# Feature Article

## Quantum Cascade Lasers in Test Benches
### — Tracing Additional Exhaust Components using the Latest Measurement Equipment under Test Bench Conditions —

Daniel SCHEDER, Matthias SCHRÖDER,

Marcus RIEKER, Hiroshi KAWAMURA

Proposed legislation as well as new after-treatment devices that comply with recent regulations lead to the need for further analysis capabilities in terms of nitrogen exhaust components such as NO and $NO_2$, $NH_3$ and $N_2O$. This study compares conventional methods, which face difficulties when measuring these compounds, with a new analyzer utilizing Quantum Cascade Lasers (QCL). After a short description of optical absorption spectroscopy in general and the QCL technology in particular, system setup and sample handling with a QCL analyzer are described. The second part covers a variety of tests conducted at different locations within the HORIBA Group and at different end user laboratories. Subjects discussed include synthetic gas tests that verify the viability of the QCL analyzer as well as engine tests that show the analyzer in comparison with conventional methods for measuring nitrous gases under real test bench conditions. Further aspects such as urea conversion with Selective Catalytic Reduction (SCR) and $NO_2/NO_X$ ratio are discussed. The study shows that QCL technology is capable of mastering the growing challenges facing emission testing.

## Introduction

### Motivation

Proposed legislation as well as new after-treatment devices that comply with recent regulations lead to the need for new analyzing capabilities in terms of new nitrogen exhaust components. Several after-treatment systems such as the Lean $NO_X$ Trap (LNT) catalyst and Selective Catalytic Reduction (SCR) have been developed for reducing $NO_X$ (NO: nitrogen monoxide / $NO_2$: nitrogen dioxide) emissions from both diesel and lean-burn gasoline engines to meet the recent stringent regulations for automobile exhaust emissions. However, to evaluate the performance of these new after-treatment devices, it is not sufficient to analyze the regulative nitrogen components such as NO and $NO_2$ only,[4] It is also important to monitor $NH_3$ (ammonia) slip from SCR catalysts during different engine running conditions.
In addition, proposed legislation such as EURO 6 and 7 or

CFR 1065 and 1066 will substantially change test methods and instruments used for measuring toxic emissions. These emission standards stipulate the measurement and regulation of new exhaust gas components. To confront global warming, the United States Environmental Protection Agency (EPA) has issued a rule requiring greenhouse gases (GHG) including $N_2O$ (nitrous oxide) to be reported.[10] Thus, an analyzer that can measure NO and $NO_2$ at the same time as $NH_3$ and $N_2O$ is a key demand. Conventional methods used for measuring nitrogen compounds have problems mastering the growing challenges posed by interferences and detection limits. This has led to the development of new analyzers utilizing a Quantum Cascade Laser (QCL) to measure NO, $NO_2$, $N_2O$ and $NH_3$.

### Principles of Optical Spectroscopy

Like conventional gas analyzers, QCL devices are based on the principles of optical absorption spectroscopy:
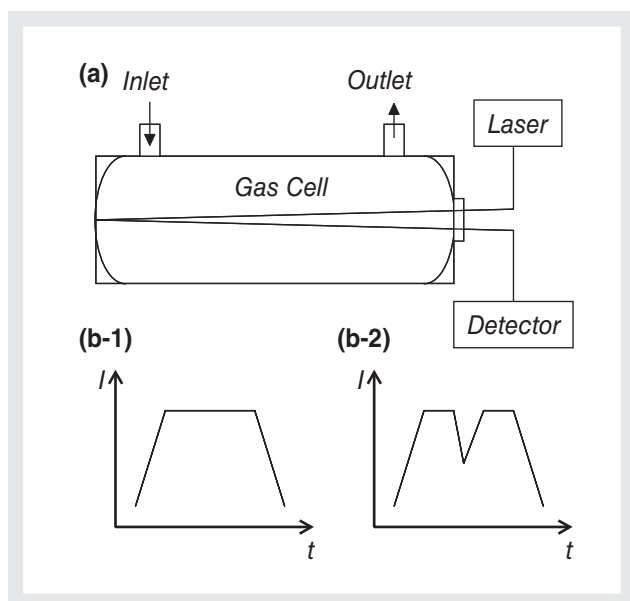
Figure 1   (a) Schematic setup of a Spectrometer; (b-1) the original pulse shape of the laser beam and (b-2) the characteristic absorption spectrum after transmission
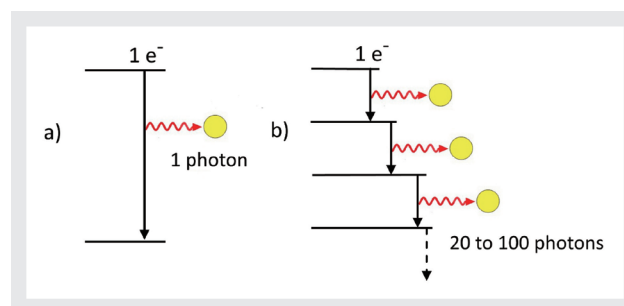


Figure 2   (a) Conventional lasers emit only one photon at one electron transition; (b) with QCL, the electron transits multiple layers, releasing several photons in the process

substances such as, in this case, exhaust components absorb energy in the form of electromagnetic waves. The molecules are transformed to a higher energy state, while the energy absorbed represents the molecular structure of a specific substance. Each component therefore shows specific wavelengths at which its absorption tendencies are most pronounced. To record the specific absorption spectrum, a laser beam is passed through the sample gas as shown in Figure 1(a). The laser pulse is reflected by mirrors and hits a detector. When the frequency of the beam is the same as the vibrational frequency of an atomic bond (depending on factors such as element mass and bond strength), absorption occurs. An examination of the light transmitted shows how much energy the component has absorbed at each wavelength, and the absorption spectrum ascertained in this way characterizes the component as shown in Figure 1(b). According to the Beer-Lambert law, the absorbance is proportional to the gas concentration. Thus, the gas concentration can be obtained from the shape of the absorption spectrum according to library data.[6], [7]

## QCL Technology

The difference between QCL and conventional exhaust gas analyzers lies in the laser technology used. QCL is a semiconductor laser based on two fundamental phenomena of quantum mechanics: tunneling and quantum confinement.[2], [3] With conventional diode lasers, the light originates from an energy gap existing between the valence and the conductance band. As shown in Figure 2(a), only one photon is released every time an electron undergoes relaxation. In contrast, a QCL element

has several thin layers of semiconductors which create a multi-level band structure consisting of separate quantum wells. This results in the electrons "cascading" down through the layers while several photons are released. For this reason, the laser strength and intensity increase considerably, Figure 2(b).

Moreover, with QCL the wavelength no longer depends solely on the band gap of the semiconductor materials applied but also on the layer thicknesses. This allows QCLs with a wide range of emission wavelengths to be manufactured using the same well-known semiconductor material systems. QCLs are able to produce light in the whole Mid-Infrared (Mid-IR) and potentially in the Far-Infrared (Far-IR) spectrum. They can therefore emit strong beams in regions in which the relevant nitrogen compounds exhibit high extinction coefficients, whereas the absorption tendency of coexisting gases is low in these regions.

## Operating Principles of QCL Spectroscopy

The principles of optical spectroscopy, which have already been discussed in Subsection of Principles of optical spectroscopy, also apply to QCL analyzers. There are, however, differences in their operation processes: supplied with electrical pulses at a constant interval, a QCL element generates light while the temperature of the laser element increases with the electric current applied. As the emitted wavelength depends on the QCL's temperature, the wavelength is tuned by its temperature and the electrical pulse.[5], [11], [12] This makes it possible to precisely adjust the wavelength to the region in which the compounds targeted for measurement absorb laser light. One pulse lasts several 500 ns and the wavelength changes with increasing temperature. The wavelength variation during a pulse of this kind is approximately 0.005 μm.

## System Setup and Sample Handling

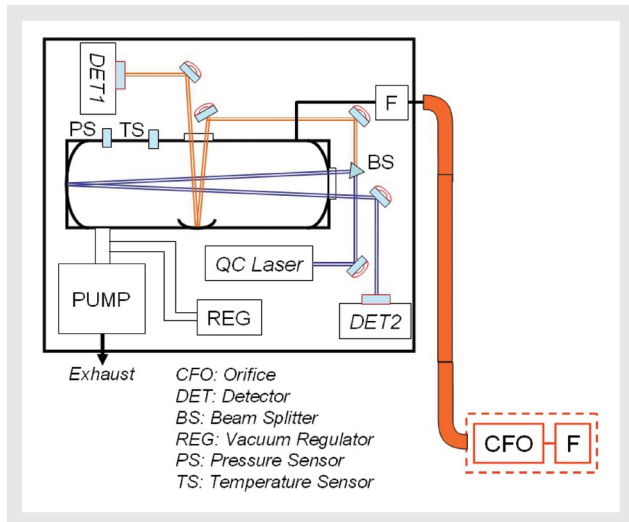It took some effort to make the QCL working principle

Figure 3   The MEXA-1400QL-NX system design allows NO, $NO_2$, $N_2O$, and $NH_3$ to be measured simultaneously at different concentrations

more viable and to meet the demands of legislation for exhaust gas measurement. The result is the HORIBA MEXA-1400QL-NX, which is already being used by several OEMs. The analyzer is capable of measuring the four most relevant nitrogen compounds simultaneously at different concentration levels, Figure 3.

## Measuring at different concentration levels

The optical path length is absolutely crucial for the measurement results. A short laser path allows the use of small optical cells and leads to rapid responses. On the other hand, a very long path length enables very low detection limits but often extends the response time. For this reason, a sophisticated design of the cell and of the mirrors in particular has been implemented in the MEXA-1400QL-NX analyzer to allow for two different path lengths with one gas cell. A short path of 0.84 m is realized with a low number of light reflections (~ 25) while a high number of light reflections (~ 100) add up to a path length of 30 m. The combination of these two paths gives way to the measurement of both high and low gas concentrations in one system configuration.[4], [8], [9]

## Measuring several gases simultaneously

To measure NO, $NO_2$, $N_2O$ and $NH_3$ simultaneously, the system design uses four QCL elements at individual wavelengths. At the chosen wavelengths, the absorption tendency of coexisting gases is expected to be low. Each laser unit in turn emits pulse light while the detector receives the whole spectrum and for each QCL one after

another.[4], [8], [9]

## Compensation of coexistent gases

Firstly, with QCL the interference caused by the spectral overlap of co-existing gases is reduced due to the fine laser beam resolution of 0.001 $cm^{-1}$. Secondly, while an absorption spectrum expands under atmospheric pressure, a sharp peak of the absorption spectrum can be obtained under low pressure. The sample gas is therefore drawn into the gas cell by a vacuum pump which creates enough vacuum (25 kPa) to reduce this pressure broadening effect significantly. These two circumstances allow reliable mathematical compensation of the interference of co-existing gases such as CO, $CO_2$, $CH_4$, $H_2O$, and hydrocarbons.[4], [8], [9]

## Rapid $NH_3$ measuring

The difficulty with $NH_3$ is that it tends to adhere to the surfaces of the sample cell and transfer lines due to its large electric dipole moment. To prevent water condensation and to minimize the dissolution of $NH_3$, the sample inlet, filter, vacuum regulator, and gas cell are heated to 113 °C. In addition to this, materials and surfaces of the transfer lines were optimized to reduce the response time to less than 5 s during $NH_3$ testing.[4], [8], [9]

## Sample handling

The MEXA-1400QL-NX analyzer works with a sample flow of approximately 8 L/min. There are thus two ways of handling emission testing samples. Firstly, the exhaust gases can be directly sampled from the exhaust in the undiluted or raw state via a transfer line as shown in Figure 4(a). In this configuration, the system response is
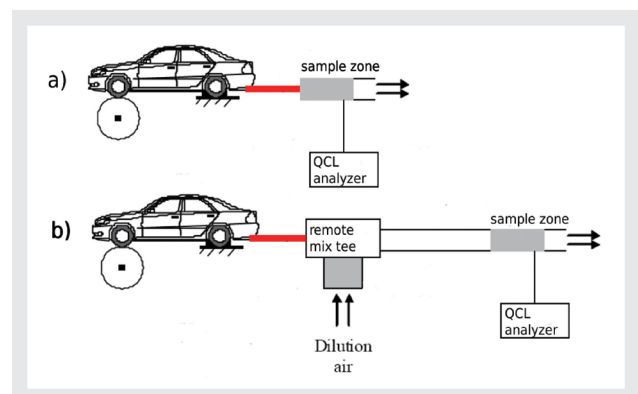


Figure 4   System diagram for vehicle tests on a chassis dynamometer. With the MEXA-1400QL-NX, the exhaust gases can either be measured directly, i.e. raw (a), or diluted with air (b).

Table 1   Synthetic gas tests performed for this study

| Test | Low Range | | | | High Range | | | |
|---|---|---|---|---|---|---|---|---|
| | NO | NO₂ | N₂O | NH₃ | NO | NO₂ | N₂O | NH₃ |
| Zero Noise | Y | Y | Y | Y | Y | Y | Y | Y |
| Span Noise | Y | Y | Y | Y | Y | Y | Y | Y |
| Linearity | Y | Y | Y | Y | Y | Y | Y | Y |
| Linearity | Y | Y | Y | Y | Y | Y | Y | Y |
| Rise Time | Y | Y | Y | Y | Y | Y | Y | Y |
| Interference Check | Y | Y | Y | Y | | | | |

very fast, and all four gases can be measured simultaneously at high concentrations. Secondly, it is possible to dilute the exhaust gases with ambient air to measure low and medium concentrations of NO, NO₂, and N₂O at the same time, as shown in **Figure 4(b)**. For bag sampling, there will be modified analyzer versions which work at lower sample flow rate.

## Test Results

The performance of MEXA-1400QL-NX was tested and verified using a variety of tests conducted at different locations within the HORIBA Group and at different end user laboratories. The following section shows some of the test results.

## Synthetic Gas Tests

Synthetic gases - like any first step of gas analyzer verification – comprise gas blends of the target species based on either nitrogen or synthetic air at known concentrations. They also for example include blends of potentially co-existing gases in the exhaust. The absolute accuracy of any gas analyzer is determined via the items listed in **Table 1**.

## Noise

The signal noise is defined here as two times the standard deviation during steady flow of a defined gas. For each component and range, the gases used here are nitrogen and the span gas, which is usually 95 % of the full-scale concentration. The zero noise results shown in **Table 2** are of special importance as they determine the lower detection limit of an analyzer.

## Linearization curve

The linearity of the instrument is examined for both the low range and the high range. In the linearity test, calibration gases of the required concentrations are generated by blending the calibration gas with N₂ at ten different blending ratios. A gas divider is used to do this automatically. The reference concentration of each sample gas is calculated from these blending ratios and the nominal gas concentration. **Figure 5** shows a typical result of a linearity test. As a quality criterion, every measured point should deviate from the expected concentration by no more than 1 % of the full scale. All measurement ranges are calibrated separately and meet the criteria of the various regional regulations (ECE, EPA) or, for simplicity's sake, each measured point should be within 2 % of the expected concentration.

Table 2   Results of noise tests as well as the pass/fail criteria

| | NO | NO₂ | N₂O | NH₃ |
|---|---|---|---|---|
| criteria (100 / 50 ppm range) | < 0.4 % F.S./100 ppm | < 0.4 % F.S./50 ppm | < 0.4 % F.S./100 ppm | < 0.4 % F.S./50 ppm |
| ZERO 2σ | 0.02 | 0.01 | 0.02 | 0.01 |

| | NO | NO₂ | N₂O | NH₃ |
|---|---|---|---|---|
| criteria (5000 / 2000 ppm range) | < 0.4 % F.S./5000 ppm | < 0.4 % F.S/2000 ppm | < 1.0 % F.S./2000 ppm | < 0.4 % F.S/2000 ppm |
| ZERO 2σ | 1.3 | 0.25 | 0.62 | 0.16 |

| | NO | NO₂ | N₂O | NH₃ |
|---|---|---|---|---|
| criteria (100 / 50 ppm range) | < 2.0 % F.S./100 ppm | < 2.0 % F.S./50 ppm | < 2.0 % F.S./100 ppm | < 2.0 % F.S./50 ppm |
| SPAN 2σ | 0.34 | 0.16 | 0.34 | 0.21 |
| criteria (5000 / 2000 ppm range) | < 2.0 % F.S./5000 ppm | < 2.0 % F.S./2000 ppm | < 2.0 % F.S./2000 ppm | < 2.0 % F.S./2000 ppm |
| SPAN 2σ | 28.81 | 11.83 | 9.71 | 15.5 |

Figure 5   Screenshot showing typical results of a linearity test

## Interference

The number of components emitted by internal combustion engines can generally be as high as 200. The concentration of each component depends largely on the type of fuel used, the chemistry of the combustion process itself and exhaust after-treatment. The major components at significant concentrations are tested for potential cross-interference with the target species of MEXA-1400QL-NX. They are listed with their criteria in Table 3.

## Rise time

The rise time of the full measurement system can be divided into two parts: the sample handling system depends on the application and differs in the dimensions and material of the transfer line and the degree of soot contamination etc. However, the analyzer is the same from unit to unit. Hence, in a first step, the full system is measured without the influence of the sample handling system, Table 4(a). It is then tested including a typical

Table 3   Gases used for the interference check

| Componets | NO | $NO_2$ | $N_2O$ | $NH_3$ |
|---|---|---|---|---|
| criteria (for 5 ppm / 10 ppm range) | +/-0.2 ppm | +/-0.1 ppm | +/-0.2 ppm | +/-0.1 ppm |
| $CO_2$_16 vol% | -0.01 | 0.00 | 0.00 | 0.021 |
| $H_2O$_16 vol% | -0.01 | 0.00 | 0.00 | 0.066 |
| $CH_4$_5000 ppm | -0.01 | -0.01 | 0.09 | 0.070 |
| $C_2H_4$_500 ppm | -0.06 | -0.00 | 0.00 | 0.073 |
| $C_2H_5OH$_500 ppm | -0.01 | 0.02 | 0.16 | 0.069 |
| $C_2H_2$_250 ppm | -0.03 | -0.01 | 0.04 | 0.048 |
| $C_2H_6$_250 ppm | -0.01 | -0.00 | 0.00 | 0.057 |
| NO_5000 ppm | – | – | – | -0.010 |
| $NO_2$_2000 ppm | – | – | 0.00 | 0.000 |
| $N_2O$_2000 ppm | 0.00 | 0.03 | – | 0.000 |
| $NH_3$_2000 ppm | 0.01 | 0.00 | 0.01 | – |

Table 4   (a) Rise time $T_{10-90}$ of the sole analyzer; (b) rise time of the full measurement system including heated filter and transfer line

(a)

| Range | NO | NO$_2$ | N$_2$O | NH$_3$ |
|---|---|---|---|---|
| criteria | < 1.5 s | < 1.5 s | < 1.5 s | < 2.5 s |
| 100 / 50 ppm | 0.8 s | 0.7 s | 0.9 s | 0.8 s |
| 5000 / 2000 ppm | 1.0 s | 0.8 s | 1.4 s | 0.9 s |

(b)

| Range | NO | NO$_2$ | N$_2$O | NH$_3$ |
|---|---|---|---|---|
| criteria | < 2 s | < 2 s | < 2 s | < 5 s |
| 100 / 50 ppm | 0.9 s | 0.8 s | 0.7 s | 3.6 s |
| 5000 / 2000 ppm | 0.9 s | 1.0 s | 1.0 s | 1.6 s |
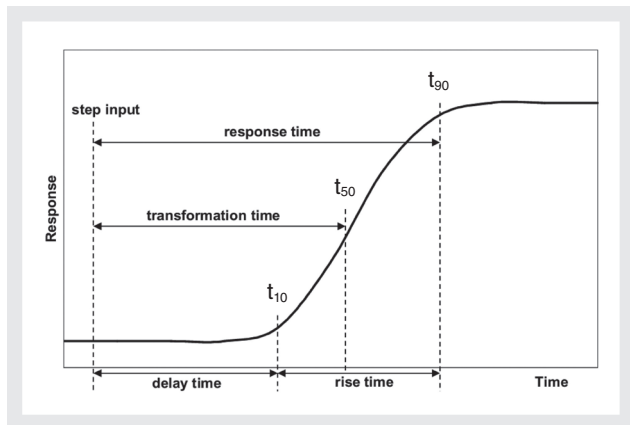


Figure 6   The rise time of a sensor is defined in ECE R49 and elsewhere

setup comprising a heated filter using a quartz glass fibre filter element and a 6 m long heated line. This is a common length which suits a high number of installations, Table 4(b).

The definition of the rise time as $T_{10-90}$ represents the duration from 10 to 90 % of a sensor's response to a step-shaped input signal as shown in Figure 6.[1]

## Engine Tests

The real engine exhaust tests shown here are examples of the possible applications of MEXA-1400QL-NX.
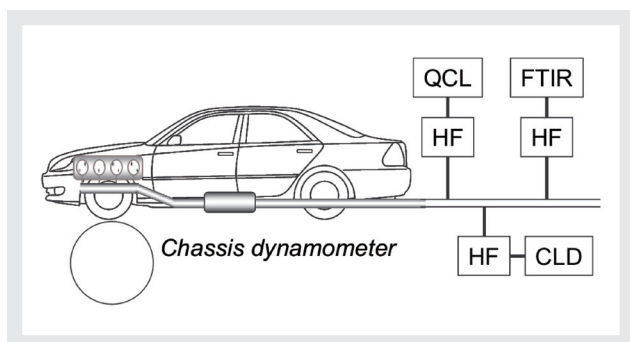First the correlation to standard, well-known measurement

systems in some selected applications is investigated. The reference systems chosen are Chemi-Luminescence (CLD) and Fourier Transform Infra-Red (FTIR) analyzers, Figure 7. Since MEXA-1400QL-NX has wider measurement ranges at both the lower and upper end of the scale, the correlation test can only cover part of the specification.

The shapes of modal traces for tailpipe sampling are similar for all three methods under investigation. Also, the absolute level of emissions is almost identical and shows qualitatively good correlation of the systems for NO gas over a Federal Test Procedure 75 (FTP-75) driving cycle as shown in Figure 8.[3]

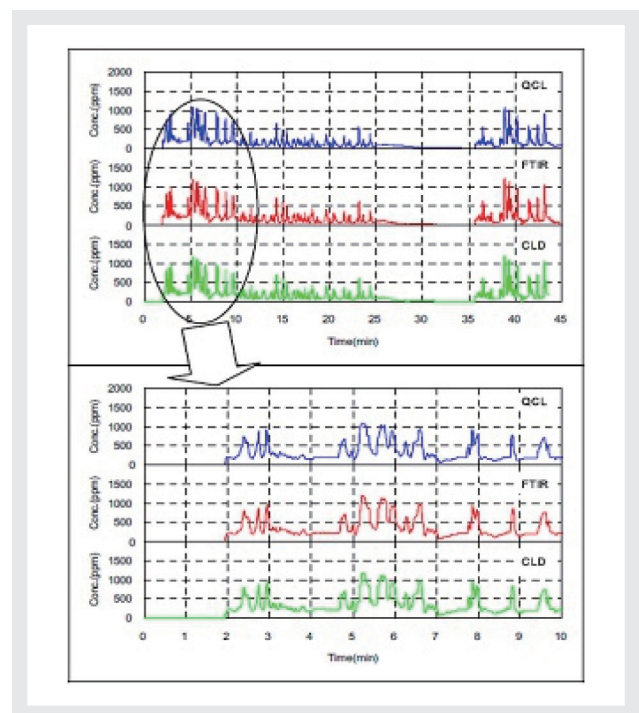More tests are conducted between 1400QL-NX and two-channel CLD sampling via a full flow dilution tunnel.



Figure 7   Setup of NO correlation test between QCL, CLD and FTIR at the sample position 'tailpipe'



Figure 8   Comparison of MEXA-1400QL-NX with three analyzers that can be used for NO measurement at the concentration levels given
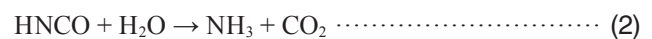
One channel of the CLD is set to NO mode and the other to $NO_X$. The parameter under investigation is the correlation between the two instruments at static speed conditions.

One important aspect must be considered when measuring $NO_X$ gases using different systems: the sample handling systems can change the oxidation stage upwards or downwards depending on the temperature conditions and the presence of substances such as soot which for example reduce $NO_2$ to NO. This effect needs to be taken into account when only nitrogen oxide is compared. The instrument with higher temperature and soot contamination is likely to show the $NO_X$ reduction effect. In the particular measurement shown in Figure 9, the averaged NO concentration is well within 3 %. This is a good agreement in view of the fact that both instruments

are calibrated using different span gas bottles and have different ranges and hence linearization curves. The $NO_X$ value of CLD and the NO and $NO_2$ value of QCL deviate by between 4% and ~ 6%. As described above, this can be partly due to the individual calibrations and linearizations. Besides sample handling effects, another potential influence on $NO_X$ measurements using CLD is the converter material. Its task is to reduce the entire $NO_X$ to NO so it can be detected. The converter generally has an efficiency of less than 100%, and this typically causes underestimation of $NO_X$. For the results shown in Figure 9, the potential influences of sample handling and converter are not investigated further here.

## Urea Conversion

The functional principle of a Selective Catalytic Reduction (SCR) catalyst is based on the conversion of $NO_X$ to $N_2$ with the help of $NH_3$. The basic principle is as follows: the $NH_3$ is typically generated from an injected aqueous urea solution or – less commonly – directly applied as a gas. The injection of $NH_3$ needs to be performed in a controlled manner since a stoichiometric reaction is required in order to avoid $NH_3$ slip.

The urea is injected via a nozzle and then decomposes into iso-cyanic acid and ammonia at a temperature of more than 133 °C (Formula 1). The iso-cyanic acid is only an intermediate product which is further hydrolyzed into ammonia at 160 °C (Formula 2):

$$(NH_2)_2CO \rightarrow NH_3 + HNCO \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

Besides the desired main reactions, a number of intermediate and unwanted substances are also produced at temperatures of 133 °C or above. These components are biuret, triuret, melamine and cyanuric acid. They are potentially dangerous due to the risk of instrument contamination and can cause false measurements. One application used during the research and development of SCR catalysts is $NH_3$ measurement directly upstream of the SCR catalyst. However, this measurement exhibits several difficulties. The urea → ammonia conversion as well as the ammonia/exhaust gas mixing may not be perfect and may create misleading results.

Figure 10 shows two examples of pre-SCR measurements with the 1400QL-NX and a FTIR instrument in parallel during a New European Driving Cycle (NEDC). In one
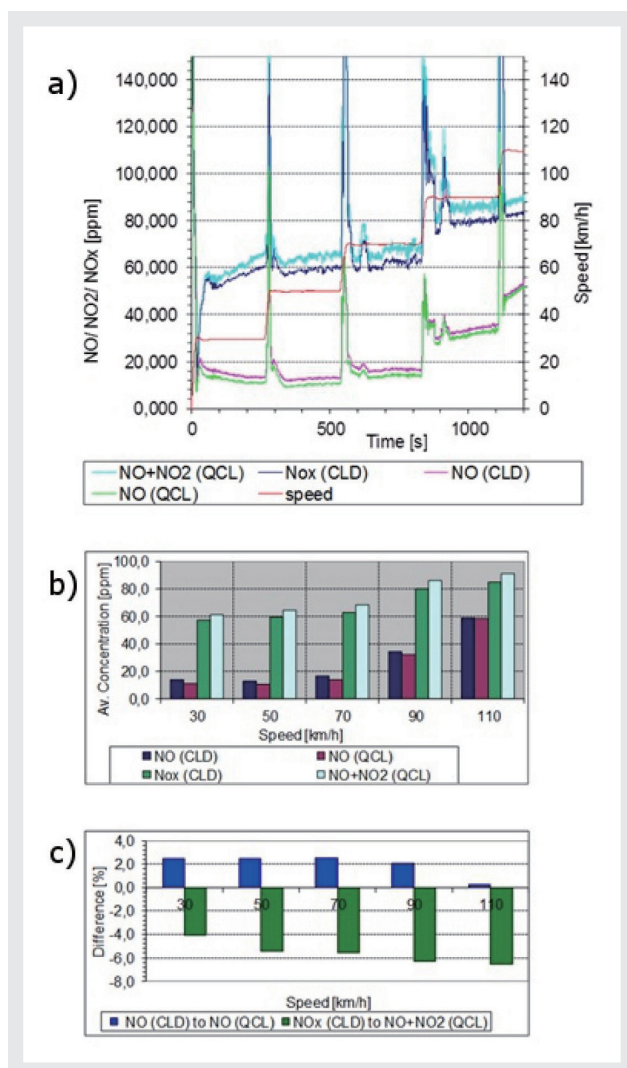


Figure 9  NO, $NO_2$ and $NO_X$ compared at five different speeds:
(a) the modal traces follow the same trend;
(b) the average values;
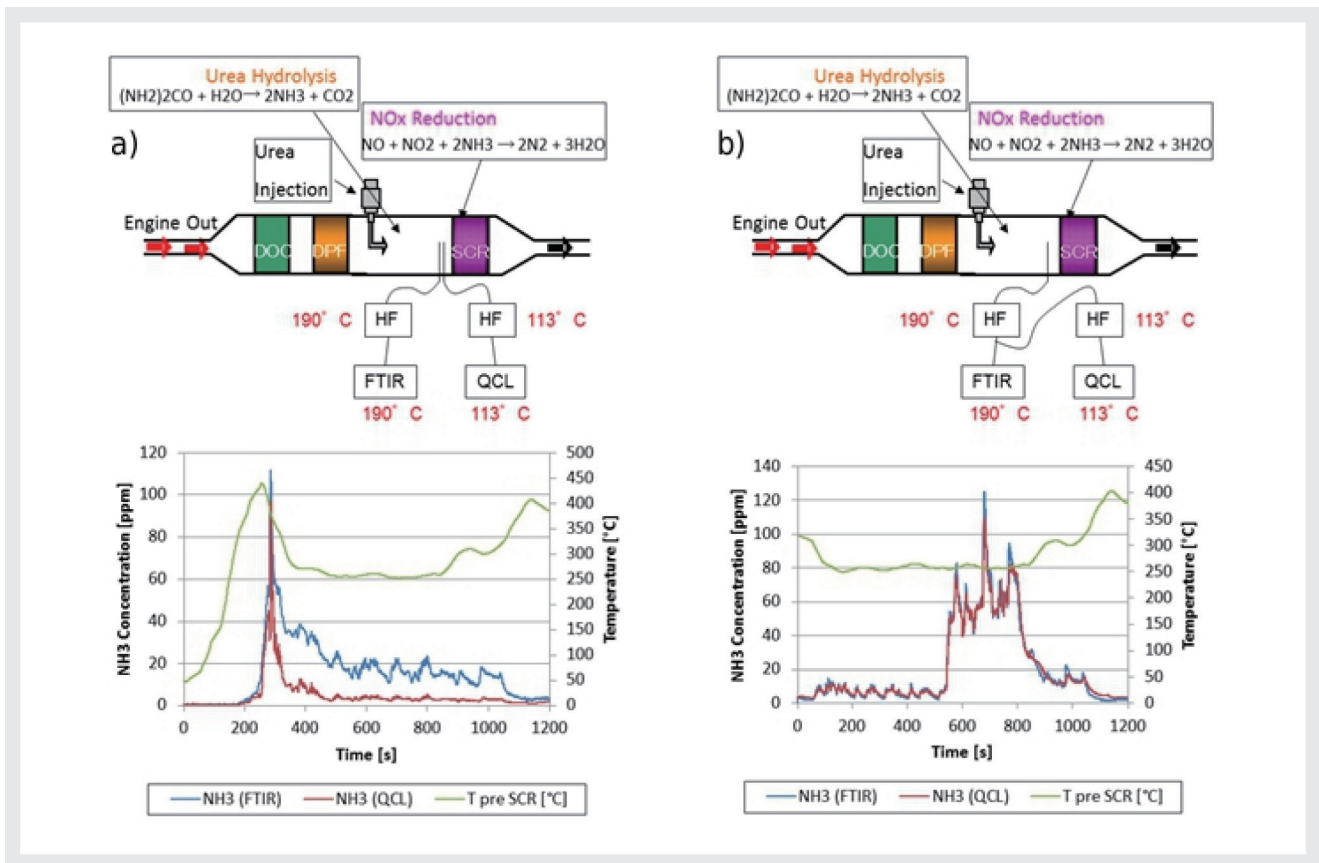(c) the differences of NO and $NO_X$ to NO and $NO_2$

Figure 10   1400QL-NX (QCL) compared to a FTIR instrument with sampling upstream of the SCR: when two separate probes and independent sample handling systems of different temperatures are used (a), the $NH_3$ trace deviates strongly. When the QCL is connected behind the FTIR heated pre-filter (b), the traces are in good accordance.

configuration, both instruments, 1400QL-NX at 113 °C and the FTIR at 190 °C, sampled exhaust gas from different probes with a spacing of only about 5 cm in between, Figure 10(a). The $NH_3$ traces showed large discrepancies. After further investigations, the 1400QL-NX was connected via a flow splitter downstream of the heated filter of FTIR, which was also heated to 191 °C. The sample handling of the 1400QL-NX itself was not changed. The measurement results showed a good correlation in this case.

It can be concluded from Figure 10(b) that the instruments themselves are equivalent. On the other hand, the differences for the Figure 10(a) configuration need to be explained. As far as it concerns non-perfect $NH_3$/exhaust mixing, this is an unlikely reason since the instrument shows no full accordance at all. The mixing behaviour should depend on flow conditions which vary throughout the test depending on the engine load etc. During idling phases of the test, the instruments would be expected to agree better. The more probable explanation for the disagreement in Figure 10(a) is the production of $NH_3$ inside the FTIR

sample handling system. The temperature conditions would allow this effect: if urea or iso-cyanic acid reached into the sample handling systems of an instrument, they would stay stable if the temperature was below their decomposition point. This is the case for 1400QL-NX since the temperature is below 133 °C. However, the FTIR heated to 191 °C may change the sample gas and allow reactions such as those shown in Formula 1 and Formula 2. It can measure ammonia plus potential ammonia in the form of precursors. In contrast, 1400QL-NX measures the real ammonia concentration present at the sample position.

## QCL and $NO_2/NO_X$ Ratio

The $NO_X$ concentration of the engine exhaust has a wide range. It depends on the air-to-fuel ratio, the combustion temperature and the pressure – and on the after-treatment system too, of course. Also, the $NO_2/NO_X$ ratio is variable between almost 0 and more than 50%.
QCL technology allows an accurate direct measurement of $NO_2$ which is useful for both low and high $NO_2/NO_X$ ratios: at low ratios, a differential method such as dual CLD is very sensitive to time alignment and inter-channel variation. Those variations can result from linearization,
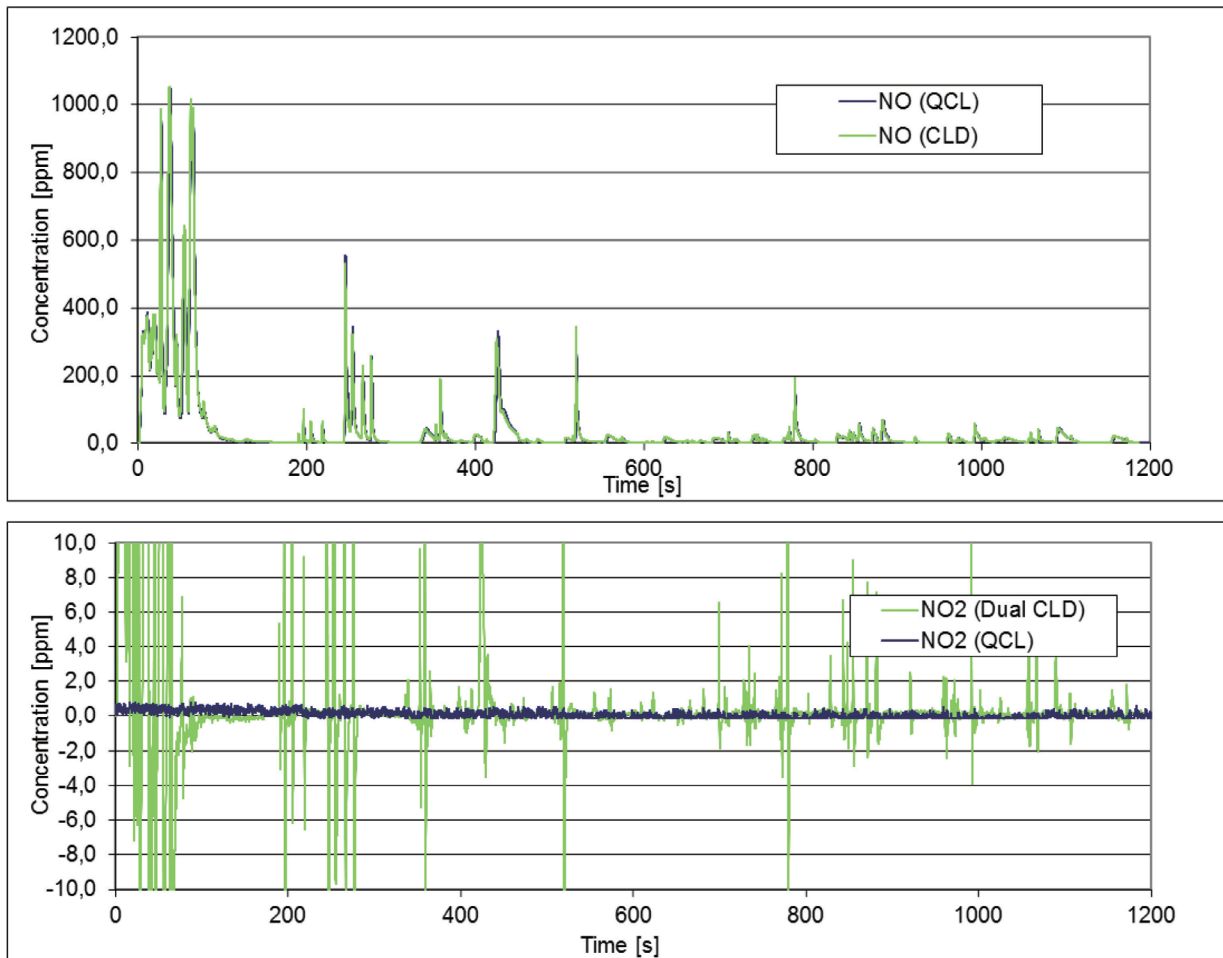
Figure 11   The direct injection gasoline vehicle (3 L, 6 cylinder) used for this study has almost no NO$_2$ emission (bottom) while NO emission (top) is relatively high

calibration, uncertainties of converter efficiency etc. Direct measurement using QCL absorption spectroscopy yields reliable results for NO$_2$ even at high NO calibrations as shown in Figure 11.

On the contrary, for high NO$_2$/NO$_X$ ratios, any uncertainty in the NO$_2$ → NO conversion efficiency has a relatively large influence on the NO$_X$ value compared to the case in which most of the NO$_X$ consists of NO. QCL without the use of converters is not affected by this and is a reliable and robust method.

## Conclusion

The working principle of absorption spectroscopy based on a Quantum Cascade Laser is shown in theory. A QCL device offers strong and highly monochromatic light of a

defined wavelength which can be selected over a wide range during manufacturing of the laser and over a small range via its operating temperature.

MEXA-1400QL-NX uses four of these lasers to realize a four-component analyzer designed for negligible interference from co-existing gases and a low limit of detection. The analyzer performance is shown for both synthetic and real exhaust gases. It correlates well with conventional methods if gas concentrations are suitable for other methods. However, MEXA-1400QL-NX shows its unique strengths and advantages in the case of low concentrations and extreme mixtures. QCL technology can be used to measure many different gas components. Choosing the right wavelength area with a suitable coefficient of extinction and minimum interference is the key issue. As the next model of the QCL series, HORIBA will introduce the new MEXA-1100QL-N2O analyzer,

which was designed for an ultra-low $N_2O$ detection limit in the order of a few ppb.

## Acknowledgements / Danksagung

### References

[ 1 ]  ECE/TRANS/WP.29/GRPE/2009/12 *Regulation No.49.*

[ 2 ]  Faist, J., Capasso, F., Sivco, D. L., Sirtori, C., Hutchinson, A. L., Cho, A. Y., Quantum Cascade Laser, *Science 264*, 1994, p. 553-556.

[ 3 ]  Faist, J., Capasso, F., Quantum Cascade Laser Mc Graw-Hill , *Yearbook of Science and Technology* 1997, p. 265-267.

[ 4 ]  Hara, K., Nakatani, S., Rahman, M., Nakamura, H., Tanaka, Y., Ukon, J., Development of Nitrogen Components Analyzer Utilizing Quantum Cas-cade Laser, *SAE Paper* 2009-01-2743, 2009.

[ 5 ]  Hill, Cory J, Yang, Rui Q., Mid-IR Semiconductor Lasers for Chemical Sensing, *SAE Paper* 2003-01-2551, 2003.

[ 6 ]  McCulloch, M. T., Normand, E. L., Langford, N., Duxbury, G., New-man, D. A., High sensitive detection of trace gases using the time-resolved frequency downchirp from pulsed quantum-cascade lasers, *Journal of the Optical Society of America* B 20, 1761, 2003.

[ 7 ]  McCulloch, M. T., Normand, E. L., Langford, N., Duxbury, G., Real-time trace-level detection of carbon dioxide and ethylene in car exhaust gases, *Applied Optics* 44 (14), 2005, p. 288-294.

[ 8 ]  Rahman, M., Development of an Ultra-Low Concentration N2O Ana-lyzer Using Quantum Cascade Laser (QCL), *SAE Paper* 2010-01-1291, 2010.

[ 9 ]  Rahman, M., Hara, K., Nakatani, S., Tanaka, Y, Emission Testing of N2O (Bag Sampling) from Diverse Vehicles by Laser Spectroscopic Motor Exhaust Gas Analyzer, *SAE Paper* 2011-01-1155, 2011.

[10]  United States Environment Protection Agency, Climate Change, Green House Gas Emissions, 2010 Inventory of Green House Gas Emissions and Sinks, *http://www.epa.gov/climatechange/index.html.*

[11]  Yang, Rui Q, Mid-IR III-V Semiconductor Diode Lasers for Trace Gas Monitoring, *SAE Paper* 2002-01-2451, 2002.

[12]  Yang, Rui Q, et al., Development of Thermoelectric Cooled Single-Mode Distributed Feedback Mid-IR Interband Cascade Lasers for Chemical Sensing, *SAE Paper* 2007-01-3151, 2007.

**Daniel SCHEDER**

European Product Manager
Engineering Department
Automotive Test System
HORIBA Europe GmbH

**Matthias SCHRÖDER**

Manager Emission Engineering
Global Product Planning Group
HORIBA Europe GmbH

**Marcus RIEKER**

Director Academic Affairs
HORIBA Europe GmbH
Prof. Dr. Sc. Hum.

**Hiroshi KAWAMURA**

Junior Corporate Officer
HORIBA, Ltd.
Corporate Officer, Executive Vice President
HORIBA Europe GmbH