VSL Dutch Metrology Institute

Measuring NO_2 by LED-based CEAS with a novel cell design

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Abstract

Nitrogen dioxide (NO_2) is a highly reactive molecule that is harmful both for human health and environment. Current methods to measure NO_2 such as chemiluminescence are highly sensitive but lack specificity. Cavity-enhanced absorption spectroscopy combines both a high sensitivity and a good specificity. A new cell design is presented based on the polymers PTFE and POM that shows an improved time response as compared to coated stainless steel.

Introduction

NO_2 is a harmful gas both for human health and environment. It is normally measured using chemiluminescence but this method has several drawbacks mainly related to the specificity. For example, heated metal catalysts are known to convert also other NO_y species. Therefore the NO_2 fraction is an upper limit measurement of NO_2.

A more specific method is needed, in particular for areas with low NO_2 levels (compared to other interfering species). Within MACPoll VSL developed an instrument to measure NO_2 at trace levels based on cavity-enhanced absorption spectroscopy (CEAS).

Principle of operation

An overview of the spectrometer is shown in Figure 1.

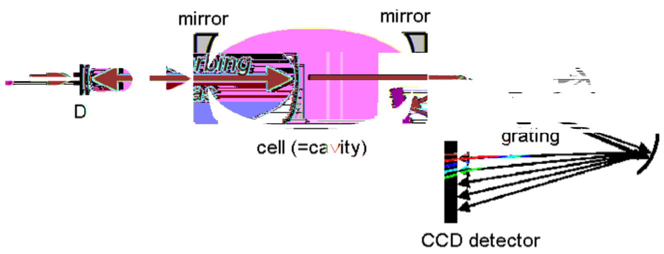

Figure 1 Schematic overview LED-based CEAS spectrometer.

As a light source a strong LED is used emitting blue light (435-470 nm). In this wavelength range NO_2 has a strong absorption band while absorption of other molecules present in the atmosphere is weak.
Light travels up to 9 km inside the cell (mirror reflectivity ~99,995 %) and is absorbed by NO_2. A spectrometer measures the transmitted light intensity. The extinction due to absorption can be calculated as follows:

$$\alpha_{abs}(\lambda) = \left(\frac{1-R(\lambda)}{d} + \alpha_{Ray}(\lambda)\right)\left(\frac{I_0(\lambda)-I(\lambda)}{I(\lambda)}\right)$$

d: cavity length
R(λ): mirror reflectivity
$\alpha_{Ray}(\lambda)$: Rayleigh scattering
$I_0(\lambda)$: reference spectrum matrix gas
I(λ): spectrum for absorbing species

A typical measurement of different NO_2 mole fraction is shown in Figure 2.

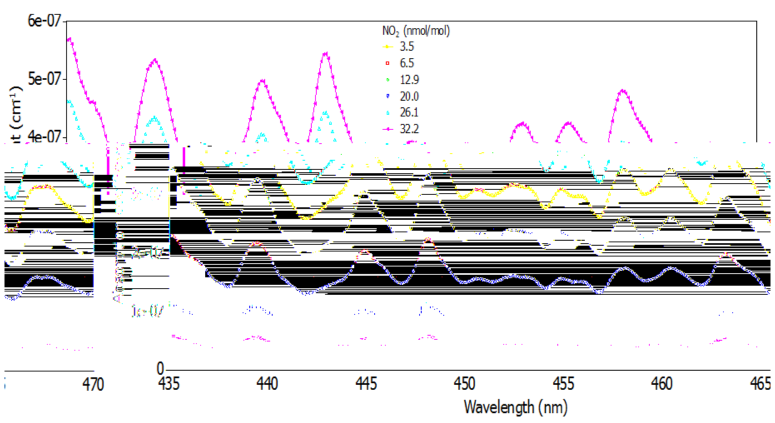

Figure 2 Measured absorption spectra for a range of NO_2 mole fractions (3.5-32.2 nmol/mol).

Novel cell design

NO_2 is a reactive molecule and it is known to interact with a variety of surfaces including many metals. In a previous design of the CEAS spectrometer we observed a slow response of the spectrometer to an <u>increase</u> step change in NO_2 mole fraction. This design was based on a flow tube of Silconert 1000 coated stainless steel and mirror holders of uncoated stainless steel.

Therefore a new cell (Figure 3) has been designed and tested in which the gas is only in contact with polymer (PTFE/POM) surfaces.

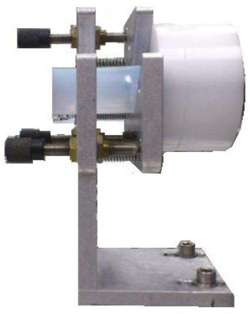

Figure 3 New cell design in which the gas is no longer in contact with metal surfaces.

Time response of the system

Figures 4A and 4B show the time response of the spectrometer using a cell based on stainless steel and PTFE/POM cell respectively.

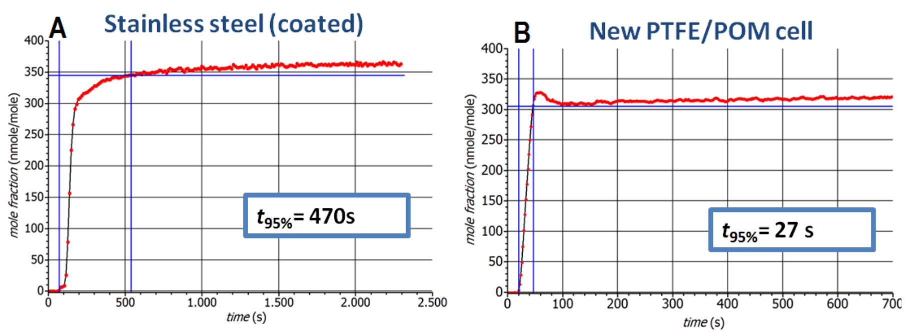

Figure 4 Response to a step change in the NO_2 mole fraction using stainless steel (panel A) and PTFE/POM cells (panel B).

A much faster response is obtained with the new cell (response time being now comparable to the filling time of the cell). Note that for a <u>decrease</u> in the NO_2 mole fraction the response time of both cells is about 30 s for both (results not shown).

Conclusions

A new cell design has been presented for the measurement of NO_2 using CEAS based on PTFE and POM. The time response of the cell has been improved drastically for a positive increase in NO_2 mole fraction.

This work was supported by the Dutch Ministry of Economic Affairs and the EMRP project MACPoll.

Ministerie van Economische Zaken

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

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