Pollutant Type: Gaseous Pollutants

Pollutant Name: Nitrogen Dioxide (NO_2), Nitrogen Oxide (NO), Nitrogen Oxides (NO_x)

Measurement Technology: Chemiluminescence method – detection of chemiluminescence from reaction of nitrogen monoxide with ozone

The measurement of NO_2 by detection of the chemiluminescence signal from the reaction of nitrogen monoxide with ozone is the reference method for ambient NO_2 measurements in Europe (EN 14211:2005). Monitors using this measurement principle measure the concentration of nitrogen monoxide (NO) and NOx (NO_x=NO+NO_2). The concentration of NO_2 is calculated by subtracting the measured NO concentration from the measured NO_x concentration.

In a chemiluminescence analyser air is fed into the reaction chamber of the analyser, where it is mixed with an excess of ozone. All NO is oxidized to NO2 by following reactions:

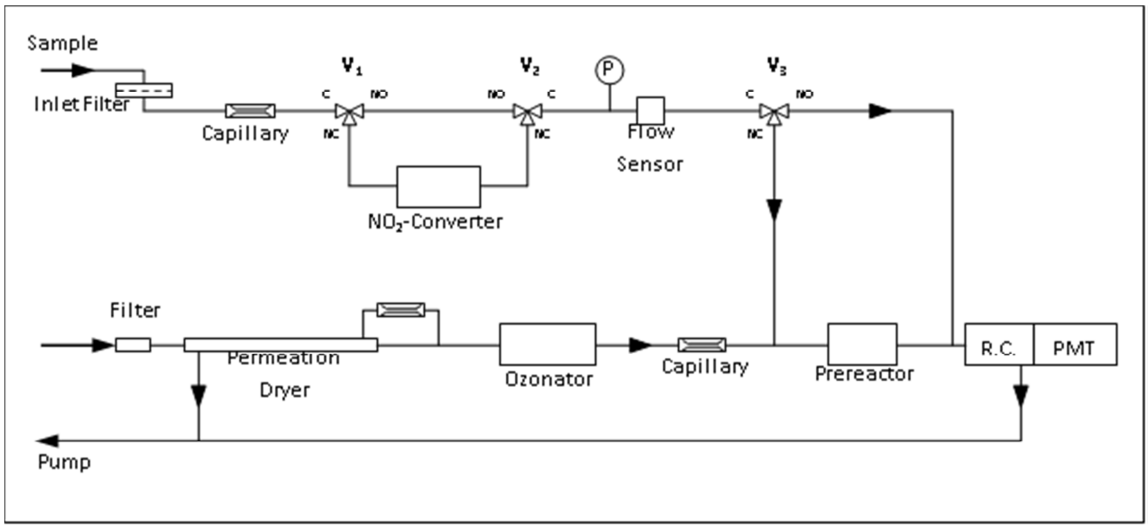
$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + h\cdot\nu$$

* = excited state of species

Infrared light that is released from the decay of NO_2* from an excited state to the ground state is detected by a photomultiplier tube. The intensity of the detected light (chemiluminescence) is proportional to the concentration of nitrogen monoxide. For determination of nitrogen dioxide, the sampled air is fed through a converter where the nitrogen dioxide is catalytically reduced to nitrogen monoxide and analysed in the same way as previously described. The chemiluminescence signal is proportional to the sum of concentrations of nitrogen dioxide and nitrogen monoxide. The concentration of nitrogen dioxide is calculated from the difference of the measured NO_x and NO concentrations.

A. Instruments with heated catalytic converters

Typical converters used for reduction of NO_2 into NO are made of a material such as stainless steel, copper, molybdenum, tungsten or spectroscopic pure carbon and are maintained at constant temperatures. The reference method for ambient NO_2 (EN 14211:2005) requires that the converter is capable of converting at least 95% of the nitrogen dioxide to nitrogen monoxide. A drawback of these converters is that other oxidized nitrogen compounds (e.g. HNO_3 and Peroxiacetyl nitrate) are reduced to NO with high efficiencies as well and can cause significant interferences (Steinbacher et al., 2007; Dunlea et al., 2007). These interferences are especially important at rural and remote sites.



Flow schematic of a typical NO-NO_x-NO_2 chemiluminescence monitor using a catalytic converter.

B. Instruments with photolytic converters

An alternative to the above mentioned catalytic converters are photolytic converters, where conversion of NO_2 is achieved by irradiation of NO_2 with UV light (< 410nm) according to following reactions:

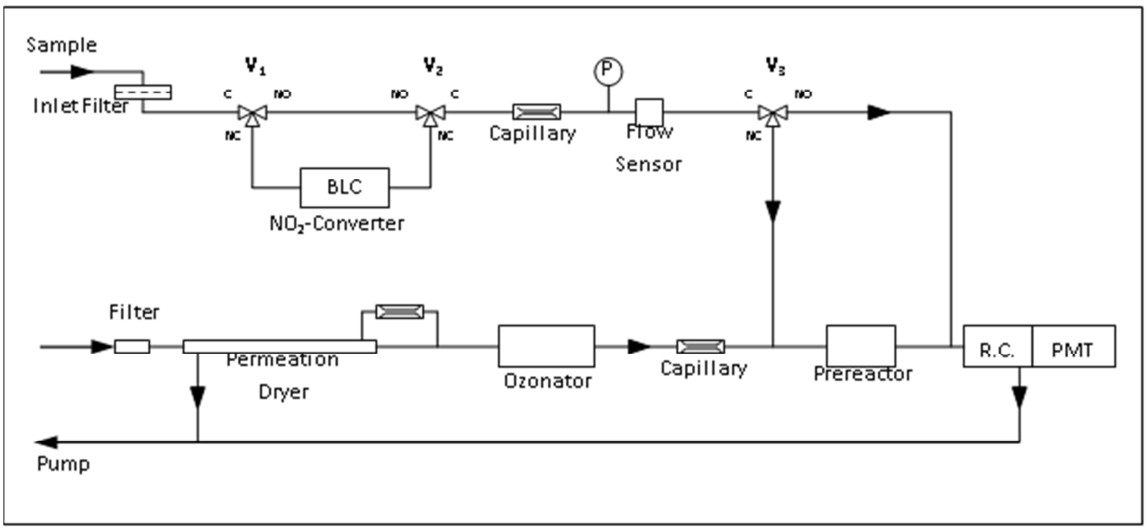
$$NO_2 + h\cdot\nu \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

leading to following equilibrium:

$$NO_2 + O_2 + h\cdot\nu \leftrightarrow NO + O_3$$

Instruments equipped with photolytic converters do not suffer from interferences to other oxidized nitrogen compounds and allow much more specific measurements of NO_2. However, the conversion efficiencies of photolytic converters are around 50% and much lower than the requirements of the European standard (EN 14211:2005). The converter efficiency of photolytic converters needs to be regularly determined for the correction of the measured signal.

There are photolytic converters available on the market that can be integrated into conventional instruments equipped with catalytic converters, more or less simply by changing the converter type (see flow schematic below).



Flow schematic of a NO-NO_x-NO_2 chemiluminescence monitor equipped with a photolytic converter (here denoted as BLC). In order to achieve a higher conversion efficiency, the pressure controller (here a capillary) has been placed downstream of the converter.

References

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Steinbacher, M., C. Zellweger, B. Schwarzenbach, S. Bugmann, B. Buchmann, C. Ordonez, A. S. H. Prevotand C. Hueglin (2007). "Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques." Journal of Geophysical Research-Atmospheres 112(D11).

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