstly, there was the interest in showing the reduction of up to 97% in toxins such as NO and NO_2 and secondly these oxides of nitrogen can be used as indicators or markers of combustion. A lot of NO_x would result from the reconstituted tobacco burning not just heating.

Consequently, NO_x has been measured in HTPs and continues to be measured in these products as part of the batch release for manufacturers.

Here the interest is in the total oxides, NO_x. It is possible that this is in part due to the very low levels of NO_2 in a gas sample and the errors that introduces. A typical HTP will have NO levels 10 to 30ppm (12 to 45µg/stick) and NO_2 levels of 1-3ppm which is not far from the noise threshold for the equipment being used – it is possible to accurately measure low levels of these gases but not necessarily in the gas matrix produced by HTP's which is still complex containing some organic molecules, water, CO and so on.

In the routine analysis of the gases from HTPs it is common to collect all gas from a smoke run and then analyse for NO_x at the end of the smoke run. This methodology lends itself to linear smoking machines where all the gas can be collected and analysed at the end of the smoke run or sub run.

In the preparation of specifications for the test of HTPs national bodies are looking at, amongst other gases and analytes, NO_x as a key analyte of interest, for example the UK draft PAS 8850 Annex D [4] refers to a method for measuring NO_x in HTP aerosol that is largely based on a standard operating procedure at a major HTP manufacturer).

There are also international moves to draw up ISO standards for Nitrogen Oxide measurement for mainstream smoke in combustible cigarettes [5].

If you are considering adding analysis of NO_x or other oxides of nitrogen to your routine test and analysis capabilities, there are several routes you can follow.

Option 1: Purchase a suitable NO_x analyser and capture a filtered gas sample and move this to the analyser ,exhaust a captured gas sample into the analyser and record readings. This has the benefit of simplicity but falls foul of two problems. Firstly there is the recording and calculation that breaks the "chain of custody" between sample formation and measurement. Errors can occur and data can be corrupted. This is a risk to be considered in a GLP environment. The second problem is one of practicality and time, gas bags on smoking machines are not really intended to be removed and replaced on routine basis.

Option 2: Buy a new smoking machine with NO_x analysis included. This is the best option from the perspective of data traceability and ease of use. However the capital outlay is high and space constraints for a laboratory may be significant. Also justifying machine replacement for what might be occasional NO_x analysis is difficult.

Option 3: Is to upgrade an existing smoking machine such as the Cerulean SM450 to include NO_x analysis alongside the existing CO analysis. This satisfies both worlds, ease of use and data integration and traceability. Cerulean are able to offer a number of upgrade packages, depending on the status of the smoking machine, that can take NO_x samples from all 20 bags, perform an analysis and integrate the results into the smoke report for print out or export to a LIMS system. Both CO and NO_x analysers can be supplied that work in the higher ranges demanded by combustible cigarettes and cigars and also in the low range needed for HTP analysis.

Enhance your SM450 to measure Oxides of Nitrogen

SM450

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