

Short communication

Tuneable diode laser spectroscopy correction factor investigation on ammonia measurement

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ABSTRACT

Current diesel engine aftertreatment systems, such as Selective Catalyst Reduction (SCR) use ammonia (NH₃) to reduce Nitrogen Oxides (NO_x) into Nitrogen (N₂) and water (H₂O). However, if the reaction between NH₃ and NO_x is unbalanced, it can lead either NH₃ or NO_x being released into the environment. As NH₃ is classified as a dangerous compound in the environment, its accurate measurement is essential. Tuneable Diode Laser (TDL) spectroscopy is one of the methods used to measure raw emissions inside engine exhaust pipes, especially NH₃. This instrument requires a real-time exhaust temperature, pressure and other interference compounds in order to adjust itself to reduce the error in NH₃ readings. Most researchers believed that exhaust temperature and pressure were the most influential factors in TDL when measuring NH₃ inside exhaust pipes. The aim of this paper was to quantify these interference effects on TDL when undertaking NH₃ measurement. Surprisingly, the results show that pressure was the least influential factor when compared to temperature, H₂O, CO₂ and O₂ when undertaking NH₃ measurement using TDL.

1. Introduction

Diesel engine vehicles have been very popular in the past decade, because of their comparative fuel economy. The ability of diesel engines to inject fuel dynamically in proportion to power demand during transient operations makes them ideal for heavy duty operations. Despite the lower carbon dioxide (CO₂) output this efficiency produces however, diesel engines generate more particulate matter (PM) and oxides of nitrogen (NO_x) (Chan et al., 1997; Majewski and Khair, 2006). NO_x refers to combined nitric oxide (NO) and nitrogen dioxide (NO₂), which are formed at the high temperatures and pressures inside engine cylinders. NO_x emissions are now at a level, in many urban areas, that are a risk to human health by causing throat, lung and eye irritations (Hsieh and Wang, 2012; Chenet et al., 2012) (Zhang et al., 2013; Boubnovet et al., 2014). NO_x also contribute to photochemical smog, ozone and acid rain. Therefore, most diesel engine vehicles must be fitted with aftertreatment systems to reduce hazardous exhaust emissions. Selective catalyst reduction (SCR) is the most effective and common treatment method based on reduction of the NO_x group (Majewski and Khair, 2006). SCR can reduce NO_x produced from a diesel engines by 90% (Chiang et al., 2010). SCR uses ammonia (NH₃) to reduce the NO_x into nitrogen (N₂) and water (H₂O). NH₃ as a gas is

difficult to handle and normally it is generated through decomposition of injected urea-water solution upstream of the SCR. However, if NH₃ is in excess through the SCR, it can lead to hazardous NH₃ being released into the environment, which is referred to as “NH₃ slip” (Suarez-Bertoa et al., 2015).

NH₃ has a toxicity limit of 20 mg/m³ and is very reactive, both with other chemicals and the materials around it (Suarez-Bertoa et al., 2015). Moreover, it contributes to particulate matter (PM) from precipitation, often in the form of ammonium nitrate and ammonium sulphate (Vaattinen et al., 2013; Huai et al., 2005), which is referred to as secondary pollution. NH₃ and particulates, as with other nitrogen compounds, cause respiratory and cardiovascular problems (Huai et al., 2005). Therefore current European standards for EURO V and Stage V engines require NH₃ to be limited to less than 10 ppm for every tailpipe concentration over the test cycle ((EC) No 582/2011) (EU Commission, 2017).

TDL (Tuneable Diode Laser) is one of the methods that can be used to measure raw NH₃. Most TDLs contain transmitter and receiver units mounted on opposite sides. Some TDL measure gas inside the sample cell which in the analyser. For this paper used type of TDL that fitted inside the exhaust pipe and measure NH₃ directly inside the engine exhaust pipe. Which means that both transmitter and receiver units are

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mounted on opposite sides inside the exhaust pipe.

The laser light from a TDL is created at a specific wavelength in the near spectral region via a diode crystal, typical wavelength near 1.512 μm for NH_3 (Huai et al., 2005) (Pisano et al., 2009; Choi et al., 2016). Tuned laser conforms to the Beer Lambert law, which means temperature and pressure can affect the spectral absorbance and effect the light intensity of the TDL (Pisano et al., 2009; Choi et al., 2016; Lenaers and Van Poppel, 2005). Therefore, most TDLs require real-time, temperature and pressure correction for the NH_3 spectrum. TDLs are also able to measure other interferences, such as H_2O , CO_2 and O_2 inside the exhaust to allow further correction of NH_3 measurements. Some TDLs can manually adjust the temperature, pressure and the other interference compounds, which otherwise have a significant effect on NH_3 measurement. Most TDL contain two units (transmitter and receiver units) that can be contaminated by exhaust gas over time which led to reduction of the measurement accuracy of the device, this can be stop by regular cleaning and maintain the units.

Most researchers report that temperature and pressure have the greatest influence when measuring NH_3 using a TDL. However, the literature does not include numerical values to quantify the extent of exhaust temperature, pressure and other interferences on NH_3 readings using TDL directly inside the exhaust pipe, because this require high cost to undertake this type of experimental test. Therefore, this paper investigates the effect of temperature, pressure and other compounds on the TDL correction factor for NH_3 measurement directly inside exhaust pipe by manually adjusting these factors within the TDL software, which means that those are not the real-time values of temperature, pressure, H_2O , CO_2 , and O_2 within the exhaust.

1.1. Experimental set up

Table 1 represents the specification of the TDL used in this experimental, in which the temperature and pressure were measured in real-time from the exhaust pipe then feeding into the TDL. H_2O , CO_2 , and O_2 have also been measured by TDL in order to do correction on the NH_3 measurements. The transmitter and receiver units of TDL were mounted on opposite sides inside the exhaust pipe.

This particular TDL can manually adjust the temperature, pressure and other interferences. Table 2 shows the range of correction factors used in this experiment. The Taguchi Orthogonal Array method was therefore used to design an experiment from those ranges. This is a method that allows the selection of a subset of combination of multiple factors from multiple levels and also balanced to ensure that all the levels of factors are considered equally (Taguchi Orthogonal Array Designs, 2012). Each correction factor was divided into five equal portions of the range as in Table 2; as a result, 25 experimental tests were generated based on the Taguchi L25 array (Table 3).

Fig. 1 is a schematic of the test rig and Table 4 show the engine specification used. The engine was run in a steady state test, which was 2200 rpm and 190 N.m for engine speed and load. The aftertreatment system used in this test was the DOC (Diesel Oxidation Catalyst) and SCR. The NH_3 slip from the aftertreatment system was detected in-situ (approximately 50 ppm), with both the receiver unit and transmitter unit located inside the exhaust. The real-time measurements of temperature, pressure and the interference compounds in the exhaust pipe were recorded and fed into the TDL before and after the test. This was

Table 1
TDL specification.

Specification	TDL
Sample Gas Flow Rate	150 kg/h
Exhaust Temperature	500 to 600 °C
T ₁₀ to T ₉₀ response time for NH_3	1 Sec
Resolution per metre	1 ppm

Table 2
Correction factor range.

Temperature	20 °C–500 °C
Pressure	950 mbar–1050 mbar
Water Correction	0%–10%
CO_2 Correction	0%–10%
O_2 Correction	0%–10%

Table 3
TDL correction factor test point based on the Taguchi L25 array.

Experiment	Temp (°C)	Pressure (mbar)	H_2O Corr. (%)	CO_2 Corr. (%)	O_2 Corr. (%)
Start Control	200	1013	10	0	0
1	20	950	0	0	0
2	20	975	2.5	2.5	2.5
3	20	1000	5	5	5
4	20	1025	7.5	7.5	7.5
5	20	1050	10	10	10
6	125	950	2.5	5	7.5
7	125	975	5	7.5	10
8	125	1000	7.5	10	0
9	125	1025	10	0	2.5
10	125	1050	0	2.5	5
11	250	950	5	10	2.5
12	250	975	7.5	0	5
13	250	1000	10	2.5	7.5
14	250	1025	0	5	10
15	250	1050	2.5	7.5	0
16	375	950	7.5	2.5	10
17	375	975	10	5	0
18	375	1000	0	7.5	2.5
19	375	1025	2.5	10	5
20	375	1050	5	0	7.5
21	500	950	10	7.5	5
22	500	975	0	10	7.5
23	500	1000	2.5	0	10
24	500	1025	5	2.5	0
25	500	1050	7.5	5	2.5
End Control	200	1013	10	0	0

applied in order to measure correct NH_3 readings for comparison with NH_3 readings from manually adjusted temperatures, pressure and other interference compounds. The real-time values for temperature, pressure and other interference compounds are presented as start control and end control in Table 3. The tests were conducted as follows:

1. Temperature and pressure were measured using external sensors in the exhaust pipe. H_2O , CO_2 , and O_2 were recorded using the TDL in the exhaust pipe at the start of the test (Start Control), as shown in Table 3. NH_3 readings were recorded three times with about 1 min intervals between each measurement.
2. The temperature, pressure, H_2O , CO_2 , and O_2 were then manually applied into the TDL for each experiment according to Table 3 and three NH_3 readings taken at 1 min intervals as before.
3. All the experiments in Table 3 were carried out in a similar way with the triplicate NH_3 values recorded for each experiment.
4. At the end of the experiments, the temperature and pressure were re-measured using an external sensor in the exhaust pipe. H_2O , CO_2 , and O_2 were also re-measured using the TDL (End Control), as shown in Table 3.

2. Data analysis and discussion

After the NH_3 readings were recorded three times as show in Table 5, it is clear that temperature, pressure and other interference compounds can have a huge effect on the TDL during NH_3 measurement. The correct NH_3 readings for the start control and end control are

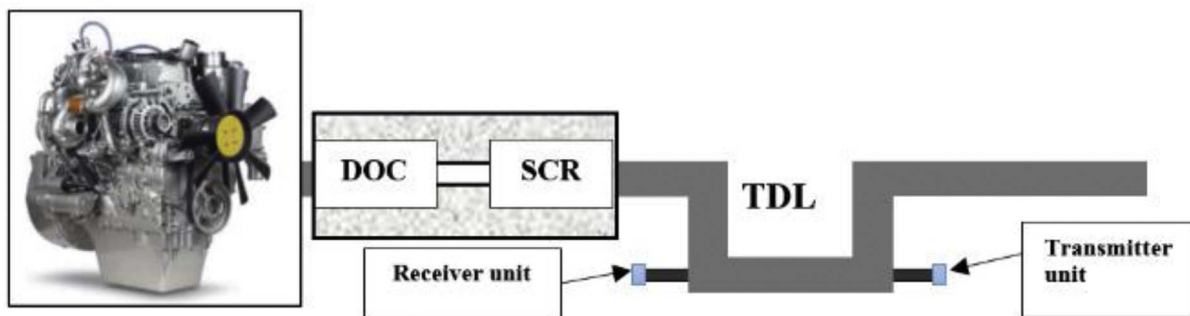


Fig. 1. Test schematic.

Table 4
Engine specification.

Engine Specification	
Engine	In-line 4 Cylinder Twin Turbo
Displacement	4.4 L
Combustion System	Direct Injection
Engine Power	130 KW

Table 5
NH3 reading.

Experiment	NH ₃ Result 1 (ppm)	NH ₃ Result 2 (ppm)	NH ₃ Result 3 (ppm)	SN _i
Start Control	56.0	53.6	56.0	
1	34.5	33.9	35.1	35.2
2	34.7	34.3	35.4	35.9
3	35.7	35.2	35.6	42.6
4	36.3	35.4	36.3	36.8
5	38.0	36.4	37.1	33.3
6	45.1	43.0	44.3	32.4
7	45.4	43.2	44.6	32
8	48.2	45.2	47.1	29.8
9	44.8	42.2	44.1	30.2
10	43.3	41.4	43.2	32.
11	66.1	65.8	66.3	48.4
12	61.6	61.8	62.1	47.8
13	62.6	62.7	63.2	45.8
14	61.0	61.4	62.0	41.7
15	65.7	65.5	65.2	48.3
16	88.5	85.5	90.2	31.4
17	93.7	91.7	95.8	33.2
18	90.8	88.5	92.4	33.3
19	91.8	91.5	93.4	39.1
20	86.6	88.2	87.9	40.3
21	128.5	131.9	128.7	36.7
22	125.3	126.2	123.7	39.9
23	116.3	119.6	119.3	36.2
24	124.9	128.6	127.7	36.4
25	124.6	130.1	130.0	32.2
End Control	53.6	56.0	56.0	

about 55.20 ppm average. However when the temperature, pressure and other interference compounds been adjusted manually, this lead to NH₃ readings completely changed and differed from the correct NH₃ readings. This is similar to suggestions by Pisano et al. and Lenaers et al (Pisano et al., 2009; Lenaers and Van Poppel, 2005), that at high temperature and pressure, the TDL spectral line shape can be broadened, which can affect the measurement intensity. The same authors also mention that water concentration can affect the TDL on NH₃ readings, so when the amount of water concentration is fed into the TDL, for the instrument to correct itself for NH₃ measurement during water interference by selecting the right spectral line, that because water can have huge absorption on the infrared spectrum.

The greatest range calculation method from Taguchi Orthogonal

Array was used to determine the most influential factor on a TDL during NH₃ measurement. The method first calculates the SN_i (Signal-to-noise ratio) value for each experiment and then averages the SN_i value for each factor in order to determine the highest rank and influence on NH₃ measurement using a TDL.

The equation below represents the SN_i calculation:

$$SN_i = 10 \log \frac{\bar{y}_i^2}{S_i^2}$$

where:

$$\bar{y}_i = \frac{1}{N_i} \sum_{u=1}^{N_i} (y_{i,u})$$

$$S_i^2 = \frac{1}{N_i - 1} \sum_{u=1}^{N_i} (y_{i,u} - \bar{y}_i)^2$$

i = recorded number

u = trail number

N_i = number of trials for recording number i

Table 5 represents the NH₃ readings, including the SN_i value for each experiment. It also contains the correct NH₃ readings at the start control and end of control. By conducting the data analysis using the Taguchi Orthogonal Array show in Table 6, the average SN_i for each level of every factor, which found that exhaust temperature has the highest influential correction factor on NH₃ measurement, which was similarly suggested by authors such Pisano et al., Choi et al and Lenaers et al (Pisano et al., 2009; Choi et al., 2016; Lenaers and Van Poppel, 2005). The next most influential factors are O₂ and H₂O, which are second and third, followed by CO₂ is fourth most influential. However, it is surprising that pressure is shown to be the least influential factor, as it does not have a huge effect on the TDL during NH₃ measurement, despite most previous research believing pressure is the second most influential factor (after temperature) on a TDL during NH₃ measurement. The reason is that the TDL software does not take pressure values into account during the measurement of NH₃. Those influence factor can affect the spectral absorbance and light intensity of the TDL during NH₃ measurement, but does not shows the amount of been effected, the

Table 6
Taguchi analysis showing the correction factor influence.

Level	Temp SNi	Pressure SNi	H ₂ O SNi	CO ₂ SNi	O ₂ SNi
1	36.76	36.80	36.43	37.95	36.57
2	31.29	37.77	38.39	36.30	36.01
3	46.41	37.54	39.92	36.42	39.63
4	35.45	36.85	35.60	37.41	39.03
5	36.27	37.22	35.84	38.10	34.94
Range	15.12	0.97	4.32	1.80	4.69
Rank	1	5	3	4	2

only way to see the effect is through the NH₃ reading. Generally, in order to achieve a good NH₃ reading using a TDL, real-time exhaust temperature, and pressure, H₂O, CO₂ and O₂ must be fed into the TDL.

3. Conclusion

This main aim of the experimental tests were to determine the extent of the influence from temperature, pressure, H₂O, CO₂ and O₂ on NH₃ measurements directly inside the exhaust pipe using TDL. Those influence factor can affect the spectral absorbance and light intensity of the TDL during NH₃ measurement.

The tests show a huge effect on the TDL during NH₃ measurement, although those values for temperature, pressure and other interferences compounds are not exactly or not real-time from the exhaust pipe, as show in Table 5.

The tests shows that temperature was the most influential correction factor, followed by O₂ and H₂O. Meanwhile CO₂ and pressure can be negligible, as both have the lowest influence. These results show that temperature, O₂ and H₂O can have a huge effect on the TDL spectrum line because the line shape can be broadened which affects the measurement intensity. Most TDL instruments adjust by compensating for these interferences, but if the values for those factors are not taken into account real-time, this still leads to errors in the TDL readings for NH₃. Overall, in order to achieve better and accurate results for NH₃ readings inside exhausts pipe using a TDL is by feeding in correct or real-time exhaust temperature, pressure, and other interference compounds present inside the exhaust.

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