

# Real-time tailpipe ammonia measurements from vehicles tested over the new Worldwide harmonized Light-duty vehicle Test Cycle (WLTC)

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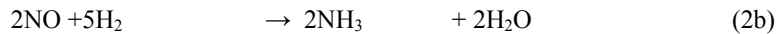
<sup>3</sup>CGS

## **1. Introduction**

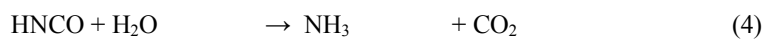
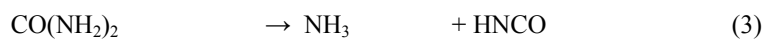
Ammonia is classified under the European dangerous substances directive (67/548/EEC) as: toxic, corrosive and dangerous for the environment. The U.S. Occupational Safety and Health Administration (OSHA) has set for ammonia an eight-hour exposure limit at 25 ppm and a short-term (15 minutes) exposure level at 35 ppm [1]. Its reaction with nitric and sulfuric acid leads to the formation of atmospheric secondary aerosols, namely, ammonium nitrate and ammonium sulfate [2, 3]. It has been reported that ammonium account for up to 17% of the total mass of PM<sub>2.5</sub> in the South Coast Air Basin [4] and that ammonium, nitrate and sulphate represent 40% of the total PM<sub>2.5</sub> in

some European cities [5]. The deposition of ammonia and/or ammonium salts leads to hypertrophication of waters and acidification of soils with negative effects on nitrogen-containing ecosystems [6-8].

. Molecular nitrogen is the aimed reaction product during the reduction of NO<sub>x</sub> over the TWC and ammonia has been found to be a secondary product during this process. In the TWC ammonia is formed via steam reforming from hydrocarbons [13] and/or via reaction of nitrogen monoxide (NO) with molecular hydrogen (H<sub>2</sub>) (through reaction 2a or 2b) produced from a water-gas shift reaction between CO and water (1) [14, 15]:



Ammonia was first identified in vehicles exhaust in 1970s [16] and after that it is commonly detected in: vehicles exhaust, road tunnel air, roadsides and urban air. As a consequence, gasoline LDVs equipped with a TWC are now recognized as an important source of ammonia in the urban areas [11, 17]. Moreover, with the recent introduction of the selective catalytic reduction system (SCR) in heavy duty vehicles (HDV) and even more recently in the diesel light duty vehicles (LDV) the potential numbers of vehicles that could emit ammonia may increase. The SCR is an after-treatment system that aims at decreasing NO<sub>x</sub> emissions by reacting NO<sub>x</sub> (NO and NO<sub>2</sub>) with NH<sub>3</sub> on a catalyst surface (reactions 5a-c). Ammonia is formed by the catalytic reaction of the urea that is injected into the system. Reactions 3-5c summarized the whole chemical pathway [18]:



Any possible over-doping of urea and/or the catalyst degradation may lead to ammonia emissions. For this reason, the Euro VI emission standards for HDV included a 10 ppm limit for the average emitted tailpipe concentration over the test cycle ((EC) No 582/2011) [19].

Measuring vehicular ammonia during chassis dynamometer experiments has been proved to be an analytical challenge. The standard dynamometer emissions measurement equipment is not adapted to measure this compound [20]. Indeed, critical sampling artifacts have been reported when ammonia was analyzed from bag samples. Ammonia can be absorbed in condensed water or react with acidic compounds present in the exhaust or along system. Previous studies have reported that ammonia sticks and it is also adsorbed on the surfaces of sampling and analysis equipment, as well as in the dilute exhaust systems' walls [20-24]. Ammonia is delayed in the CVS making time-resolved ammonia analysis from the CVS tunnel extremely difficult [22]. As a result, exhaust tailpipe measurements have been considered to be the most appropriate approach for measuring vehicular ammonia emission on chassis dynamometer tests.

It has become necessary to find suitable techniques to measure ammonia emissions from vehicles exhaust during the new World harmonized Light-duty vehicle Test Procedure (WLTP) that will be soon used for type approval of LDV in the European Union and potentially other countries who are signatories to the UN-ECE. Therefore, in the present study three different analytical techniques: HR-FTIR, HORIBA MEXA 1440 QL-NX, and CGS BLAQ-Sys, were used to evaluate the feasibility of the online ammonia emissions measurement from a series of four different LDV over the WLTC.

EURO VI regulation for HDV specifies FTIR and Laser Diode Spectrometer (LDS) in either "in-situ" or extractive modes as measurement principles to be used for the measurement of ammonia from HD exhaust. Either technique must meet certain criteria, such as: a sample path (sampling line, pre-filter(s) and valves) made of stainless steel or PTFE and heated to  $463 \pm 10$  K ( $190 \pm 10$  °C) in order to minimize ammonia losses and sampling artefacts; spectral resolution of the laser (for the near infrared) or spectral resolution of the ammonia wavelength (for the FTIR) within  $0.5 \text{ cm}^{-1}$ ; minimum detection limit of  $< 2$  ppm under all conditions of testing; system response time  $\leq 20$  s; among others. The purpose of the campaign was to study the proposed analytical methods and also sampling temperatures for the WLTP, both of which are, in some cases, different to that specified in the EURO VI regulation. The most important being the sampling temperature issue.

## 2. Experimental

**Four light duty vehicles were tested as part of the Validation Phase 2 (VP2) exercise of the World harmonized Light-duty vehicle Test Procedure (WLTP) conducted in the Vehicle Emission Laboratory (VELA) at the European Commission Joint Research Centre (EC-JRC) Ispra, Italy during September 2013. Three groups, CGS, HORIBA and the Sustainable Transport Unit of the JRC, took part in the measurement and analysis of the four vehicles exhaust emissions over the WLTC class 3, version 5.3** (see Fig1) (see Section 2.1). The vehicles consisted of two diesel vehicles (DV1 and DV2), one flexi-fuel vehicle (FFV) and a gasoline vehicle (GV). The detailed description of the vehicle's features is available in Table 1. A certified diesel fuel with 5% bio-diesel content (henceforth B5) was used in the two diesel vehicles, DV1 and DV2, while a certified gasoline containing 5 % ethanol (hereinafter E5) was used in the FFV and the GV. The fuels specifications are summarized in the Table 1 of the supplementary information. The vehicles were selected to cover the different potential ammonia emitters. DV2 was chosen as a reference diesel vehicle on the basis that no ammonia should be detected.

**Table 1.** Vehicles description.

<b>Denomination</b>	<b>DV1</b>	<b>DV2</b>	<b>FFV</b>	<b>GV</b>
Combustion type	Diesel	Diesel	Flex-fuel gasoline/EtOH	Gasoline
EU emission standard	Euro 6	Euro 5	Euro 5a	Euro 5
After-treatment	DPF, SCR	DPF	TWC	TWC
Fuel	B5	B5	E5	E5
Fuel system	TDI	TD	DI	GDI
Engine displacement (cm <sup>3</sup> )	1968	1560	1596	1390
Engine power (kW)	105	84	132	132
Odometer (km)	22362	18871	24334	38541
Vehicle weight (kg)	1712	1282	1481	1194

The VELA 2 facility includes a climatic test cell with controlled temperature and relative humidity (RH) to mimic the different ambient conditions (temperature range: -10 to 35 °C; RH: 50%). Triplicated tests were performed on a chassis dynamometer (inertia range: (454–4500) kg), designed for two and four-wheel drive LDV (two 1.22 m roller benches – Maha GmbH, Germany). The emissions exhaust is fed to a Constant Volume Sampler (CVS, HORIBA, Japan) using a critical Venturi nozzle to regulate the diluted exhaust flow rate (CVS flow range: (3 - 30) m<sup>3</sup>/min). A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions. A UEGO type sensor was connected to the tailpipe to follow the air to fuel ratio. The tests were conducted at test cell temperature of 23 °C, and at 50 ± 2% RH. The temperature refers not only to the cell temperature but also to the vehicle's oil temperature, ± 1 °C, at the beginning of each test. Vehicles were kept inside the climatic cell under the described conditions for 20-24 hours.

### *2.1 Worldwide harmonized Light-duty vehicle Test Cycle (WLTC)*

In 2009 a road map for a world-harmonized light-duty vehicle test procedure (WLTP) was proposed by the World Forum for Harmonization of Vehicles Regulations (WP.29) of the United Nations Economic Commission for Europe (UNECE). Since the beginning of the WLTP process, the European Union had a strong political objective, set by its own legislation (Regulations (EC) 443/2009 and 510/2011) [25], to implement a new and more realistic test procedure by 2014.

The formal text for the phase 1a version of the light-duty vehicle Global Technical Regulation (GTR) was adopted by GRPE in 2013. The GTR specifies globally harmonized performance-related equipment specifications and test procedures. The phase 1a describes the development of the Worldwide harmonized Light-duty driving Test Cycle (WLTC) and associated test procedure for the common measurement of criteria compounds, CO<sub>2</sub>, fuel and energy consumption.

Three different driving cycles were developed, on the bases of the vehicle's power-to-mass ratio and its maximum speed, to represent three different vehicle classes. The vehicles tested in the present study are under the class 3

(power/mass >34 kW/ton and maximum speed >120 km/h), which is the highest power and speed class. Fig1 illustrates the version 5.3 of the speed profile for this class.

The Worldwide harmonized Light-duty driving Test Cycle (WLTC) is a cold-start driving cycle, where the vehicle and its components (oil, coolant, catalyst, etc) are at 23 °C at the beginning of each test. The driving cycle consists of four phases with different speed distributions (see Fig1) and it intends to be representative of the real world driving conditions being based on real world vehicle journeys from several countries. The length of the entire cycle is 1800 seconds and is comprised of the low speed (589 s), medium speed (433 s), high speed (455 s) and extra-high speed (323 s) phases. Moreover, it reaches a maximum speed 131.3 km/h and is about 23.3 km long.

## 2.2 Analytical instrumentation

### 2.2.1 HR-FTIR spectrometer dedicated to automotive emission

A High Resolution Fourier Transform Infrared spectrometer (HR-FTIR – MKS Multigas analyzer 2030-HS, Wilmington, MA, USA) allowed measuring the concentration of up to 20 exhaust compounds by a multivariate calibration based on a factory developed model. The absorption in the Mid-InfraRed range of several nitrogen species usually emitted in vehicle exhaust is displayed in the Fig1 of the supplementary information. As described by this figure, the areas where individual species absorb the IR often overlap. For instance, the absorbance of water, displayed with inversed scale in the upper part of the graphic, can cover the specific absorption wavelength of NO<sub>2</sub>. Consequently, the calibration model has been developed following different steps. Firstly, a PCA has been carried out to extract the informative region of the spectra for every individual species. Then, these informative regions were compared in order to isolate the specific wavelength area where no other species absorbs. These specific wavelengths were finally used to compute a multiple least-squares regression (MLR) model which aimed to predict the volume concentration of the compound. For each wavelength selected, the model assumed a linear relationship between concentration and absorption. For each compound, standard gas cylinders of several concentration levels were used to calibrate the model.

Implementation of the FTIR spectrometer for exhaust gas measurement required the acquisition of an averaged background spectrum from N<sub>2</sub>. This daily background spectrum was systematically subtracted to the new spectra registered by the instrument. The calibration of the instrument was based on a factory developed multivariate model.

CO, CO<sub>2</sub> and NO<sub>x</sub> measurements from the previously described analyzers were used to check the HR-FTIR calibration model. The limit of detection for ammonia, as well as for the other compounds, was estimated with the values obtained from the measurement of the background air, by assuming 3 times the standard deviation of the measured value to the averaged value, and for ammonia was found to be equal to 0.3 ppm.

HR-FTIR spectrometers dedicated to real time analysis of automotive emission must have a high acquisition frequency in order to register fast changes of volume concentration resulting from sharp accelerations. The output signal can be used to monitor the fluctuation of pollutant emission along the speed profile. Furthermore, the CO and/or NO signals were precisely synchronized using the CO or NO<sub>x</sub> instantaneous measurement at the tailpipe obtained using the non-dispersive infrared (NDIR) or the chemiluminescence detector (CLD), respectively, so that all instruments would be align to the very same time.

The HR-FTIR (Multigas analyzer 2030 MS - MKS, Wilmington, MA) reached 5 Hz acquisition frequency with a multipath gas cell of 5.11 m. It is equipped with a Michelson interferometer (spectral resolution: 0.5 cm<sup>-1</sup>, spectral range: 600-3500 cm<sup>-1</sup>) and a liquid nitrogen cooled mercury cadmium telluride detector. The raw exhaust was sampled directly from the vehicle's tailpipe with a PTFE (politetrafluoroetilene) heated line and a pumping system (flow: ca. 10 L min<sup>-1</sup>, T: 191 °C) in order to avoid the wall adsorption and/or dissolution of hydrophilic compounds (i.e. NH<sub>3</sub>, NO<sub>2</sub>, carbonyls, or ethanol) in condensed water. The residence time of the raw exhaust gas in the heated line before the FTIR measurement cell was less than 2 seconds. The measurement temperature was set to 191 °C, with a working pressure of 1013 hPa (±20). The compounds were monitor at 5 Hz, averaged and presented at 1 Hz.

### 2.2.2 HORIBA MEXA 1440 QL-NX. Quantum Cascade Laser Infra-Red Spectrometer (QCL-IR).

MEXA 1400QL-NX is an analyzer for the direct measurement of four nitrogen compounds (NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>) simultaneously in automobile exhaust gas on real-time by using Infrared Absorption Spectroscopy (IR Spectroscopy) as the measuring principle. By combining the new technology of Quantum Cascade Laser (QCL) light source and precisely adjusted long dual-path optical cell, it has realized high sensitivity for low concentrations with a limit of detection which complies with the current European legislative requirements. Furthermore, the QCL

has a wide dynamic range (i.e. 0-5 ppm to 0-2000 ppm) for the measurement of ammonia emissions in the exhaust gas. The MEXA 1440 QL-NX has a wavelength resolution close to  $0.006 \text{ cm}^{-1}$ .

The analyzer utilizes a high resolution spectrum and a highly vacuum optical cell in order to minimize the interference offered by the co-existing gases. Moreover, ammonia response has been improved by using a vacuum sample transfer line maintained at temperature of  $113^{\circ}\text{C}$  which ensures shorter residence time and minimum adsorption of ammonia on the surface of the walls. The temperature is optimized to prevent the decomposition of urea or its by-products and ensures a selective measurement of pure ammonia.

The analyzer can be used for the measurement of exhaust gas components from various fuel and engine types. MEXA 1400QL-NX consists of three main components – Main Control Unit, analyzer unit and heated filter (FH-01). The MCU serves as an instrument for the calculation of the emissions and for the display of the measured concentration. The analyzer unit contains the core of the MEXA 1400QL-NX – the sensor including QCL element, gas cell and optics, as well as a sample handling system specifically designed for the measurement of  $\text{NH}_3$ . The heated filter is connected to the analyzer unit via a heated line. The sampling of the exhaust is conducted via a stainless steel sampling probe covered with a heated jacket in order to avoid cold spots. The FH-01 contains a quartz filter element specifically designed to minimize the desorption of the ammonia molecules present in the exhaust gas.

### 2.2.3 CGS- BLAQ-Sys compact Test Bench.

The BLAQ-Sys Compact has specifically been designed for measuring traces of ammonia in engine exhaust gases. It contains a heated sampling probe, heated dilution system and an integrated photo-acoustical analyzer with a Quantum Cascade Laser (QCL).

The technology of the ammonia analyzer is based on the periodic absorption of laser light by ammonia in the sample gas and the subsequent generation of pressure waves. The laser light is generated by a quantum cascade laser, and the resulting pressure waves are measured with small microphones. The higher the concentration of ammonia, the higher the amplitude of the pressure waves.

By calibrating the instrument with a gas mixture containing a known concentration of ammonia, the amplitude of the microphone signal can be associated with a concentration of ammonia in the sample gas.



The design of the measurement cell is optimized for maximum amplification of the signal generated by ammonia and for maximum attenuation of external sound and vibration. A sketch of the measurement concept is shown in Fig. 2 of the SI. The wavelength range that is covered during a measurement is chosen after extensive research on the spectral absorption features of ammonia and the gases that can be expected in the sample gas. For ammonia the measurement is performed by scanning the laser parameters in such a way, that a wavelength range around  $965.4 \text{ cm}^{-1}$  ( $10.3 \text{ }\mu\text{m}$ ) is covered, so the ammonia peak can clearly be recognized and quantified automatically (see Fig.3 of the SI).

Ammonia molecules tend to stick to the surface of commonly used materials in the exhaust gas measuring technology (e.g. untreated stainless steel). Therefore only materials exhibiting minimum ammonia adsorption effects like PFA, PTFE and coated stainless steel have been used throughout the complete sampling system and analyzer in the BLAQ-Sys system. This assures that the concentration of ammonia is hardly altered by adsorption/desorption effects before it is measured.

The raw exhaust gas is sampled from the tailpipe with a coated stainless steel CGS extraction probe and transferred via a heated 1/8" PFA raw gas line (flow: ca  $1 \text{ L min}^{-1}$ , T:  $190^\circ\text{C}$ ) to the CGS Dilution Unit (DU) (T:  $100^\circ\text{C}$ ). The dilution module in the DU contains an injector pump which sucks the raw exhaust gas through a PTFE sample gas filter (PTFE Membrane;  $1\text{-}2 \text{ }\mu\text{m}$ ;  $\varnothing 47 \text{ mm}$ ). The filter membrane was replaced before every new measuring cycle. Dry instrument air is used to dilute the sample gas flow in the ratio 1:10. The diluted raw exhaust gas is transferred via a heated 3/8" PFA sample gas line (flow: ca  $11 \text{ L min}^{-1}$ ; T:  $100^\circ\text{C}$ ) to the mobile BLAQ-Sys instrument cabinet. The ammonia analyzer extracts a fraction of the gas flow with its internal pump that is placed behind the heated measurement cell (gas flow:  $90 \text{ ml min}^{-1}$ , T:  $50^\circ\text{C}$ ,  $500 \text{ hPa}$  working pressure). The volume of the measurement cell including an inline acoustical filter is  $6 \text{ ml}$ . The ammonia analyzer has a maximum measurement range of  $0 - 250 \text{ ppm}$  and its detection limit is  $0.2 \text{ ppm}$  (3 times standard deviation).

During the measurement campaign, the BLAQ-Sys system was daily calibrated over the dilution unit with zero air (synthetic air) and a calibration mixture of  $50 \text{ ppm}$  ammonia in synthetic air. The time required for performing the calibration measurement was 20 minutes.

## 2.2.4 Regulated emission measurements

Although the scope of the experiments was to test the feasibility and quality of the vehicular exhaust ammonia measurements, regulated compounds were also measured using standard methodologies defined by the related regulation to assure the performance of the vehicles used. CO, NO<sub>x</sub>, THC, non-methane hydrocarbons (NMHC) and particulate matter are regulated for vehicle emission. These pollutants were not analysed directly at the tailpipe of the vehicle, but after dilution of the raw exhaust. This avoids water condensation in the sampling line and also simulates the dilution process occurring in the atmosphere. For regulatory purpose, a collection step from the CVS, either in a bag (gaseous pollutant), or on a filter (particulate pollutant), was carried out. The obtained results are summarized in Table 2.

**Table 2.** Average emission factors (mg/km) for the regulated compounds and CO<sub>2</sub> (g/km) over the WLTC. Euro 5-6 spark and compression ignition emission limits (units, mg/km).

Vehicle	THC	THC +NO <sub>x</sub>	NMHC	CO	NO <sub>x</sub>	CO <sub>2</sub>	PM
<b>DV1</b>	4 (±3)	188 (±7)	2 (±1)	115 (±9)	184 (±5)	156 (±4)	0.2 (±0.1)
<b>DV2</b>	8 (±3)	467 (±31)	6 (±3)	290 (±19)	458 (±32)	124.5 (±0.7)	0.5 (±0.1)
<b>FFV</b>	80 (±20)	141 (±18)	74 (±20)	470 (±131)	61 (±7)	151.0 (±0.5)	2.0 (±0.1)
<b>GV</b>	29 (±11)	50 (±8)	24 (±10)	309 (±23)	22 (±3)	137.4 (±0.5)	1.4 (±0.2)
<b>Euro 5 S.I.<sup>1</sup></b>	100	-	68	1000	60	-	5.0
<b>Euro 6 S.I.<sup>1</sup></b>	100	-	68	1000	60	-	4.5
<b>Euro 5 C.I.<sup>2</sup></b>	-	230	-	500	180	-	5.0
<b>Euro 6 C.I.<sup>2</sup></b>	-	230	-	500	80	-	4.5

<sup>1</sup>S.I. = spark ignition emission limits mg/km; <sup>2</sup>C.I. = compression ignition emission limits mg/km

The CVS bag sampling method requires the collection of the diluted exhaust with a constant sampling flow rate from the dilution tunnel into a bag, thus, obtaining a representative sample of the total gas which passed through the dilution tunnel during the sampling period. Then, a series of analyzers were connected to the exhaust bags. Once the sampling period was finished, the collected gas was drawn towards the corresponding analyzers. The regulated

emissions from all vehicles were measured with the following analyzers: non-dispersive infrared (NDIR for CO/CO<sub>2</sub>), a chemiluminescence (CLD for NO<sub>x</sub>) and a heated (191 C) flame ionization detector (FID for THC) (HORIBA, Kyoto, Japan) (see Fig1).

Another set of analyzers similar to the one used for gaseous regulated emission measurement was directly connected at the tailpipe of the vehicle. These sensors can monitor online the dynamic volume concentration of the pollutants over the cycle driven, with 1 Hz frequency. This measurement methodology for the raw gas measurement is not indicated in the scope of the legislation; however, the outputs were mostly informative and useful in the framework of this project. Indeed, these comprehensive data were correlated with other dynamic parameters such as velocity of the vehicle, temperature of the catalyst, and instantaneous fuel consumption. The integration of the recorded signals provided valuable quality control information when compared with the emission factors resulting from the bags and they prove to be useful for the alignment of the HR-FTIR signals (see HR-FTIR measurements)

### **3. Results and Discussion**

#### *3.1 Regulated compounds*

Four light duty vehicles were tested as part of an intercomparison exercise of the Worldwide Light-duty vehicle Test Procedure (WLTP) that was conducted in the VELA 2 at the EC-JRC. The quantification of the regulated compounds emitted by these vehicles is of major interest in order to assess the well performance and functioning of the tested vehicles. The regulated emissions were measured according to the WLTP GTR. The obtained emission factors together with the Euro 5-6 spark and compress ignition emission limits are summarized in Table 2.

Most regulated compounds and ammonia emissions showed very good repeatability, demonstrating the suitability of the testing procedure. An example of the repeatability achieved for CO<sub>2</sub> emissions, oil temperature and exhaust temperature can be seen in Fig2.

DV1, a Euro 6 diesel LDV equipped with a diesel particle filter (DPF) and SCR system, emitted on average 184±5 mg/km of NO<sub>x</sub>. This value doubles the Euro 6 NO<sub>x</sub> limit (80 mg/km). Clearly, DV1 did not comply with the THC + NO<sub>x</sub> limit (170 mg/km) either. The high NO<sub>x</sub> emissions could suggest a mal functioning of the SCR system. The DV2, a Euro 5 diesel LDV equipped only with a DPF, did not comply with the Euro 5 NO<sub>x</sub> nor THC + NO<sub>x</sub>

emission limits, the average emission were  $458\pm 32$  and  $467\pm 31$  mg/km, respectively. In the case of the FFV, average emission factors of NO<sub>x</sub> and NMHC were within the Euro 5 limits when taking into account the uncertainties ( $1\sigma$ ). The other regulated pollutants, THC, CO and PM, were below emission limits. Finally, the GV comply with the Euro 5 emission standards.

### 3.2 Ammonia emissions and measurement

Fig3 illustrates the ammonia emission profiles obtained from the four tested vehicles (DV1, DV2, FFV and GV) using the three analytical instruments: HR-FTIR, HORIBA MEXA 1440 QL-NX QCL-IR, and CGS BLAQ-Sys. Table 3 shows the average and maximum concentration (ppm) measured for each vehicle by each instrument. The presented averages were obtained from the three tests that were performed per vehicle and the errors refer to one standard deviation.

**Table 3.** Average ammonia concentration from the four testes vehicles, DV1, DV2, FFV and GV using HR-FTIR, HORIBA MEXA 1440 QL-NX, and CGS BLAQ-Sys.

Vehicle	Concentration	JRC HR-FTIR	HORIBA QCL-IR	CGS BLAQ-Sys
<b>DV1</b>	<b>Average<sup>1</sup></b>	<b>0.5</b> ( $\pm 0.1$ )	<b>0.1</b> ( $\pm 0.1$ )	<b>0.2</b> ( $\pm 0.1$ )
	Max	1.0	0.8	6.6
<b>DV2</b>	<b>Average<sup>1</sup></b>	<b>0.5</b> ( $\pm 0.1$ )	<b>0.1</b> ( $\pm 0.1$ )	<b>0.2</b> ( $\pm 0.1$ )
	Max	1.0	0.5	2.0
<b>FFV</b>	<b>Average<sup>1</sup></b>	<b>20</b> ( $\pm 7$ )	<b>21</b> ( $\pm 7$ )	<b>23</b> ( $\pm 11$ )
	Max	135	272	190
<b>GV</b>	<b>Average<sup>1</sup></b>	<b>22.3</b> ( $\pm 0.6$ )	<b>24</b> ( $\pm 1$ )	<b>24</b> ( $\pm 2$ )
	Max	155.0	587	229

<sup>1</sup>Average concentration (ppm) of the three tests performed per vehicle. Max refers to the maximum concentration registered value (ppm) during the three tests.

The average ammonia concentrations measured from the raw exhaust of DV1, diesel vehicle equipped with a SCR system, by the three instruments were, for the three test, extremely low (see Table 3). Most of the time the concentration of ammonia was close or below the limit of detection (LOD) of the HR-FTIR (0.3 ppm) and the HORIBA MEXA 1440 QL-NX (0.2 ppm) instruments. However, while the HR-FTIR and the HORIBA MEXA

1440 QL-NX measured concentration of ammonia close to the LOD over the whole cycle, the CGS BLAQ-Sys detected some ammonia at the very beginning of low phase of the WLTC (see Fig3). The comparison of the unattended profile observed by the CGS BLAQ-Sys with those of several other compounds obtained using the HR-FTIR revealed that the CGS BLAQ-Sys had a cross-interference from the ethylene emitted during cold start (see Fig4). As Fig4 illustrates, this cross-interference was also present during the tests performed with the other vehicles. Still, the average ammonia concentration measured with the BLAQ-Sys did not differ from those obtained with the HR-FTIR and the HORIBA MEXA 1440 QL-NX due to the low concentration of the interfering ethylene and also because ethylene is only emitted during the cold start so it is “diluted” along the cycle.

The high NO<sub>x</sub> emission factors measured for the DV1 and the absence of any ammonia at its raw exhaust reinforce the hypothesis of a malfunctioning of the vehicle’s SCR system, making the comparison with previous studies pointless.

The DV2 was used as the reference diesel vehicle, from which no ammonia emission was expected to be measured. In fact, the HR-FTIR and HORIBA MEXA 1440 QL-NX instruments did not detect any ammonia over the WLTC. The CGS BLAQ-Sys detected low emissions of ammonia. However, the observed profile corresponds exactly to that of the ethylene emitted during the cold start and measured with the HR-FTIR (see Fig4), confirming that no ammonia was emitted as the other two instruments suggested.

The average ammonia emission concentrations measured from FFV and GV’s raw exhaust were the same, within uncertainties, for the two vehicles and the three instruments (see Table 3). The two vehicles, tested over the WLTC, resulted into two different ammonia emission profiles that were consistently and evenly reproduced by all three analytical instruments (see Fig3). The HORIBA MEXA 1440 QL-NX monitors and reports the ammonia concentrations at 10 Hz frequency, as a consequence higher maximum ammonia concentrations were constantly obtained for the two vehicles (272 and 587 ppm for FFV and GV, respectively). For the same reason the peaks that this instrument produces are sharper and better defined. Thus, the average ammonia concentrations obtained with the HORIBA MEXA 1440 QL-NX are the same than those obtained with the HR-FTIR and the CGS BLAQ-Sys. The average ammonia emission concentrations measured from FFV and GV over the WLTC at 23 °C (from 20±7 to 24±2 ppm) are in very good agreement with the average of the ammonia concentrations reported for a series of Euro 5 gasoline vehicles tested over the NEDC at 22 °C (22 ppm) [26]. In that study the same type of flexi-fuel vehicle

was tested using the E5 blend over the NEDC at 22 °C. The reported average ammonia emitted over the NEDC was 7 ppm, while over the WLTC was around 21 ppm (see Table 3). Moreover, the maximum ammonia concentration measured for FFV over the WLTC was, at least, one order of magnitude higher (135-272 ppm) than over the NEDC (14 ppm). These results suggest that the higher concentrations of the ammonia emissions are due to the dynamism, and still realism, of the new cycle.

#### **4. Conclusions**

Four light duty vehicles were tested as part of the Validation Phase 2 (VP2) exercise of the WLTP. The raw vehicles' exhaust was analyzed in real-time using three different instruments, HR-FTIR, HORIBA MEXA 1440 QL-NX, and CGS BLAQ-Sys. The obtained average ammonia concentrations and the emission profiles reveal that the three instruments are all suitable to measure ammonia from the vehicles raw exhaust. The CGS BLAQ-Sys presented a cross-interference from a co-existing compound (ethylene) emitted from the tailpipe during the cold start. Still, the results showed that all three instruments are in good agreement, presenting no significant differences. The three instruments also present a very good reproducibility. It is then perfectly feasible to measure ammonia at the vehicle exhaust with an online method guaranteeing the reproducibility and repeatability of the results.

The HORIBA MEXA 1440 QL-NX was operating at 113 °C as opposed to 190 °C of the other instruments. The results indicate that temperature of the sampling and analyzer is not important as long as there is no condensation.

The FFV and the GV showed similar average ammonia emission concentrations than those reported for a fleet of gasoline LDV in a previous study [26]. The comparison of the results obtained for FFV with those from a similar vehicle tested over the NEDC [26] suggest that a vehicle that was studied using the NEDC could present higher emissions of ammonia if tested under the same conditions over the more dynamic WLTC. Implementation and adjustment of complementary devices such as oxidizing catalysts right after the SCR [27] or after the TWC, or an appropriate feedback and control technology to maintain precise air/fuel ratio [28] may be necessary when LDV ammonia emissions limits will be introduced.

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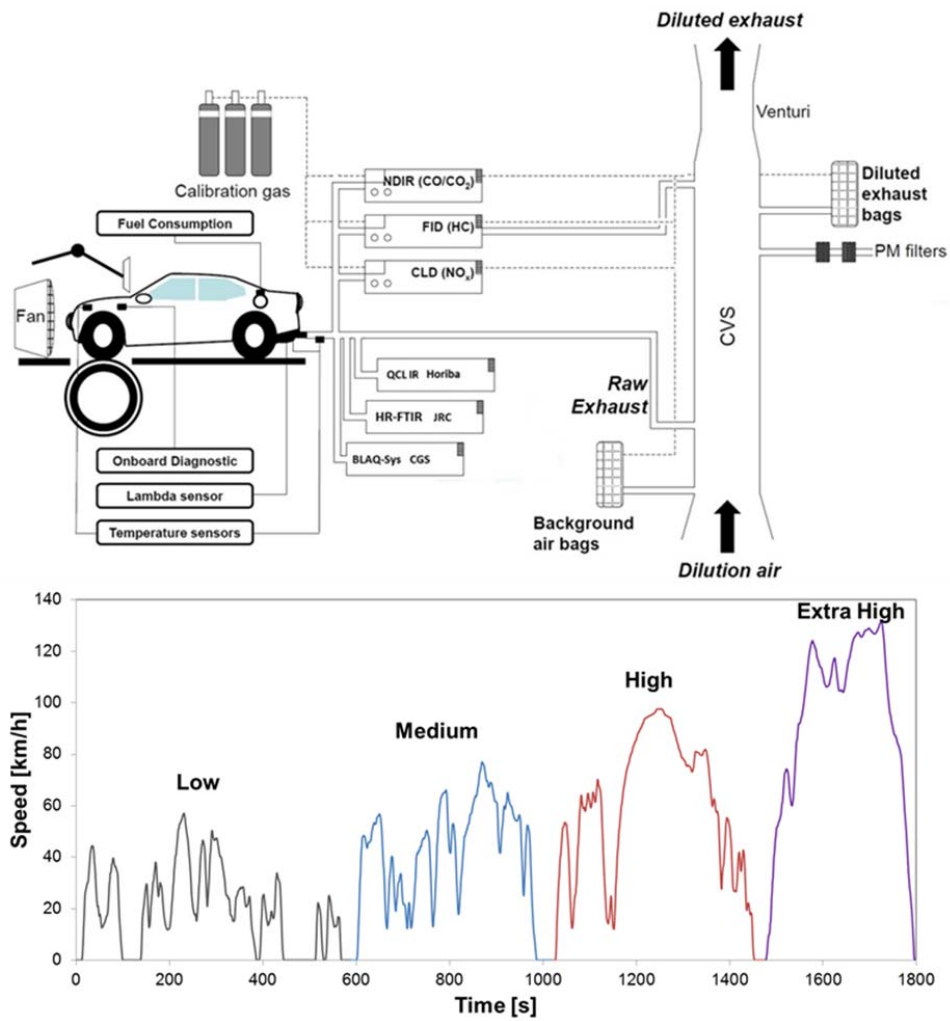
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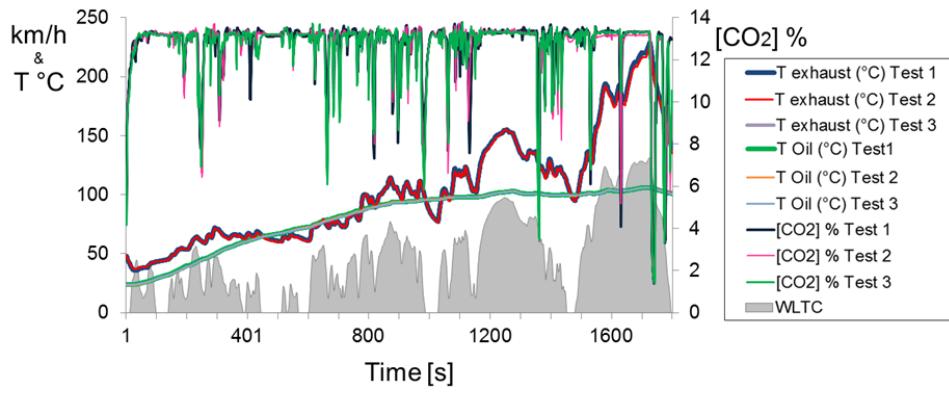
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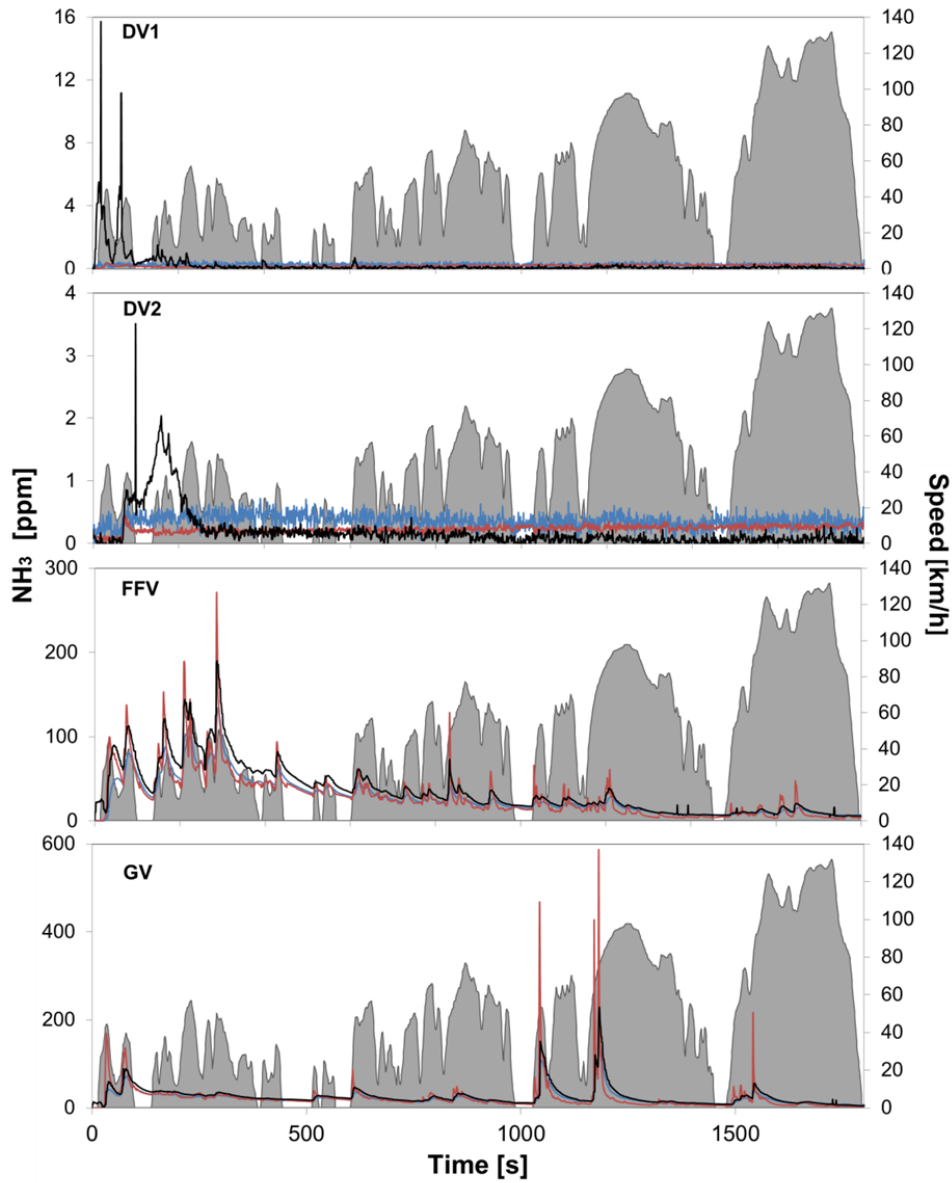
**Fig1.** Schematic diagram of the experimental setup (top) and Worldwide harmonized Light vehicle Test Cycle (WLTC) (bottom). Each color represents one of the four phases that form the cycle.



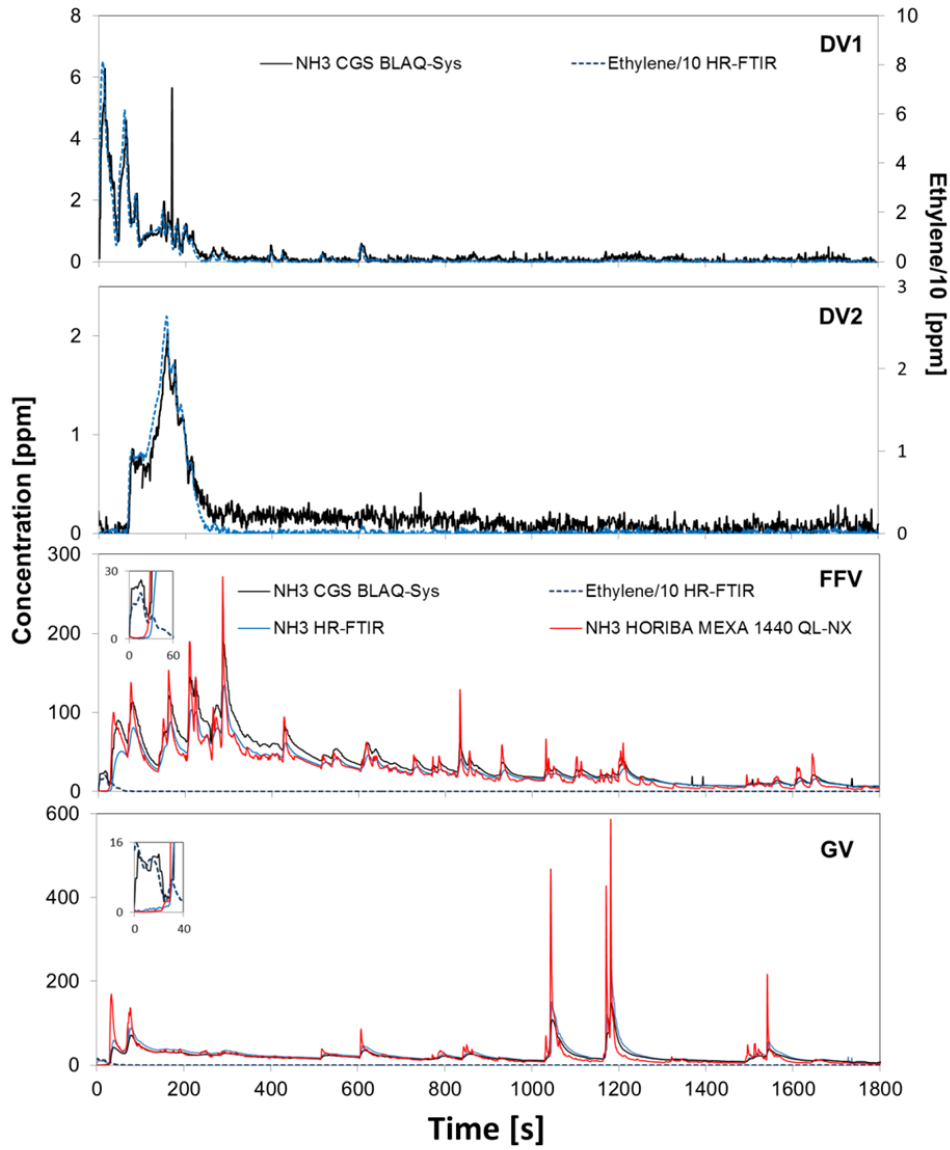
**Fig2.** Representation of some setup capabilities (exhaust temperature, CO<sub>2</sub> emissions, Oil temperature) and repeatability for the three tests performed for FFV over the WLTC.



**Fig3.** Real-time ammonia emission concentration for vehicles DV1, DV2, FFV and GV over the WLTC measured by HR-FTIR (blue), HORIBA MEXA 1440 QL-NX (red), and CGS BLAQ-Sys (black).



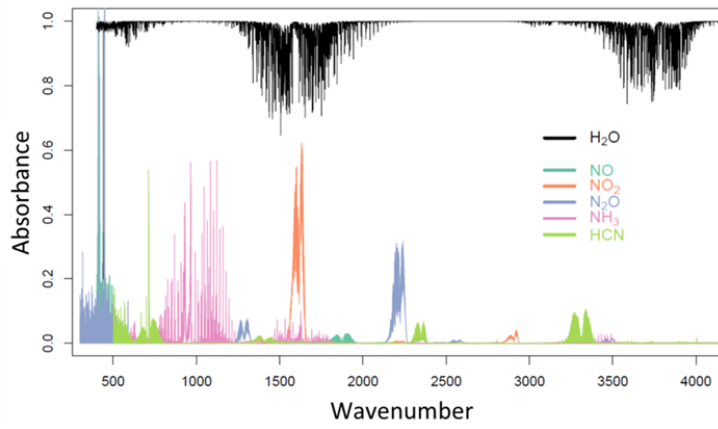
**Fig4.** Concentration of ammonia measured by HR-FTIR (blue), HORIBA MEXA 1440 QL-NX (red), and CGS BLAQ-Sys (black), compared with one tenth of the concentration of ethylene, measured by HR-FTIR (dotted blue) over the WLTC. Ethylene concentration for DV1 and DV2 is found on the right axis.



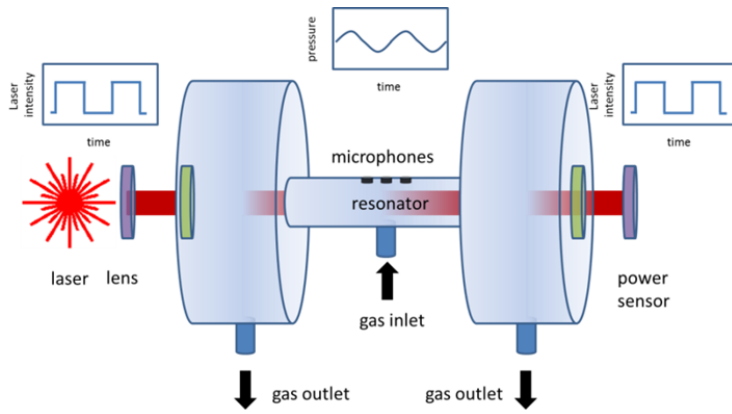
**Table 1 SI.** Fuels specifications.

Parameter	Method	Unit	E5	Parameter	Method	Unit	B5
RON	EN ISO 5164	-	101.2	Cetane Number	EN ISO 5165	-	52.4
MON	EN ISO 5163	-	90.4	Density at 15 °C	EN ISO 3675	-	835.5
Density at 15 °C	EN ISO 3675	kg/m <sup>3</sup>	751.8	Sulfur	EN ISO 20846	kg/m <sup>3</sup>	3.9
DVPE	EN 13016-1	kPa	65.0	Viscosity at 40 °C	EN ISO 3104	mm <sup>2</sup> /s	2.53
Sulfur	EN ISO 20846	mg/k g	<3.0	Lubricity at 60 °C	ISO/DIS 12156	µm	127
Net Heating Value	ASTM D3338	MJ/k g	42.02 0	Net Heating Value	ASTM D4868	MJ/k g	42.9 4
Carbon	ASTM D3343	% (V)	85.14	Carbon	ASTM D5291	% (V)	86.1
Hydrogen	ASTM D3343	% (V)	13.16	Hydrogen	ASTM D5622	% (V)	13.1
Oxygen	EN 13132	% (V)	1.7	Oxygen	Calculated	% (V)	0.7
Ethanol	EN 13132	% (V)	4.7				

**Fig1 SI.** FTIR spectra of typical vehicular emitted nitrogen species and H<sub>2</sub>O.



**Fig2 SI.** The modulated laser light is directed from the left to the right through the measurement cell, resulting in a pressure modulation that is measured by microphones; the pressure amplitude is proportional to the  $\text{NH}_3$  concentration.





**Fig3 SI.** Absorption spectra from NH<sub>3</sub>, H<sub>2</sub>O and CO<sub>2</sub>, the vertical axis represents the fraction of the light that is absorbed in 1 cm of ambient air at a pressure of 0.5 bar.

