

Measuring NO_x during periodic technical inspection of Diesel Vehicles

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Supplementary Information

1. NO_x mission factors calculation for light-duty vehicles testing with malfunctioning SCR system over a WLTC

For the set of WLTC tests performed with a functioning SCR system, NO_x emissions (mg/km) are reported as measured from the bags according to (EC, 2017a). For the test performed without AdBlue injection the final emission factor evaluation was performed, depending on the available data, as follows: for LD1 and LD2, by integration of the calculated instantaneous NO_x mass emissions measured at the vehicle's tailpipe, while for LD3 and LD5 NO_x emissions are reported as measured from the bags. LD1 and LD2 instantaneous NO_x mass emissions calculation was based on the exhaust flow rate calculated as difference between the total flow and dilution air flow of the constant volume sampler (CVS) for LD1 and on the exhaust flow rate signal recorded at the OBD port for LD2. For LD5, it was not possible to perform the WLTC test simulating a malfunctioning of the SCR system. The detailed description of the measurement equipment is provided in "Experimental setup and procedure for the aftertreatment system warm-up evaluation tests" section in the main text.

2. NO_x-PTI equipment

Analyser #1 was a 4 gas analyser commercially available, MID approved (for CO, CO₂, HC and O₂ measurement) equipped with NO_x electrochemical sensor. It included a particulate filter on the sampling line in order to protect the gas analyser and a water separator. These analysers are calibrated in the standard way throughout Europe and the world, in accordance with OIML recommendations. A similar approach is used to calibrate the NO_x sensor. It uses a cylinder of standard gas with a NO_x concentration of 1800 ppm. This value is consistent with the range of 0 to 5000 ppm, given that this measurement is linear. The adjustment is made at one point. It should be noted that the set-up and response times are long. The sampling flow was ~6.7 l/min and the measuring frequency was 1 Hz.

Analyser #2 was equipped with NO and NO₂ electrochemical sensors (NO_x provided as NO + NO₂). It included a water trap and particle filter to remove the moisture from the sampling flow. An additional module, the gas conditioning unit (GCU) featuring a cooling fan, a cooling rod and a water trap, was also fitted in the sampling line. GCU aimed at removing water from the flue gas sample to ensure accurate measurement of NO₂. Manufacturer specified that in presence of the GCU unit the measurement had to be considered as dry. The sampling flow was ~0.6 l/min. The measuring frequency was 0.5 Hz. NO and NO₂ were calibrated respectively with 94.3 ppm and 203 ppm reference gas cylinders.

Analyser #3 was equipped with a CLD compact module. It contained a reaction/measurement chamber in which NO from the sample gas reacts with ozone (O₃). The radiation generated by the

reaction was amplified and measured using a photomultiplier tube (PMT). The NO concentration is proportional to the amount of radiation. The ozone required for the measurement was generated from the ambient air by means of an ozone generator. The sensor was pressure and temperature stabilized, so that a constant measurement was possible. The sample gas was freed from ozone in the ozone destroyer before it leaved the measuring device as exhaust gas. The measuring device was operated in a vacuum, which was generated by the pump. As specified by the manufacturer the negative pressure in the probe lowered the dew point, preventing the water in the probe/measuring section from condensing out. The measuring chamber, on the other hand, was heated. Eventually the measurement was considered as wet. The sampling flow was ~ 5.5 l/min. The measuring frequency was set at ~ 20 Hz (not constant). Analyser #3 was calibrated by the manufacturer with a nominal 1000 ppm NO reference cylinder, linearity was checked over 10 points (tolerance $\pm 1\%$ FS), zero (tolerance ± 0.5 ppm) and span (tolerance ± 10 ppm) drift were checked over 8 hours. Rise time (t_{10-90}) and limit of detection (LOD), calculated as 2σ over 10 s, were also provided, being respectively 1.2 s (target < 5 s) and 0.056 ppm (target < 0.5 ppm).

Analyser #4 was commercially available, MID approved (for CO, CO₂, HC and O₂ measurement) and retrofitted with an NO electrochemical sensor for automotive application from Envitec (Wismar, Germany). Water was removed from the sampling flow by a coalescent filter placed at the inlet of the apparatus. The water separator design and installation followed the OIML R 99 (OIML, 2008) requirements. The sensor was calibrated by the manufacturer with two NO reference cylinders with nominal concentration of 200 ppm and 800 ppm. The relative deviation reported at 200 ppm during the span verification was 3%. The manufacturer also specified a $< \pm 2\%$ signal drift per month, underlining the importance of a consistent maintenance and calibration. The reported repeatability was 2% of the signal. The sampling flow was ~ 3.9 l/min and the measuring frequency was set at ~ 2 Hz (not constant).

Device #5 was an integrated Portable Emissions Measurement System (iPEMS) equipped with a proprietary cartridge system, (3DATX, n.d.) This system allowed emissions measurement for CO₂, CO and HC using a non-dispersive infrared (NDIR) spectrometer, and NO, NO₂ and O₂ using three-electrode electrochemical sensors. The system is equipped with a condensate unit featuring a chiller (flow temperature at the exit $\sim 10\div -15^\circ\text{C}$) to remove the moisture from the sample gas. An external water trap was also installed to remove additional condensation that might have collected in the tube after the chiller. Regarding the NO and NO₂ sensors, the manufacturer specified for both a $\pm 2\%$ repeatability. NO and NO₂ concentration results from the device were reported on a dry basis. The sampling flow was ~ 2 l/min. The electrical signals are acquired at 100 Hz, averaged over a 1 s duration to produce a 1 Hz electrical signal, which is converted to a 1 Hz concentration value. This device was already used in the framework of PTI in a recent study (Thomas et al., 2023).

3. Tables

Table S1. Summary of the light-duty vehicles tested at the JRC in the 2020–2022 period, in the framework of the Market Surveillance activity (Bonnell et al., 2022; Gruening et al., 2023) and used for the ATS heating time analysis in this work. All the tests used feature a cold start, preceded by a soak time as foreseen in EC regulation 2017/1151 (EC, 2017a) for RDE test.

Year	Vehicle	# test	Engine	Standard	Category
2020-2021	#1	1	ICE	Euro6d- TEMP	M1
2020-2021	#2	2	ICE	Euro6d- TEMP	N1-Class3
2020-2021	#3	2	ICE	Euro6d- TEMP	N1-Class3
2020-2021	#4	1	ICE	Euro6d	M1
2020-2021	#5	2	ICE	Euro6d	M1
2020-2021	#6	3	ICE	Euro6d- TEMP	N1-Class3
2020-2021	#7	2	ICE	Euro6d- TEMP	M1
2020-2021	#8	2	ICE	Euro6d- TEMP	M1

2020-2021	#9	2	ICE	Euro6d- TEMP	M1
2020-2021	#10	1	ICE	Euro6d	M1
2022	#11	2	NOVC HEV	Euro 6d	M1
2022	#12	1	ICE	Euro 6d	N1-Class2
2022	#13	2	ICE	Euro 6d	N1-Class3
2022	#14	2	ICE	Euro 6d-TEMP	M1
2022	#15	1	ICE	Euro 6d	N1-Class3
2022	#16	1	ICE	Euro 6d-TEMP	M1
2022	#17	1	ICE	Euro 6d-TEMP	M1
2022	#18	1	ICE	Euro 6d	M1
2022	#19	1	ICE	Euro 6d-TEMP	N1-Class3

Table S2. Summary of the heavy-duty vehicles tested at the JRC in the 2020–2023 period and used for the ATS heating time analysis in this work. All the test considered features a cold start.

Year	Vehicle	# test	Engine	Standard	Category
2020	#1	4	ICE	Euro VI D	M3-Class3
2021	#2	5	ICE	Euro VI E	N3
2023	#3	4	ICE	Euro VI E	N3
2023	#4	4*	ICE	Euro VI E	N3

*Two tests were performed using hydrotreated vegetable oil (HVO) as fuel instead of Diesel.

4. Figures

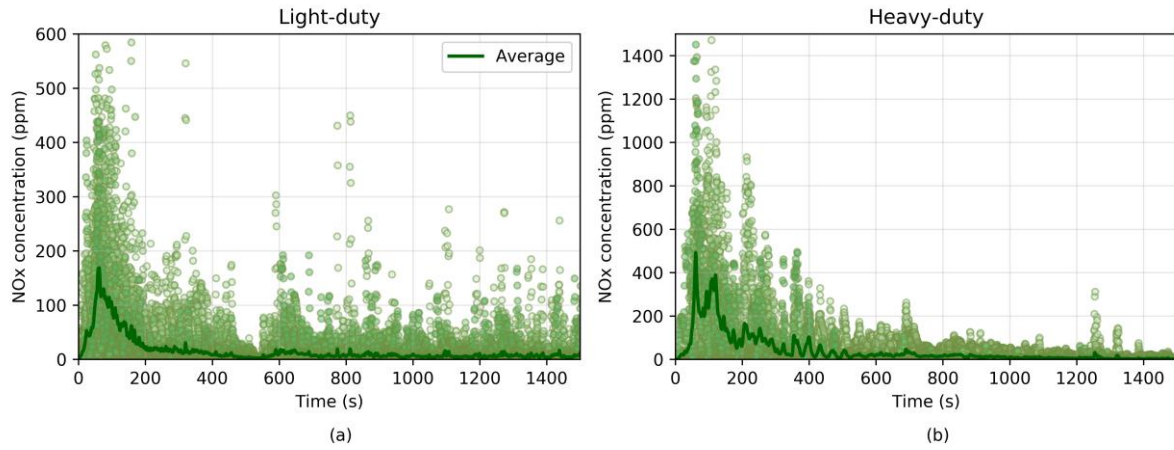


Figure S1. (a) NOx concentration during RDE tests for Diesel light-duty vehicles tested at JRC in the framework of Market Surveillance (Bonnel et al., 2022; Gruening et al., 2023). (b) NOx concentration during WHVC and ISC tests for Diesel heavy-duty vehicles tested at JRC. The solid line represent the average of the modal emissions obtained, while NOx concentration trends for all tests are represented by circles. Both graphs are zoomed in the first 1500 seconds of each test. Additional details on the methodology applied could be found in “Statistics from on-road and laboratory datasets” section.

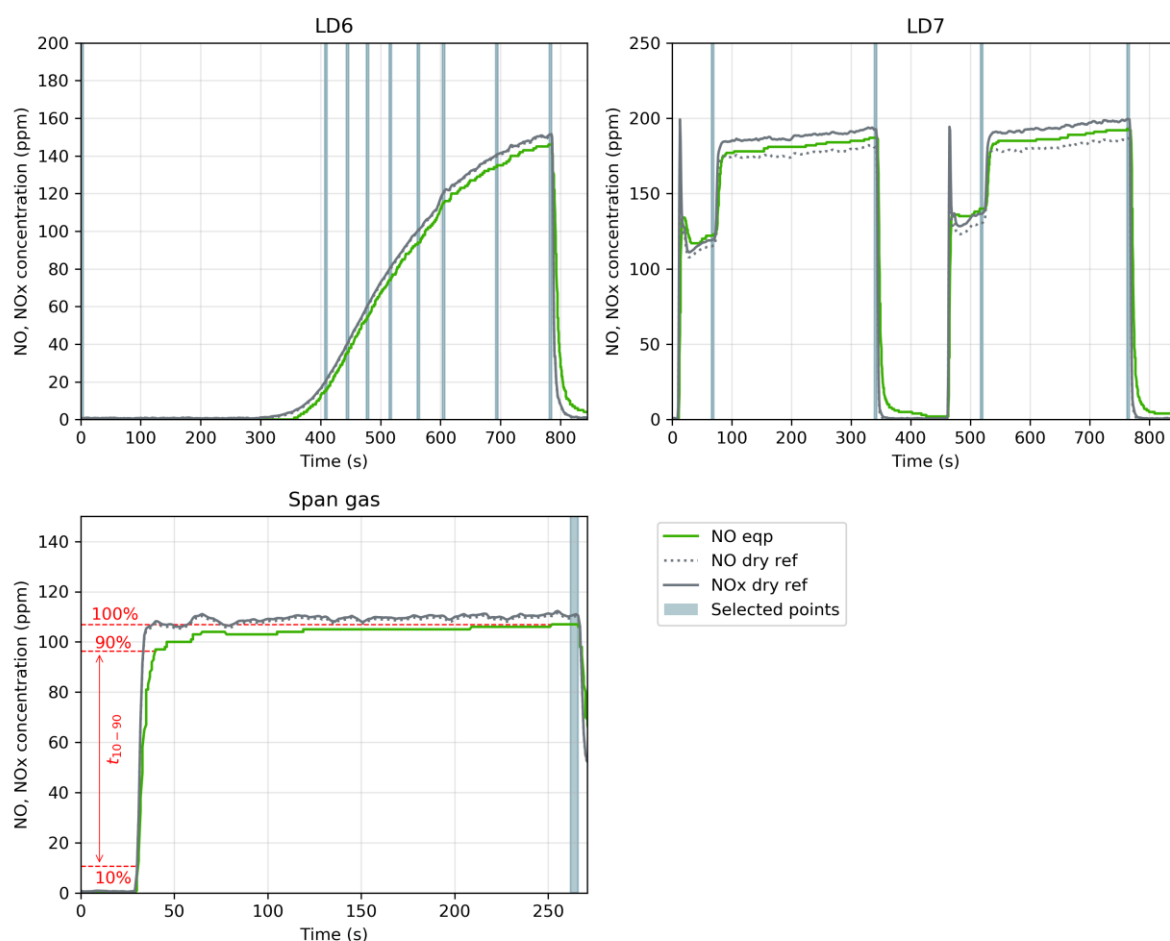


Figure S2. Graphical visualization of the selected points used for comparing analyser #4 against the reference equipment in LD6, LD7 and span gas testing. The same approach was also applied for the other equipment. Analyser #4 measured NO concentration in solid light green line, NO (dotted line) and NOx (solid line) concentration from reference equipment are displayed in grey. Light blue bands highlight the different 5 seconds sections used to evaluate the averages of the PTI-analyser and the reference equipment. In the span gas test, a schematic of how t_{10-90} was evaluated is reported.

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