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## Investigations of emissions of reactive substances $\text{NO}_2$ and $\text{NH}_3$ from passenger cars

Public concern and complaints regarding ambient air in zones of dense traffic pertains to two compounds of nitrogen, nitrogen dioxide ( $\text{NO}_2$ ) and ammonia ( $\text{NH}_3$ ); both are toxic and strongly irritant, such that legal limitations are under discussion. This paper contributes to measuring methods as already in part proposed by GRPE subgroup WLTP-DTP (Worldwide Light Duty Test Procedures – Diesel Test Procedures) for  $\text{NO}_x$ .

Despite legally lowered  $\text{NO}_x$  emission levels, lumping both,  $\text{NO}_2$  and  $\text{NO}$ , levels of  $\text{NO}_2$  have risen in cities and agglomerations as a result of both, deployed catalytic exhaust after-treatment devices and low sulphur Diesel fuels. In present tests two different combinations of  $\text{NO}_2$  measuring methods as proposed by WLTP were checked on Diesel cars for practicability in handling and accuracy. These integral, indirect methods ( $\text{NO}_2 = \text{NO}_x - \text{NO}$ ) have been found as useful tools for estimate of  $\text{NO}_2$  and with use of appropriate analyzers a satisfactory accuracy was attained.

Furthermore, attention was brought to ammonia ( $\text{NH}_3$ ) emitted by gasoline engines with three way catalysts (TWC) which ought not to be ignored while on the other hand SCR systems for Diesel engines are strictly regulated. Emission levels of more recent TWC turned out to be mostly below 20 ppm  $\text{NH}_3$ . Vehicle of older technology exhibited significantly higher levels, about 10 times more.

As chemical reactions depend on pressure and temperature (= i.e. flow condition in CVS-tunnel) as well as concentrations, doubts need to be considered on accuracy of results based on chemical reactive substances. Nevertheless, clear tendencies regarding changes of concentrations of  $\text{NO}_2$  and  $\text{NH}_3$  along the path-way could not be observed.

Key words: exhaust emissions, reactive substances  $\text{NO}_2$  and  $\text{NH}_3$

### 1. Introduction

Nitrogen dioxide  $\text{NO}_2$  and ammonia  $\text{NH}_3$  are not limited by the present exhaust gas legislation for passenger cars and the possibilities of limiting them are discussed.

Some increase of atmospheric pollution by  $\text{NO}_2$  can be observed in the dense traffic areas, in spite of general reduction of  $\text{NO}_x$  [1–3]. It is due to the combined effect of an increased proportion of Diesel vehicles with oxidation catalysts (DOC) or with passive DPF regeneration systems (CSF) in the fleet, together with the use of low sulphur fuels. Oxidation catalyst, often used as a key element of the DPF regeneration concept, increase the ratio of  $\text{NO}_2/\text{NO}_x$  in the exhaust gas, which is of big concern, since  $\text{NO}_2$  is more toxic than  $\text{NO}$  [1]. Some particulate filters technologies are especially problematic as they form  $\text{NO}_2$  on purpose to regenerate the filter continuously.

Several contributions on  $\text{NO}_2$ -production in the Diesel aftertreatment systems and on the  $\text{NO}_2$  measuring procedures were performed by the authors in the past [4, 5].

From them, as well as from experiences of other authors [6–8], it can be generally stated, concerning the  $\text{NO}_2$  emission of Diesel engines, that:

- with Pt-coated catalyst (DOC), or with catalyzed soot filter (CSF), there is a maximum of  $\text{NO}_2/\text{NO}_x$ -ratio typically when exhaust gas temperatures range around 350°C; there is a higher potential for  $\text{NO}_2$ -formation with higher Pt-content in the coating,

- lower  $\text{NO}_2$ -productions appear with higher spatial velocity,
- higher S-content in the fuel also causes a lower  $\text{NO}_2$ -production (this by directly influencing the catalysis and by quicker ageing of the catalyst),
- weaker catalytical activity and consequently lower  $\text{NO}_2$ -concentration appear with used DOC/DPF and/or when these devices are loaded with soot.

Modern gasoline cars are equipped with three way catalysts (TWC), which efficiently convert  $\text{NO}_x$  and the resulting amount of  $\text{NO}_2$  is negligible.

It was nevertheless stated and analyzed in several test programs of the Swiss Federal Laboratories EMPA that gasoline vehicles may emit quite considerable peak values of Ammonia  $\text{NH}_3$  [9–11]. This happens especially during Lambda deviations to the rich mixture in dynamic engine operation.

High  $\text{NH}_3$  emission peaks may occur with modern  $\text{NO}_x$ -storage catalysts, when switched to rich operation for deNO<sub>x</sub>-regeneration [12]. Ammonia originates in the atmosphere from natural and anthropogenic sources and it has a relatively short life time in the range of hours. It reacts with nitrogen oxides and sulphur oxides forming ammonium nitrate and sulphate.

In near exposure  $\text{NH}_3$  is toxic and has to be minimized.

Both compounds  $\text{NO}_2$  and  $\text{NH}_3$  are reactive and the question appears how should they be measured?

In WLTP there are some proposals of measuring  $\text{NO}_2$  from bags and from diluted gas.

In the present project direct measurements (from undiluted and diluted exhaust gas) were performed at different sampling points in the exhaust- and CVS- system and in different operating conditions. These results were compared with the simultaneous measurements from diluted gas in the sampling bags.

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## 2. Tested vehicles

Two Diesel cars were used to investigate  $\text{NO}_2$  emissions.

Figure 1 shows the vehicles on the chassis dynamometer and Table 1 represents the most important data of the vehicles. The Opel was used twice in different testing periods (9 months apart). The results will be defined as vehicle 1 and vehicle 2.



Fig. 1. Diesel vehicles for research of  $\text{NO}_2$

Table 1. Data of Diesel vehicles

Vehicle	Vehicle 1 and 2 Opel Astra DI16V	Vehicle 3 BMW 320d
Cylinder	4	4
Overall displacement [ $\text{cm}^3$ ]	1994	1995
Power [kW]	60	110
Injection type	DI	DI
Fuel	Diesel	Diesel
Weight empty [kg]	1390	1600
Transmission	m5/front	m6/rear
Matriculation	20.01.1998	30.09.2004
Turbocharging	yes	yes
Exhaust aftertreatment	DOC	DOC
Emission level	Euro 2	Euro 4

Three gasoline cars were used to study the release of  $\text{NH}_3$ . Figure 2 and Table 2 represent these vehicles. The Renault is representing an older TWC technology with Lambda control.



Fig. 2. Gasoline vehicles for research of  $\text{NH}_3$

Table 2. Data of Gasoline vehicles

Vehicle	Renault 18 Break vehicle 4	Volvo V60 T4f vehicle 5	Peugeot 306 Break 1.6 vehicle 6
Cylinder	4	4	4
Overall displacement [ $\text{cm}^3$ ]	2164	1596	1587
Power [kW]	74	132	72
Injection type	MPI	DI	DI
Fuel	Gasoline	Gasoline	Gasoline
Weight empty [kg]	1110	1554	1250
Transmission	m5/front	a6/front	m5/front
Matriculation	01.04.1985	27.01.2012	2001
Turbocharging	no	yes	no
Exhaust after-treatment	TWC	TWC	TWC
Emission level	Euro 0	Euro 5	Euro 3

The fuels used were from the Swiss market, summer quality:

- Diesel  $\text{S} < 10$  ppm according to SN EN 590 and
- Gasoline RON 95 according to SN EN 228

The lube oils were not changed and not analyzed.

### 3. Test Methods and Instrumentation

The vehicles were tested on a chassis dynamometer, each one at the same operating conditions and with warm engine (see "Test procedures").

#### 3.1. Chassis dynamometer

The following test systems were used:

- Roller dynamometer: Schenk 500 G5 60
- Driver conductor system: Tornado, version 3.3
- CVS dilution system: Horiba CVS-9500T with Roots blower
- An automatic air conditioning in the hall (concerns the intake- air of the engine and the dilution air of CVS).

The driving resistances of the test bench were set according to the legal prescription.

To study  $\text{NO}_2$  emissions at constant speeds and sometimes in WLTC the driving resistance was increased to obtain a higher exhaust temperature near to the maximum of  $\text{NO}_2$  production.

#### 3.2. $\text{NO}_x$ and $\text{NH}_3$ analysis

The chemiluminescence measuring method uses the effect that during the oxidation of NO to  $\text{NO}_2$  by means of ozone  $\text{O}_3$ , a part of  $\text{NO}_2$  is emitting a luminous radiation. This chemiluminescence signal is detected photo-electrically. When  $\text{O}_3$  is present in excess the signal is proportional to the NO concentration of the sample gas.

In order to measure  $\text{NO}_2$  in the sample gas, it has first to be converted into NO. To accomplish this chemical reduction the sample gas is passed through a converter heated to more than  $400^\circ\text{C}$ .

Modern converters contain metallic active material, which allows better selectivity of  $\text{NO}_2$ . Since sample gas normally contains both NO and  $\text{NO}_2$ , it is possible to measure the sum  $[\text{NO}] + [\text{NO}_2] = [\text{NO}_x]$  in the converter channel.

One of the used  $\text{NO}_x$ -analyzers, the Horiba chemiluminescence analyzer (CLA) – not heated is equipped with one converter and can selectively indicate NO, or  $\text{NO}_x$ .

Another  $\text{NO}_x$ -measuring system used is the EcoPhysics CLD 822 CM hr. (chemiluminescence detector), a heated analyzer with heated measuring line. This detector is equipped with a double reactor chamber and with two  $\text{NO}_2 \rightarrow \text{NO}$  converters and allows simultaneous readings of NO,  $\text{NO}_x$  and  $\text{NO}_2$ .

Both analyzers were systematically calibrated with the zero and span-gases and fulfilled all quality requirements.

The third measuring system used was the FTIR (Fourier Transform Infrared) Spectrometer (AVL SESAM), which offers the possibility of simultaneous, time-resolved measurement of approx. 30 emission components – among others: NO,  $\text{NO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$  and  $\text{N}_2\text{O}$ .

The FTIR measuring principle is a measurement with IR light. Contrary to NDIR with a narrow wave length area by means of an optical filter, the scan area of the IR wave length by use of the FTIR measuring principle is large. The principle of FTIR is that the gas to be analyzed is led through a cuvette with an IR light source at one end that is sending out scattered IR light, and a modulator that "cuts"

the infrared light into different wave lengths. At the other end of the cuvette a detector is measuring the amount of IR light to pass through the cuvette. Like the NDIR measuring principle, it is the absorption of light at different wave lengths that is an expression of the concentration of gases to be analyzed. By data processing, Fourier Transformation mathematics is used to turn the measured absorption values into gas concentrations for the analyzed gases. As the light, when using the FTIR measuring principle, is modulated into many different wave lengths, it is possible to analyze many different gases in the same instrument.

FTIR is calibrated by the data processing software and it does not need the continuous calibration.

The detection limit for all  $\text{NO}_x$  measuring systems is in the range of 0.5 to 1.0 ppm, which for the investigated vehicles and the applied driving cycle is equivalent of 0.01 to 0.02 g/km.

### 4. Test procedures

The vehicles were tested on a chassis dynamometer at two constant speeds 30 km/h and 50 km/h and in the dynamic driving cycle WLTC (Worldwide Light Duty Test Cycle), always with warm engine. As conditioning and warm-up the first 1000s of WLTC (part 1 and part 2) were used.

The exhaust gases were measured with FTIR at different sampling positions (SP) along the exhaust flow path and also from the bags. At the end of the CVS-tunnel and in the bags CLD and CLA were also used.

The sampling positions were: tailpipe, tube to CVS (non-diluted), CVS after dilution and CVS at the end. The resulting dilution factors (DF) were for vehicle 1 at 30 km/h in the range of 9 and at 50 km/h in the range of 6.

At constant operation the measuring system was switched from SP to SP. The dynamic cycles were performed for each SP successively.

In this way the thermal state of the engine and exhaust was repetitive and responded to the operating conditions.

#### 4.1. $\text{NO}_2$ sampling positions

Figure 3 represents the sampling positions for Diesel vehicles. SP1 and SP2 are for undiluted and SP3 for diluted gas. The braking force of the chassis dynamometer was increased at constant speeds to obtain the maximum possible  $\text{NO}_2$ -values and to make better visible the investigated effects. In the driving cycle WLTC this simulation of slope was not done (except of one trial with the Opel with a slope

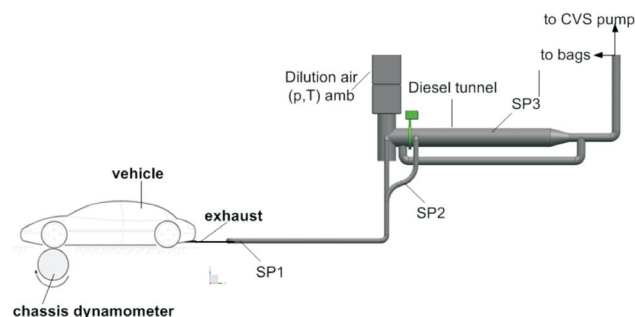


Fig. 3. Sampling positions SP for Diesel vehicles – testing  $\text{NO}_2$



of 3%). The slope at constant speeds was 3% for vehicle 1 and 2 and it was 5% for vehicle 3. The slope (the braking force) was adjusted for each vehicle in order to obtain higher temperatures of the DOC and significant  $\text{NO}_2$ -concentrations at 30 km/h.

#### 4.2. $\text{NH}_3$ sampling positions

Figure 4 represents the sampling positions for gasoline vehicles. SP1 and SP2 are for undiluted and SP3, SP4 and SP5 for diluted gas.

The braking resistances were not increased i.e. responded to the horizontal road.

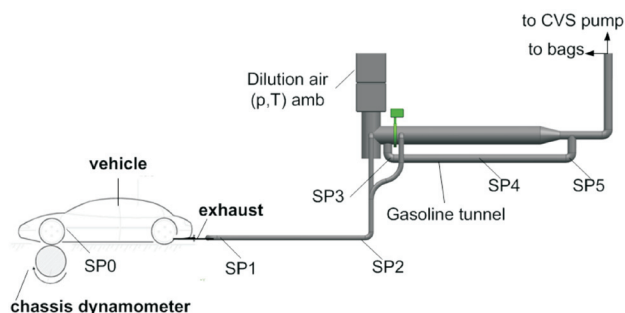


Fig. 4. Sampling positions (SP) for Gasoline vehicles – testing  $\text{NH}_3$

#### 4.3. Driving cycle

In terms of the driving cycles an approach to find a homogenized world-wide driving cycle was started with the on-going development of the harmonized WLTP world-wide light duty test procedure. The WLTC (world-wide light duty test cycle) should represent typical driving conditions around the world and is developed based on combinations of collected in-use data and suitable weighting factors by an expert group from different countries. This cycle has been used also in this study, Fig. 5. It represents different driving situations, like urban, rural, highway and extra-highway.

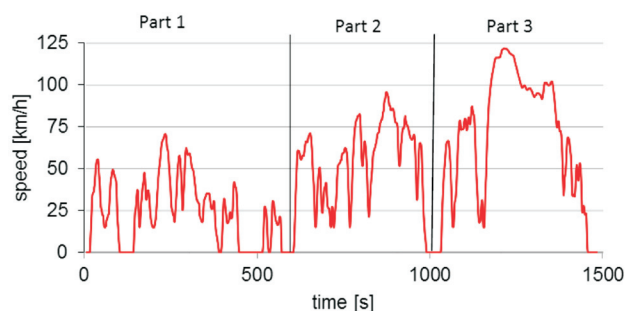


Fig. 5. WLTC driving cycle

### 5. Results

#### 5.1. $\text{NO}_2$ Emissions of Diesel vehicles

In some test series the driving resistances were increased (simulation of slope) in order to increase the  $\text{NO}_2$ -values and to better study the  $\text{NO}_2$  transport.

Figure 6 represents the  $\text{NO}_2$ -concentrations (ppm) at  $v = 30$  km/h, at different sampling positions (SP) and in bags. The increased driving resistance (3% slope) was applied for both vehicles. (Remember that vehicle 1 and vehicle 2 is

physically the same car, but used in different test sessions, 9 months apart).

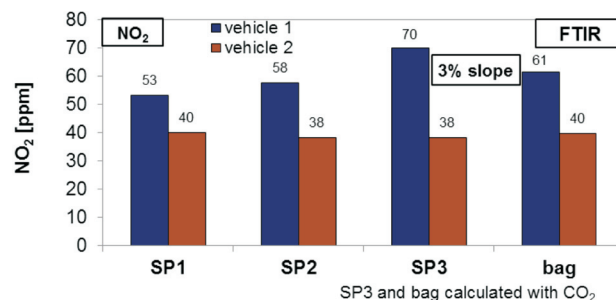


Fig. 6.  $\text{NO}_2$ -Emissions at different SP's and  $v = \text{const } 30$  km/h

The tendency of increasing  $\text{NO}_2$  from SP1 to SP3 for vehicle 1 is not confirmed for vehicle 2.

At sampling position SP3 the exhaust gas is diluted and the dilution factor (DF) is calculated with  $\text{CO}_2$  concentration.

The estimate of values from diluted gas is influenced by the dilution factor (DF). Tests were performed with DF calculated from CO or NO, but the lowest dispersion was found for  $\text{CO}_2$ . This dispersion is in the range of  $\pm 3\%$ .

In both tests the results from bag-measurement are similar to those of different sampling positions (SP).

The concentrations of  $\text{N}_2\text{O}$  and  $\text{NH}_3$  (not represented here) were negligible, ( $\text{N}_2\text{O} \sim 2$  ppm,  $\text{NH}_3 < 0.3$  ppm mostly zero).

Comparing the repetition results with Opel Astra after 9 months (vehicle 2) with the previous results (vehicle 1) clear differences of  $\text{NO}_x$  - and  $\text{NO}_2$ -emissions were found.

The  $\text{NO}_2$ -differences are represented in Fig. 6. As a reason for these differences the EGR-valve is considered. The tested car is equipped with EGR-valve, which, according to the state of deposits, can vary on resulting EGR-rate at similar operating conditions of the engine. In reality the car was used at mostly low operating profiles before the 1st test campaign and it was used over longer periods at high operating profiles before the 2<sup>nd</sup> test campaign.

To confirm the hypothesis about the EGR-valve fouling the pneumatic control of this valve was deactivated for some tests and showed the expected impacts on  $\text{NO}_2$  and  $\text{NO}_x$ .

The increased  $\text{NO}_2$ -emission of vehicle 1 from SP1 to SP3 in Fig. 6 may be explained with the influence of EGR-valve over the measuring time at  $v = \text{const}$  (over 1 h). The bag-values (as average) confirm the values at SP1, SP2 and SP3.

The question: "what happens with  $\text{NO}_2$ , if we increase EGR-rate at steady state operation?" cannot be simply answered, because there is an interference of contradictory effects at certain operating conditions, like reducing  $\text{NO}_x$  (and  $\text{NO}_2$ ), but increasing the exhaust temperature ( $t_{\text{exh}}$ ) and with it a possible increase of the  $\text{NO} \rightarrow \text{NO}_2$  conversion in the catalyst, if the  $t_{\text{exh}}$ -range was below the  $\text{NO}_2$  maximum production. This topic offers questions for further investigations.

For legislation or for the real world application nevertheless a dynamic operation is required.

In order to show the influences of slope and of EGR some repetitions of WLTC's were performed, one of them with deactivated EGR.

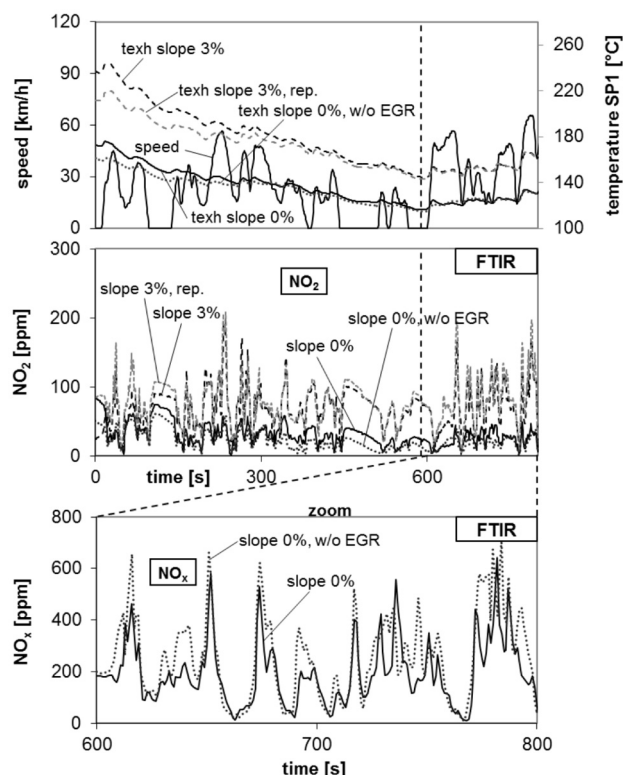


Fig. 7.  $\text{NO}_x$  and  $\text{NO}_2$ -emissions in WLTC with and w/o EGR, with slope 3% and w/o slope, vehicle 2, SP1

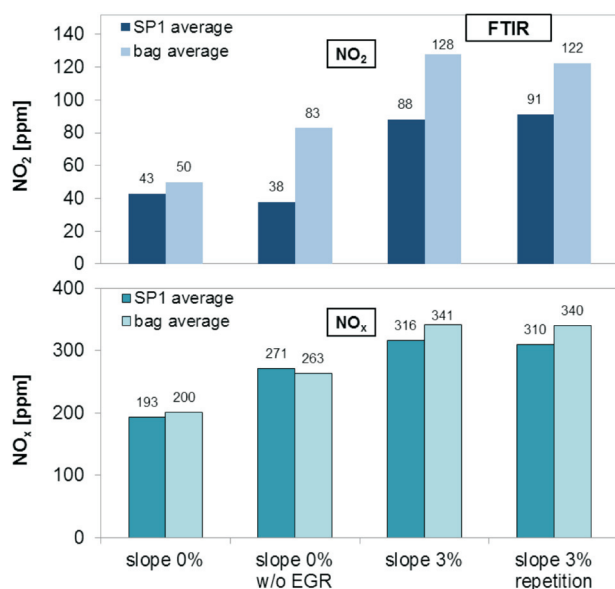


Fig. 8.  $\text{NO}_x$  and  $\text{NO}_2$ -emissions in WLTC with and w/o EGR, with slope 3% and w/o slope, vehicle 2

Figure 7 shows the traces of  $\text{NO}_2$  and  $\text{NO}_x$  in a part of WLTC, at SP1, performed with and without EGR and with and without slope. A slope of 3% causes clearly higher exhaust temperature, in average, an increase of about  $50^\circ\text{C}$  was observed. Deactivated EGR increases the  $\text{NO}_x$ -peak values.

In the phases of zero-load (ex. 450–500 s) in the driving cycle  $\text{NO}_2$ -concentration increases depending on the temperature of the oxidation catalyst (maximum of  $\text{NO} \rightarrow \text{NO}_2$  conversion in the temperature range  $300\text{--}350^\circ\text{C}$ ). With slope of 0% these  $\text{NO}_2$ -values are lower and DOC temperature is cooler. Without EGR  $\text{NO}_2$ -emission in the mentioned time-interval is lower than with EGR.

The repetitivity of  $t_{\text{exh}}$ - and  $\text{NO}_x$ -time plots is good.

Figure 8: a comparison of average  $\text{NO}_2$ - and  $\text{NO}_x$ -values in WLTC confirms: both emissions are higher at higher engine load (slope 3%); deactivated EGR increases  $\text{NO}_x$  and decreases (or keeps constant)  $\text{NO}_2$  at tailpipe (SP1), but in the bags  $\text{NO}_2$  w/o EGR increases.

There is for this vehicle and this configuration of exhaust gas lines and sampling a tendency of outstandingly higher  $\text{NO}_2$ -values measured in the bag. This suggests a supplementary  $\text{NO}_2$  production in the bag.

Nevertheless, there are other possible reasons for deviations between undiluted (SP1) and diluted (bag) results. These reasons are: estimate of the dilution factors and the possible fluctuations of emission source during the long time of test (measuring at each SP one WLTC after the other). With these reasons the authors explain the differences of  $\text{NO}_x$  between SP1 and bag.

The comparison of results at different SP's at 50 km/h for all 3 vehicles is given in Fig. 9.

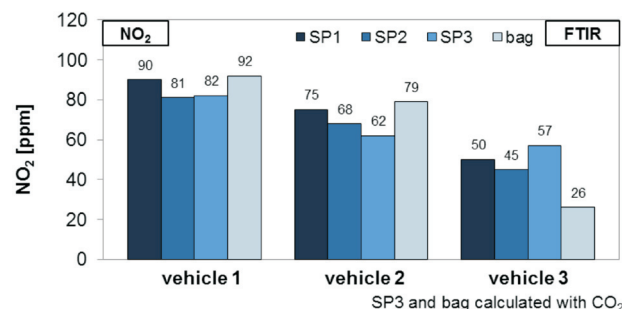


Fig. 9. Comparison of  $\text{NO}_2$ -results at different SP's and 50 km/h

There are no clear tendencies and small differences between the values at SP1, SP2 and SP3. It can be supposed, that this is more an effect of emission fluctuation during the time of switching the sampling sonde from SP1 to SP3, than any reactivity effects of  $\text{NO}_2$ . On one side, the vehicle speed is not absolutely constant, but fluctuates by approximately  $\pm 1$  km/h, on the other side, there are no clear, repetitive, regular effects showing increasing, or decreasing  $\text{NO}_2$ , which would be an indication of reactivity.

The bag-values are for vehicle 1 and 2 in the range of SP-values, while for vehicle 3 they are much lower.

The  $\text{NO}_2$ -emissions of vehicle 2 were on average lower during the repetition tests than for vehicle 1. This is explained with the cleaner EGR-valve (after more high-load operation) – the driving resistance was the same (3% slope). For vehicle 3 a slope of 5% was applied.

Figure 10 compares the results from FTIR in WLTC. In the bags, after dilution, there is for vehicle 1 and 2 some generations of  $\text{NO}_2$ - an effect, which is confirmed in

repetition tests. Vehicle 1 was driven with 3% slope, while vehicle 2 with 0% slope, which is the reason for different  $\text{NO}_2$ -levels. For vehicle 3 there is generally a decline of the  $\text{NO}_2$ -values along the gas way and the total average (over the cycle), the bag-value is lower, than value at the tailpipe (SP1).

It can be summarized for the investigated diesel vehicles that the  $\text{NO}_2$ -concentrations in bags are generally higher for vehicle 1 and 2 and generally lower for vehicle 3, than the tailpipe values (SP1).

According to the conditions of flow, temperature and concentrations the  $\text{NO}_2$  can be increased or reduced in the bags. The condition and functionality of EGR-valve offer further influences on  $\text{NO}_2$ .

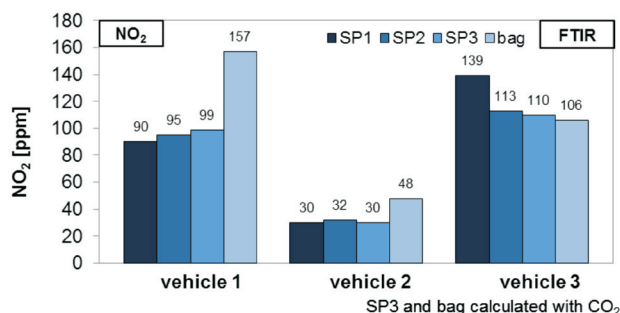


Fig. 10. Comparison of  $\text{NO}_2$ -results in WLTC at different SP's

## 5.2. WLTP-DTP measurement guidelines

The guidelines proposed by WLTP for  $\text{NO}_2$  legal measuring procedures consider the feasibility with the present installations (CVS) and analyzers.

Two methods set-up #1 and #2 are possible to perform with the present equipment. They propose an indirect estimate of  $\text{NO}_2$  by measuring continuously  $\text{NO}$  (with CLD) during the driving cycle and measuring  $\text{NO}_x$  from the bag. With the consideration of all necessary corrections  $\text{NO}_2 = \text{NO}_x - \text{NO}$ . Set-up #1 uses for all measurements one kind of analyzer whereas set-up #2 uses two analyzers.

In the applied method with 2 CLD-analyzers (set-up #2) the FTIR, or CLA were used as one of the CLD's in the present tests. CLD and CLA can be considered as equivalent systems, concerning the measuring principle and the calibration.

Figure 11 shows the comparisons of  $\text{NO}_2$ -results obtained in the WLTC warm with all vehicles and with different measuring methods: WLTP-DTP set-up #1 and #2 and time-resolved measurements with FTIR and CLD Eco.

Table 3. Measuring constellations according to WLTP-DTP in Fig. 11

Variant	Measurement	
	NO modally in CVS	$\text{NO}_x$ in bags
Set-up 1: CLA	CLA	CLA
Set-up 1: CLD	CLD	CLD
Set-up 2: FTIR & CLA	FTIR	CLA
Set-up 2: CLD & CLA	CLD	CLA
Set-up 2: CLA & FTIR	CLA	FTIR

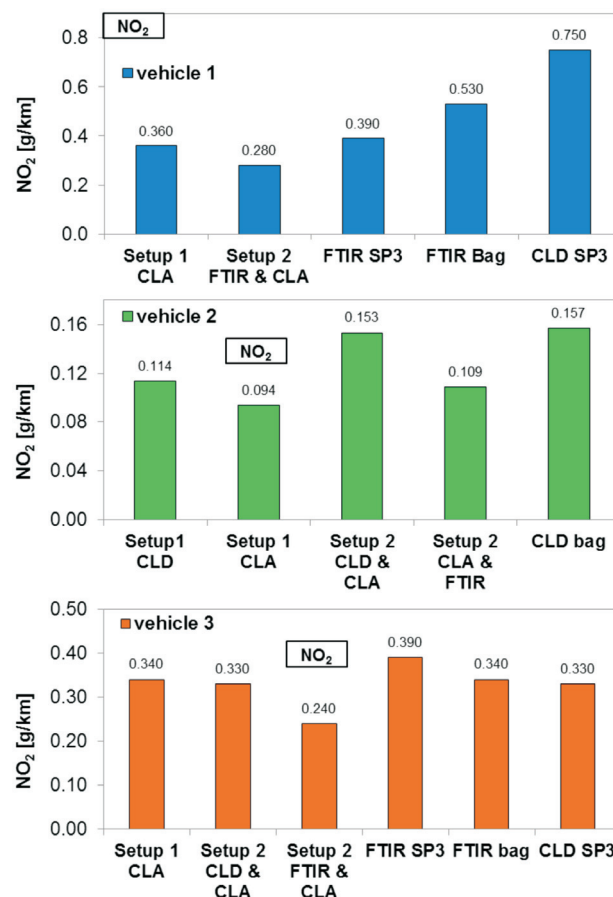


Fig. 11. Comparison of  $\text{NO}_2$ -results measured according to WLTP with different sets of analyzers

Table 3 explains the different variants of measuring constellations of set-ups #1 and #2, which are represented in Fig. 11.

There are different factors influencing the results (Fig. 11). For vehicle 1 the big dispersion of estimated  $\text{NO}_2$  is first of all an effect of varying EGR during the different tests – especially for “FTIR Bag” and for “CLD SP3” – test series with highest  $\text{NO}_2$ -values.

It has been found, that FTIR, due to its internal calibration indicates usually slightly higher  $\text{NO}$ - and  $\text{NO}_x$ -value, than CLD or CLA. This can partly explain the lower value of “set-up 2 FTIR and CLA”, where FTIR measured on-line “NO” and CLA was used for bag “ $\text{NO}_x$ ”. (In the descriptions of set-up 2 in this figure the 1st system was used for on-line  $\text{NO}$  measurements and the 2nd system was used for summary bag  $\text{NO}_x$ ).

For vehicle 2 there are two groups of  $\text{NO}_2$ -values: in the range of 100 mg/km and 150 mg/km. The dispersion of each group is quite little and the difference between them is a result of combination of emitting and of measuring dispersion. The average  $\text{NO}_2$ -level is clearly lower than for vehicle 1, but the interference, or irregularities of the EGR-valve cannot be excluded.

For vehicle 3 there is especially low  $\text{NO}_2$ -value for “set-up 2 FTIR and CLA”. It comes out, that FTIR should not be used in set-up 2 together with another measuring principle (CLD or

CLA). If the results with FTIR would be left out of consideration, the remaining results with CLA and CLD are well corresponding to each other with a relative dispersion of 3%.

From these considerations, it can be said, that when there is a constant emission level of the car and if no FTIR (in this case) is used for set-up #2, the WLTP set-up #1 and #2 yield similar  $\text{NO}_2$ -results. These results are comparable with the off-line measurements from the bag or with the on-line time-resolved and integrated measurement in the diluted gas in CVS tunnel (SP3).

The use of “mixed” measuring techniques for set-up #2, like CLD and FTIR is not recommendable.

Figure 12 represents the integral average  $\text{NO}_x$ -values in WLTC (warm) obtained with different analyzers at SP3 (in diluted gas). This example shows vehicle 1 (with 3% slope) and vehicle 3 (0% slope). The analyzers are: FTIR, CLD (heated), CLA (cold) and bags (FTIR).

It can be remarked, that the cold measurement with CLA indicates overall the lowest  $\text{NO}_x$  concentrations. The integrated FTIR on-line measurements show for both vehicles higher values than those from bags.

The differences of some [ppm] are small but they can influence the estimate of low concentrations of  $\text{NO}_2$ , which is calculated as:  $\text{NO}_2 = \text{NO}_x - \text{NO}$ . These results confirm the recommendation of using the same type of measuring system for  $\text{NO}_2$ -estimates with set-up #2.

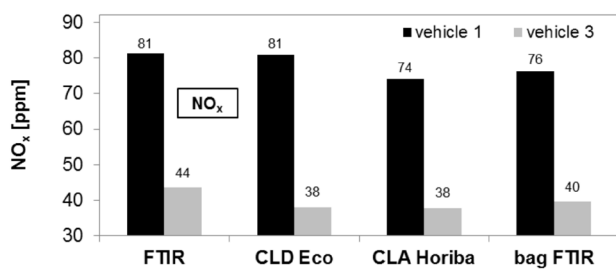


Fig. 12.  $\text{NO}_x$  in diluted gas (at SP3) with CLA-Horiba, CLD Eco. and FTIR in WLTC

### 5.3. $\text{NH}_3$ emissions from gasoline vehicles

Comparisons of  $\text{NH}_3$ -emissions of all vehicles (vehicle 4, 5 and 6) at all sampling positions are represented in Fig. 13 for 30 km/h and in Fig. 14 for 50 km/h. The average level of  $\text{NH}_3$  of vehicle 4 (with older technology) is clearly higher, than for both newer vehicles.

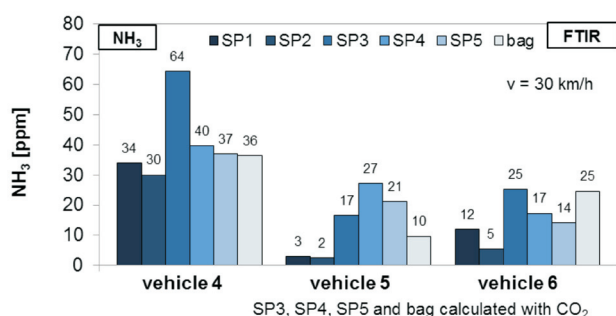


Fig. 13. Comparison of  $\text{NH}_3$ -concentrations (ppm) at constant speed 30 km/h

For vehicles 5 and 6, there are generally increased values of  $\text{NH}_3$  at SP3 and the following SP's (calculated with DF). SP3 is the first measuring position after the dilution of gas.

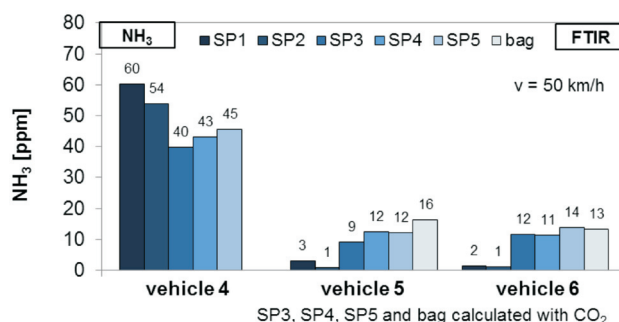


Fig. 14. Comparison of  $\text{NH}_3$ -concentrations (ppm) at constant speed 50 km/h

Figure 15 shows an example of time courses of diluted and undiluted emissions of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  during the test of vehicle 5 at  $v = 30$  km/h. The time intervals of measurements and of switching the sampling sonde between the sampling positions (SP's) are visible. The undiluted values are obtained by multiplying the diluted values with DF.

At 50 km/h two CVS flows and consequently two dilution factors DF have been applied – Fig. 16 represents the integral average values. It can be seen, that with a double DF the values at SP3 to SP5 and bag are also nearly doubled. This means, that the low  $\text{NH}_3$ -values which were measured in diluted gas were at the detection limit of the FTIR and did not represent the real  $\text{NH}_3$ -concentrations any more.

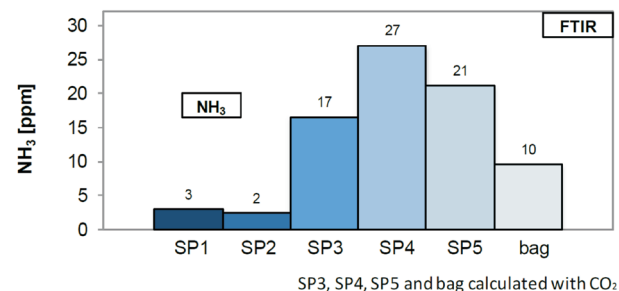
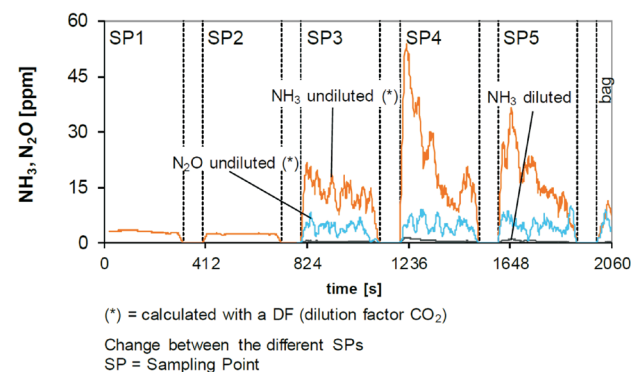


Fig. 15. Influence of dilution on  $\text{NH}_3$ -emissions at  $v = \text{const } 30$  km/h vehicle 5; DF: 34.1



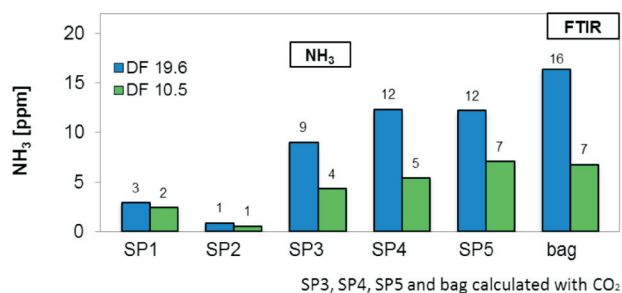


Fig. 16. Influence of dilution factors on  $\text{NH}_3$ -emissions at  $v = \text{const } 50 \text{ km/h}$  vehicle 5; DF: 19.6 and 10.5

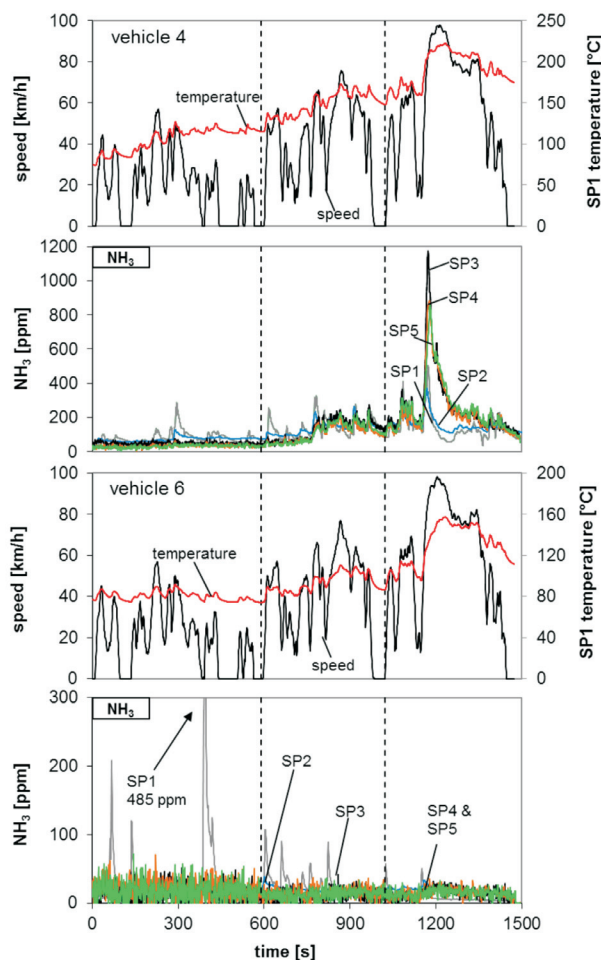


Fig. 17.  $\text{NH}_3$ -emissions in WLTC warm

This influence – measurements at the detection limit – is believed to be the major reason of non-valid results from diluted gas. The other postulated reasons – inhomogeneities in the flow, reactivity and store-release of  $\text{NH}_3$  – are at these low concentrations most probably of lower importance.

Figure 17 represents the  $\text{NH}_3$ -concentrations in the WLTC for vehicles 4 and 6. Concentrations were measured at different sampling positions in undiluted (SP1 and SP2) and in diluted (SP3, 4 and 5) exhaust gas. There are some high peaks of  $\text{NH}_3$ , which occur systematically in all tests of the same vehicle and in the same operating profile of the cycle, like for vehicle 4 near to 1170 s. These peaks are the results of rich Lambda-excursions connected with higher

exhaust gas temperatures. Another type of  $\text{NH}_3$ -spikes arrive randomly (only in one measurement) and are an effect of stochastic “release” from the exhaust system, like for vehicle 6 near to 400 s. They are most probably originating from the store-release effects of  $\text{NH}_3$  and/or of  $\text{NH}_3$  precursor substances.

Figure 18 compares the results of all gasoline vehicles (vehicle 4, 5 and 6) in WLTC, as integral average values. There is again a higher  $\text{NH}_3$ -emission level of the older vehicle 4.

There is a very good repetitivity of results (from SP to SP) for vehicles 5 and 6 from on-line measurements.

The bag values of the newer vehicles with relatively low emissions level tend to be higher than the average of all SP's. For the high emitting vehicle it is an inverse tendency: the bag value of this vehicle is substantially lower than on-line data would suggest. This indicates a tendency of reduction of  $\text{NH}_3$  in the bag in case of high emission and increase of  $\text{NH}_3$  in the bag in case of low emission.

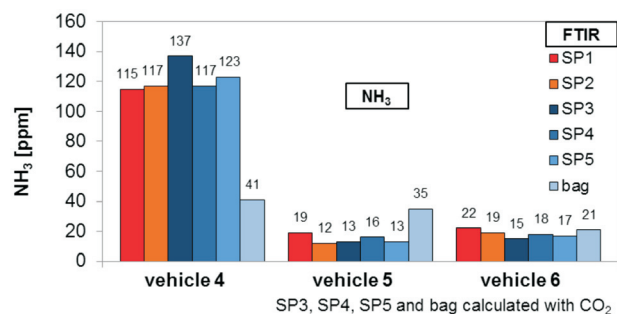


Fig. 18. Comparison of  $\text{NH}_3$ -results in WLTC

## 6. Conclusions

After investigations and repetitions of tests with Diesel and gasoline vehicles the following can be concluded:

### $\text{NO}_2$ from Diesel cars with oxidation catalyst

- At steady state operation, the  $\text{NO}_2$ -concentrations in bags are generally higher for vehicle 1 and 2 and generally lower for vehicle 3, than the tailpipe values (SP1).
- According to the conditions of flow, temperature and concentrations in CVS-tunnel (due to different dilution factors with different vehicles)  $\text{NO}_2$  can be increased or reduced in the bags, albeit based on the present results it is supposed, that the emission fluctuations during the measuring period constitute the principal influence on the observed effects.
- The present  $\text{NO}_2$ -results at constant speed operation do not indicate any regular, systematic changes of concentrations from SP to SP, which would indicate a chemical reactivity. Further research in this respect is recommended.
- The WLTP set-up #1 and #2 yield similar  $\text{NO}_2$ -results, like the direct measurement from the bag, or like the time-resolved and integrated measurement in the diluted gas in CVS tunnel; this on the condition, that no emission changes occur in the test period and unified, well calibrated measuring systems are used.
- The investigated indirect, integral WLTP- $\text{NO}_2$ -measuring methods have been found as useful tools to estimate the  $\text{NO}_2$ -levels.



- Comparisons of  $\text{NO}_2$ -levels with other vehicles are not recommendable, since the present research was focused on the testing procedures and the  $\text{NO}_2$ -emissions of vehicles were increased by increasing the driving resistances of chassis dynamometer.

#### $\text{NH}_3$ from gasoline cars with TWC

- The vehicle with older technology had an approximately 10x higher  $\text{NH}_3$ -emission level, than the newer vehicles.
- In single phases of the WLTC the relationships of bag-values and the average SP-values are varying: there is a tendency of lower  $\text{NH}_3$  in the bag for high emitting case and a tendency of slight increasing  $\text{NH}_3$  in the bag for the low emitting cases.
- The results from diluted gas (also bag-values) in WLTC correspond better with the results from undiluted gas than at constant speeds; this is because of different emission profiles and different estimates of dilution factors in both operating modes.

- In certain acceleration events of WLTC high peaks of  $\text{NH}_3$  emissions are observed; some of these peaks are repetitive (originating from rich Lambda-excursions) and some of them are stochastic (originating from store-release effects of  $\text{NH}_3$ ).
- Emission level of newer vehicles, regarded as average of all SP's, is mostly below 20 ppm  $\text{NH}_3$ .
- The  $\text{NH}_3$ -concentrations in diluted exhaust gas in CVS-tunnel (SP3, SP4, SP5) and in bag are for modern, low-emitting vehicles close to the detection limit of FTIR and the results are biased from detector noise.
- The direct, undiluted measurement of  $\text{NH}_3$  at tailpipe (SP1) can be recommended as the best variant. This direct measurement avoids the possible problems of: detection limit, contamination from dilution air, adsorption/desorption in CVS-tunnel and artefacts in the bag.

The present paper contributes to the experiences and knowledge about testing and emissions of  $\text{NO}_2$  and  $\text{NH}_3$  from passenger cars.

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## Disclaimer

The opinions expressed in this manuscript are those of the authors and should in no way be considered to represent an official opinion of the institutions BAFU, ASTRA, EMPA, AEEDA, TTM, AFHB.

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## Definitions/Abbreviations

AEEDA	Association Européenne D'Experts en Depollution des Automobiles	GRPE	Groupe Rapporteurs Pollution Energie (UNO ECE)
AFHB	Abgasprüfstelle FH Biel, CH	HC	unburned hydrocarbons
ASTRA	Amt für Strassen (CH)	HD	heavy duty
BAFU	Bundesamt für Umwelt, (FOEN)	IR	infrared
CLA	chemiluminescent analyzer	JRC	EC Joint Research Center
CLD	chemiluminescent detector	NDIR	non dispersive infrared
CVS	constant volume sampling	NO	nitrogen monoxide
DF	dilution factor	$\text{NO}_2$	nitrogen dioxide
DI	Direct Injection	$\text{N}_2\text{O}$	nitrous oxide
DOC	Diesel Oxidation Catalyst	$\text{NO}_x$	nitric oxides
DTP	Diesel Test Procedures	OBD	on-board diagnostics
EC	European Commission	SP	sampling position
ECE	Economic Commission Europe	texh e	xhaust temperature
ECU	electronic control unit	TTM	Technik Thermische Maschinen, CH
EGR	Exhaust gas recirculation	TWC	three way catalyst
EMPA	Eidgenössische Material Prüf- und Forschungsanstalt	ULSD	ultra low sulphur Diesel
FOEN	Federal Office of Environment (BAFU), CH	VERT	Verification of Emission Reduction Technologies
FTIR	Fourier Transform Infrared analyzer	WLTC	worldwide harmonized light duty test cycle
		WLTP	worldwide harmonized light duty test procedure

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