# WLTP Additional Gases Working Group

## HORIBA Proposal for Additional Measurement Technique for Nitrogen Compounds ($NO$, $NO_2$, $N_2O$ and $NH_3$)

## Introduction

The measurement method for NO and NO2 (NOx) concentrations in automotive exhaust gas is currently specified as the chemiluminescent analyser (CLA) or the Ultra-violet Resonant Absorption Spectroscopy analyser (UV-RAS).

The measurement of ammonia (NH3)[1] concentration directly from un-diluted exhaust gas is currently proposed using the following techniques :-

- Laser Diode Spectroscopy (LDS)
- Fourier Transform Infra-Red (FTIR)

The measurement of nitrous oxide (N2O) is required under the US Greenhouse Gas (GHG)[2] legislation and is currently specified by the US EPA CFR (Environmental Protection Agency Code Of Federal Regulations) using infra-red analysers, specifically :-

- Non-Dispersive Infra-Red (NDIR)
- Fourier Transform Infra-Red (FTIR)
- Photo-Acoustic Infra-Red (PA-IR)

HORIBA requests that the Working Group considers the addition of a new type of Infra-Red analyser to the techniques already specified or proposed for the above NO, NO2 (NOx), N2O and NH3 gases.
Recent developments in design and fabrication has created a new type of laser source known as Quantum Cascade Lasers (QCL) that have the ability to emit in the mid infra-red region that is ideal for the measurement of the above nitrogen gases (as well as others) that are generated in automotive exhaust.

## Quantum Cascade Laser Infrared (QCL-IR) Spectroscopy

Suitable designed and manufactured Quantum Cascade Lasers (QCL) emit coherent radiation in the mid-infrared region where the various nitrogen compounds have strong absorption. This laser's optics can give a ultra-fine resolution of the infrared spectrum. Therefore an analyzer using QCL-IR spectroscopy can minimise the interference caused by the spectral overlap of co-existing gases in engine exhaust.

Figure 1 (a) shows a schematic representation of QCL-IR spectroscope. Sample gas is fed into the gas cell and a laser pulse irradiates into the gas cell. The laser radiation emitted as continuous pulse is detected after a multiple reflection between two mirrors in the gas cell. From it's inherent design and control, the wavelength of QCL radiation slightly varies with time therefore it is possible to scan the constant width of the wavelength in a particular region. If there is no gas component in the cell which absorbs within the predetermined scanning wavelength band, a time resolved spectrum as shown in Figure 1(b-1) is observed. On the other hand, when there is a gas component which offers absorption in the band, a time resolved spectrum as shown in Figure 1(b-2) is observed. According to the Beer-Lambert law, absorbance is proportional to the concentration of gas. So, the gas concentration can be obtained from the absorption spectrum with a predetermined correlation[3].

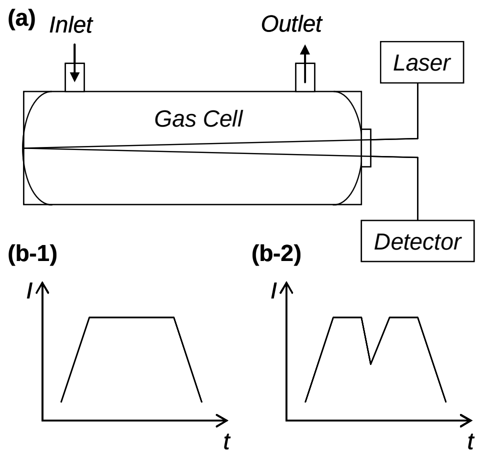


Figure 1 : Schematic of QCL-IR analyzer

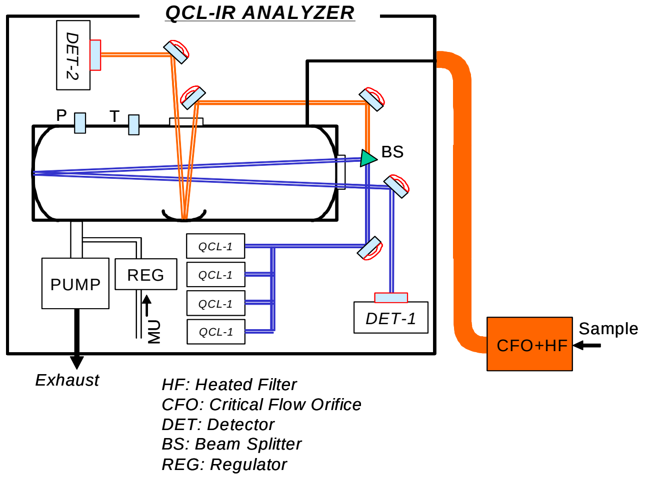


Figure 2: Block diagram of the system[3]

## QCL-IR analyzer

Figure 2 shows the block diagram of a QCL-IR analyzer for measuring, as an example, NO, $NO_2$, $N_2O$ and $NH_3$. Four laser elements corresponding to one measurement component respectively are used in the device. The lasers are very stable as they are operated at almost room temperature to irradiate lat target wavelengths therefore no extreme low temperature cooling is necessary. The wavelengths of the respective laser elements are selected and controlled at a region where a spectrum peak exists with almost no or negligible interference from other measurement gases. Theoretically CO, $CO_2$, $H_2O$ and hydrocarbons could be interference gases of nitrogen components analyzer using mid-infrared, but it is has been shown that these gases have no affect on the QCL-IR analyzer's measurement of the concentration of NO, $NO_2$, $N_2O$ and $NH_3$ when using the QCL based analyzer with the optics design proposed in this document[3].

The analyzer design shown has two paths in a single sample cell; the short path with only few light reflections and the long path with multiple light reflections. The combination of two path lengths in a single cell in this analyzer allows measuring both high concentration and low concentration gases at the same time and provides a wide dynamic measurement range should it be necessary for the specific application.

Rise times ($T_{10}$-$T_{90}$) of a QCL-IR analyzer for NO, $NO_2$ and $N_2O$ are less than 2 seconds[3], and less than 5 seconds of the raise time for $NH_3$ is achieved by carefully selecting the sampling components and temperature of heated line[4]. These rise times satisfy requirements of all transient test procedures currently being used in the world.

Examples of measurement result are shown in figures 3 to 6. Diesel and gasoline vehicles were run under FTP-75 driving schedule and the exhaust samples were taken from the tailpipe. QCL-IR analyzer shows very good agreement with CLD and FTIR analyzers.

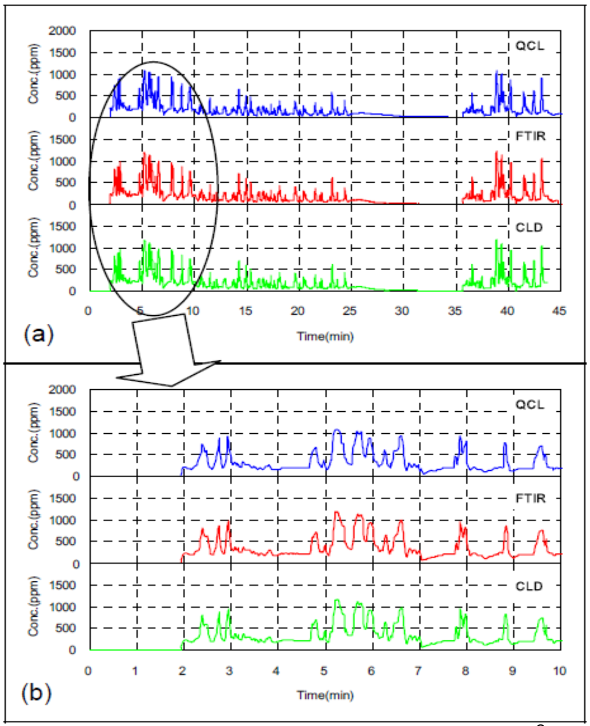

Figure 3: NO emission from diesel vehicle[3]

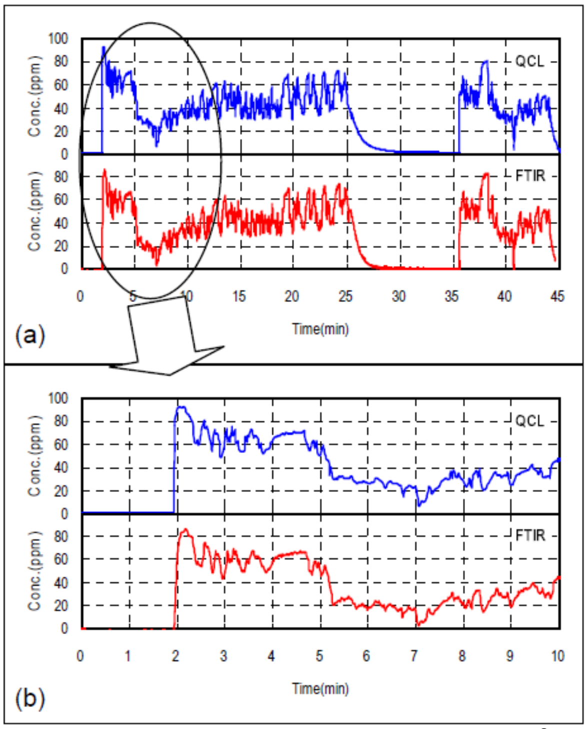

Figure 4: $NO_2$ emission from diesel vehicle[3]

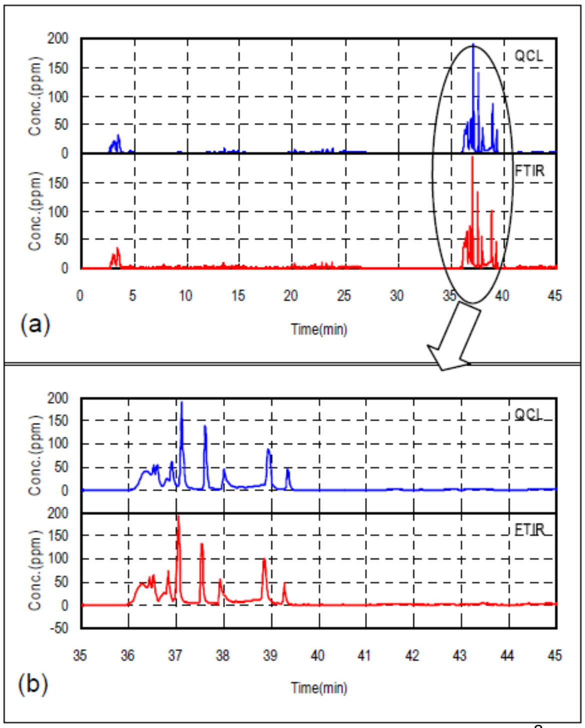

Figure 5: $N_2O$ emission from gasoline vehicle[3]

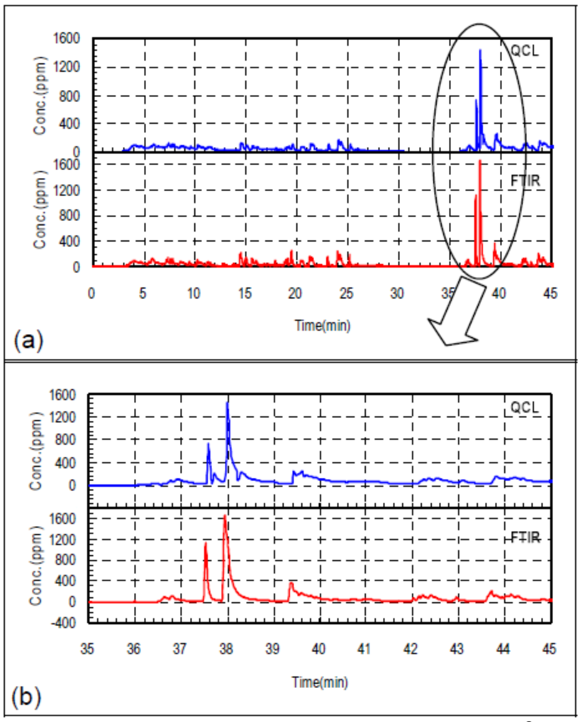

Figure 6: $NH_3$ emission from gasoline vehicle[3]

## References

1. REGULATION (EC) No 595/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
2. http://www.epa.gov/climatechange/emissions/ghgrulemaking.html
3. Hara K, at al, "Development of Nitrogen Components Analyzer Utilizing Quantum Cascade Laser", SAE Paper No. 2009-01-2743
4. Hara K et al. "Development of Nitrogen Components Analyzer Utilizing Quantum Cascade Laser (2)", Proceedings of 2010 Annual Congress of Society of Automotive Engineers of Japan, No. 20105340

## Definitions / Abbreviations

$NO$: nitric oxide

$NO_2$: nitrogen dioxide

$N_2O$: nitrous oxide

$NO_x$: oxides of nitrogen

$NH_3$: ammonia

QCL: quantum cascade laser