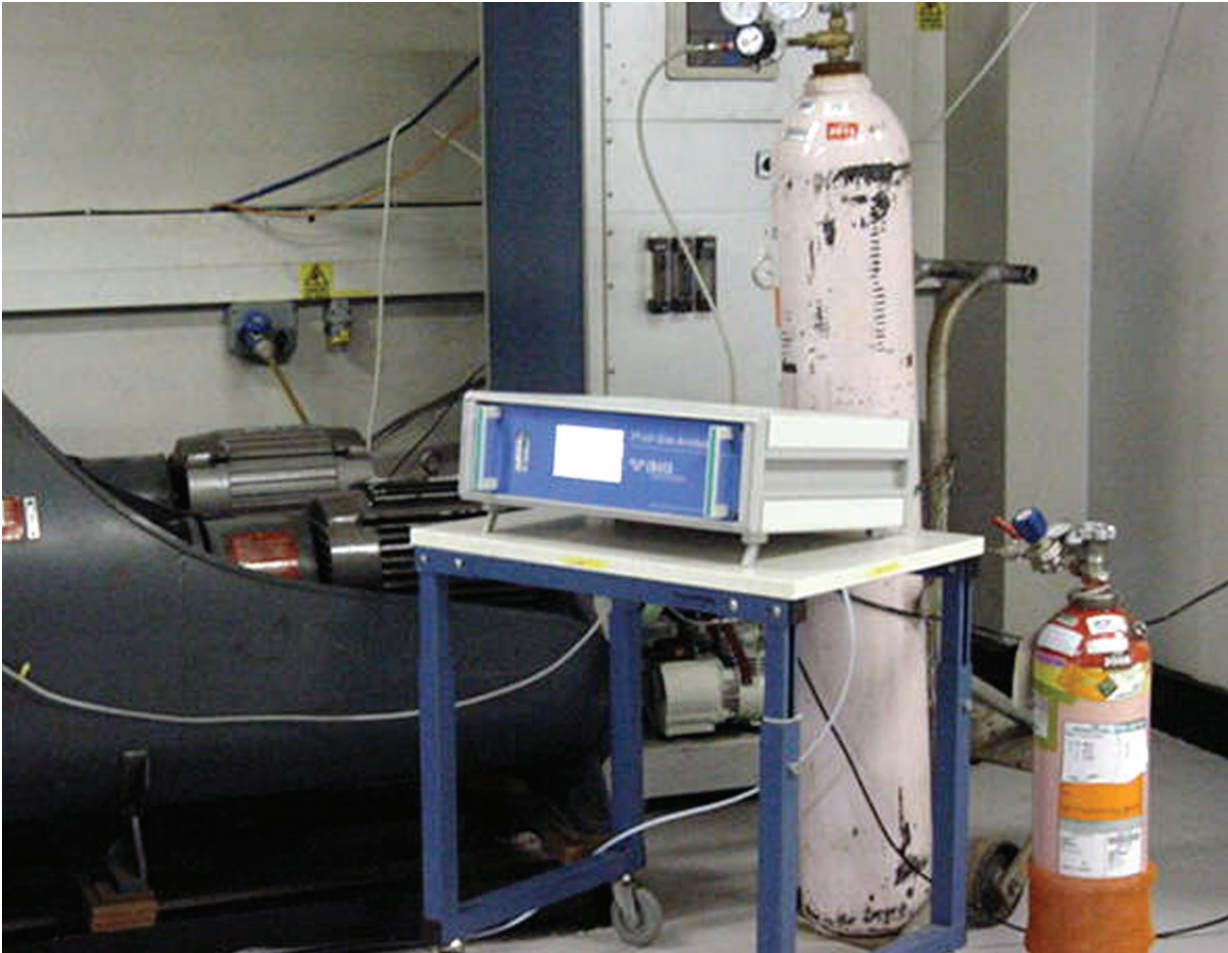


Ammonia Monitoring for DENOX PROCESS

By Philippe Minghetti and Rachid Mouflih

The aim of this article is to look at the problems and some of the solutions which have been developed for monitoring ammonia (NH₃) in DeNO_x process.



Introduction

The European directive 2001/81/EC of 23rd October 2001 has for objective to limit the emission of pollutants and ozone precursors in order to improve the protection of the environment and human health.

National emission ceilings, taking the years 2010 and 2020 as benchmarks, has been fixed for every European countries concerning the nitrogen oxides (NO_x), ammonia (NH₃), sulphur dioxide (SO₂) and volatile organic compounds (VOC).

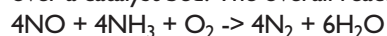
The NO_x, coming for more than 70% from combustion in vehicles and power plants, are responsible for a very significant increase of the respiratory diseases as bronchitis and asthma, especially for children and old people.

A recent three-country European study [1] found that air pollution causes 6% of all deaths, and thus kills many more people than traffic accidents.

The nitrogen oxides NO and NO₂ directly regulate O₃ production rates and indirectly influence aerosol abundances in the urban, rural, and remote troposphere. Emissions of NO_x are thus responsible for the major components of photochemical smog.

DeNO_x process

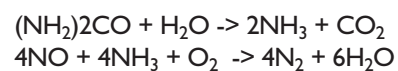
Selective catalytic reduction (SCR) is a well developed and widely used method for reducing NO_x emissions in the flue gas of a stationary combustor. The process involves the reduction of NO (and NO₂) to N₂ with approximately stoichiometric amounts of ammonia over a catalyst bed. The overall reaction is:



The selective non-catalytic reduction process

(SNCR), also known as the thermal DeNO_x process, reduces NO by addition of ammonia in the flue gas without the use of a catalyst. Ammonia is injected in the high temperature region of the boiler to reduce NO to N₂ thermally by the same overall reaction as occurs in SCR shown above.

Selective catalytic reduction systems have also potential for reducing emissions of NO_x in exhausts of heavy-duty diesel vehicles. A solution of inexpensive urea stored on the vehicle is injected into the exhaust upstream of the SCR catalyst. Urea when heated liberates ammonia, initiating the SCR deNO_x process on the catalyst surface above 250 °C:



Therefore the process has to be controlled to keep the ammonia slip in the exhaust [2].

Ammonia plays an important role in the transport of acidifying pollutants and is also involved in formation of secondary particulate matter aerosols in the atmosphere.

Ammonia may also give formation to ammonium salt that might plug equipment downstream of the SNCR process.

Some of these ammonium salts are hygroscopic and corrosive like ammonium bisulphate (NH₄HSO₄).

Scoop of existing methods for ammonia monitoring

a) Chemiluminescence with NH₃ converter

The chemiluminescence is based on the light emission coming from the chemical reaction between ozone

(O₃) and nitrogen monoxide (NO) as shown in the following equation: $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{light}$

The ammonia (NH₃) must be first converted to NO by a high temperature converter (about 800 °C). As NO and NO₂ might be present at high concentration in the sample, the measurement is done alternatively through and bypassing the converter to subtract the NO_x background. This operation introduces a delay of a few seconds that is not compatible with short response time that is needed, especially on motor exhaust applications.

The chemiluminescence is subject to quenching effect with the main combustion gases that are H₂O and CO₂, producing a de-calibration of the instrument.

b) FT-IR

The FT-IR spectrometry is based on a Michelson interferometer. The signal is recorded as a function of the optical path difference between the fixed and the movable mirror. Then a Fourier Transform is applied from this interferogram to obtain the spectrum as a function of wavelength.

The advantages of this technique are a higher spectral resolution and a typically higher throughput in intensity (no slit aperture required) compared to a classical IR spectrometer.

The FT-IR is a powerful method but its inherent high cost, long setting up and risk of interferences with the main combustion gases as H₂O, CO, CO₂, CH₄, BTX limit strongly his application for deNO_x process.

c) NIR DLAS (Near Infrared Diode Laser Absorption Spectroscopy)

The first and second overtones of the rotational=vibrational modes of many gases molecules generate absorption bands in the near infrared (0.8 – 3 μm).

The absorption spectroscopy is based on the Beer-Lambert law on one of the absorption bands of the NH₃ in the near infrared. The light is produced by a laser diode with a current modulation to scan the selected absorption band.

One of the main difficulties is to select an absorption band free from other absorption bands coming from the combustion gases: H₂O, CO, CO₂, CH₄, BTX.

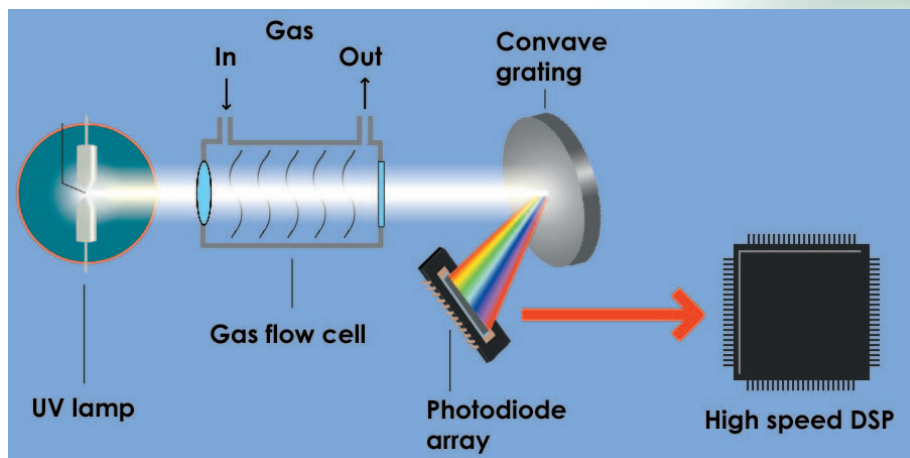
Long-term wavelength stability is one of the most important problems on laser diode. It will require time to time a temperature adjustment by a highly qualified operator to avoid failure.

As the absorption typically drops by an order of magnitude for every higher overtone, a multi-pass cell is generally necessary to achieve a correct sensitivity, that increases the cost of the instrument as well as the response time as the volume of a multi-pass cell is significantly higher than a single pass cell.

Moreover, particulates in the gas limit strongly the maximum acceptable optical path.

d) FT-UV (new method)

The measurement principle is based on the UV absorption spectrum of the ammonia gas (NH₃) in the UV range (figure). The periodic structure of the



absorption bands coming from the different levels of rotational energy of the gas molecules is analysed by performing a Fourier Transform on the absorption spectrum.

The main problem is to compute the spectrum in real time (that means in less than a second) that usual microprocessors are unable to do. Hopefully, high speed DSP (Digital Signal Processor) recently appeared on the market are able to perform this kind of calculations in a few tens of milliseconds.

The selectivity is guaranteed by the typical periodic structure of ammonia, different from any other gases. Typical measuring ranges are from a few ppm to tens or hundreds of ppm.

Other gases as NO_x may be measured simultaneously by the spectrograph for a low additional cost.

The fully solid-state measuring system is represented on the figure below. A xenon flash mode lamp having a 10 years typical lifetime is used as UV light source.

A second microprocessor takes in charge all the auxiliary functions: measurement display, trend graph, 4-20 mA output, data logging, checking, zeroing, calibration.

Conclusion

The FT-UV method appears to be the most suitable method for ammonia monitoring on deNO_x process, whatever for power generator or motor benches. Ultra-fast response time, high selectivity, no risk of interference with the major emission gases as H₂O, CO, CO₂, CH₄, moderate cost and very low maintenance are the main advantages of this technology.

Real applications of this technology on heavy-duty vehicle exhaust bench have confirmed these advantages.

The possibility to monitor NH₃ together with NO/NO₂ on the same instrument offer to the user a complete tool for deNO_x process control and/or optimisation.

Bibliography

- [1] Künzli, N. et al. Public health impact of outdoor and traffic-related air pollution: a European assessment. *Lancet*, 356: 795–801 (2000).
- [2] CONCAWE, report no. 99/62, Potential of exhaust after treatment and engine technologies to meet future emissions limits
- [3] Gunther, Barkley, Kolbezen, Blinn, Staggs - University of California, Vol28, no12, 1956. Quantitative Microdetermination of Gaseous Ammonia by Its Absorption at 204.3 nm

AUTHOR

Mr Philippe Minghetti and Mr Rachid Mouflih

Awa Instruments SAS

15 Chemin du Vieux Chene, F-38240 Meylan ZIRST – France

Tel +(33) 476 41 86 39 Fax +(33) 476 41 92 27

e-mail: sales@awa-instruments.com

www.awa-instruments.com