NITROGEN SPECIES MEASUREMENT INVESTIGATION USING TWO DIFFERENT FTIR

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Abstract- Current diesel engine after-treatment systems, such as Selective Catalyst Reduction (SCR), use ammonia (NH_3) to reduce the Oxides of Nitrogen (NO_x) into Nitrogen (N_2) and water; however, if the reaction between ammonia and NO_x unbalance this can lead either ammonia or NO_x being released into the environment. Ammonia is classified as dangerous compound for the environment; therefore, accurate measurement of ammonia is essential. Fourier Transform Infrared (FTIR) is one of the most common method used to measure raw emissions from engine exhaust pipes, due to its capability to measure multi-type emissions at the same time. However, not many FTIRs that can measure gas from engine exhaust, and most of them has different characteristics and specifications. These can affect the emission measurement from exhaust pipes and lead to uncertainties in meeting compliance demands. The work of this paper compares two FTIR that have different specifications. These FTIRs, have been compared under well controlled laboratory conditions. The concentration of ammonia and NO_x from diesel engines has been measured under different engine load and speed. The ammonia readings from each FTIR are plotted into a graph and analysed, the results show that one of the FTIR produces a lower reading compare to the other FTIR. A Chemical Luminance Detector (CLD) was used to measure the NO_x and then compared with both FTIRs. After analysed those dataset, the results clearly show the FTIR specification can affect the emission measurement from diesel engines exhaust.

Index Terms- Ammonia, CLD, Diesel Engine Emission, FTIR, NO_x.

I. INTRODUCTION

Large diesel engine vehicles commonly use after-treatment systems to reduce the hazardous exhaust emissions. Selective catalyst reduction (SCR) is the most effective and common treatment of the hazardous Oxides of Nitrogen (NO_x) group using the reduction method, it has been deployed since 1970 [1]. SCR can reduce NO_x produced from a diesel engines by 90% [2]. SCR, use ammonia (NH_3) to reduce the NO_x into nitrogen (N_2) and water; however, if ammonia is over-injected into SCR, it could lead to ammonia being released into the environment referred to as “ammonia slip” or if insufficient ammonia has been injected could lead to NO_x being released into environment [3].

Ammonia is also hazardous with a toxicity limit of 20 mg/m^3 and reacts with other chemicals around it [3], and contribute to particulate matter (PM), from precipitation sometimes referred to as secondary particulate matter. Often these are ammonium nitrate and ammonium sulphate [4], [5]. Concerns over the effect on human health of these particulate from ammonia is based on problems caused by respiratory and cardiovascular diseases [5]. In this content NO_x, refers to nitric oxide (NO) and nitrogen dioxide (NO_2), formed under high temperature and pressure inside the engine cylinders. NO_x emissions contribute to photochemical smog, ozone, acid rain. In human health, NO_x can cause eye, throat and lung irritations [6]–[11].

Due to high absorption, ammonia cannot be measured using dilution tunnel, it must be measured directly in the exhaust pipe. Fourier Transform Infrared (FTIR) spectroscopy is one of the most common methods used to measure ammonia and NO_x concentrations in diesel exhaust pipe. This device uses a Michelson interferometer to split an infrared beam into two different optical paths that are analysed to create more sensitive spectral information. The two beams respond differently to chemicals and the results are compared using the Fourier transform software to reduce cross-interference and to generate more accurate quantitative analysis [12].

Chemical Luminance Detector (CLD) is also a method that used to measure NO, it does not measure ammonia, it converts any NOx into NO which it then reacts with ozone (O_3), which will become NO_2 and oxygen (O_2) with the release of energy in the form of optically measurable fluorescent radiation (hv) or light, this happen in high temperature 475 °C about 98% of NO_x converted to NO [13]. This is called chemical luminescence radiation or light, in which light intensity is proportional to the amount of original nitrogen monoxide; it uses a photomultiplier tube to measure the light [1].

There is one previous work by [13] investigated ammonia interference effect on NO_x measurement

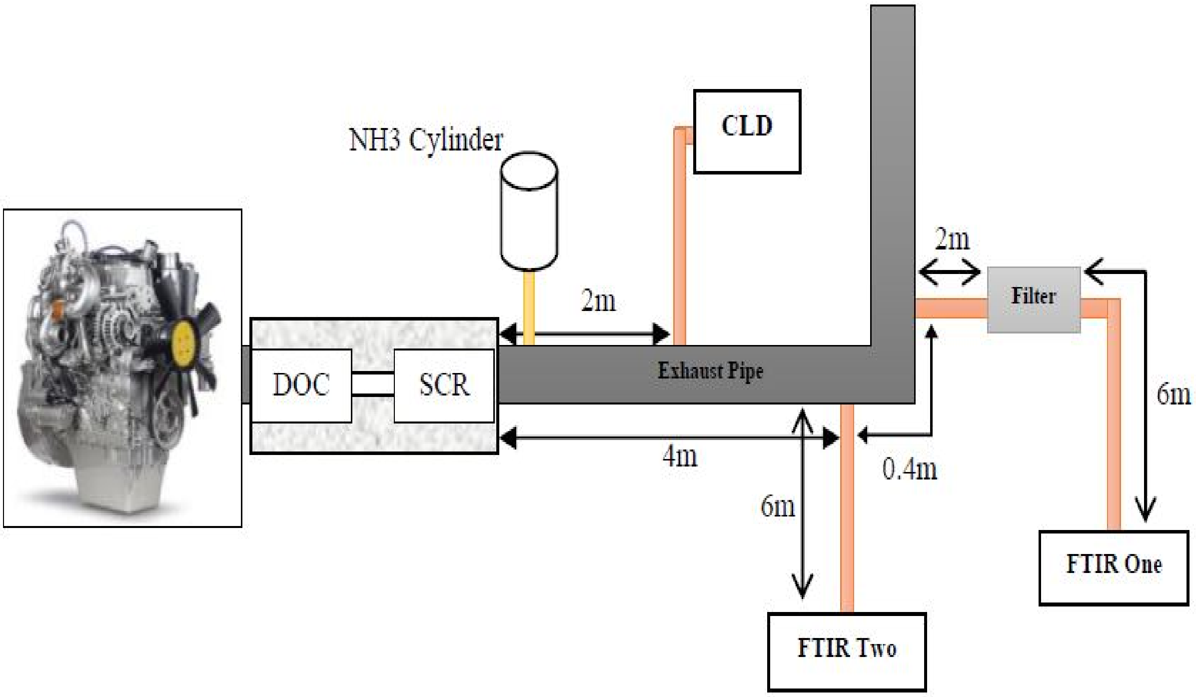

Fig 1. Schematic of the Test

using FTIR and CLD. The authors conclude that FTIR shows no effect on NOx measurement when NH_3 is present; however, careful calibration is necessary to improve the accuracy of measurement. The author believes the FTIR measurement for NO_2 is an error but does not explain in more detail. For CLD, the authors suggest that CLD is not the best method for measuring NO_x when ammonia is present, because during NO_x convert to NO at 475 °C, about 6% of NH_3 has also been converted to NO, depending on the type of converter material.

The most common temperature and flow rate for a heated sample line for ammonia measurement are 190 °C ±2, and 10 to 15 l/m [3], [4], [13], [14]. Heated sample line materials, such as steel and polymer, have been tested and the conclusions were that ammonia absorption in the polymer heated sample line was found to be significantly lower than the stainless steel and coated stainless steel heated sample line at the same length, bore size and flow rate [4], [14]. There are several manufactures of FTIR system in the market that can be used to measure engine emissions, as this lead to a problem of selecting the right FTIR that can measure raw engine emission more accurately. Therefore, the main aim of this paper was to compare two FTIR that has different specifications, in measuring ammonia and NO_x (NO and NO_2). A CLD was also used to measure the NO_x and then compared with both FTIRs.

II. EXPERIMENTAL SET UP

The two FTIR Specifications show in Table 1, the FTIR one has higher temperature, flow rate and response time then FTIR two. The experimental diesel engine (see Table 2) included a Diesel Oxidation Catalyst (DOC) and SCR. There were concerns about insufficient ammonia being produced from SCR for this test, and a separate ammonia source (99.98% grade) cylinder was used to insert ammonia into the exhaust gas stream in a needle valve, the ammonia being inserted after DOC and SCR.

However, the amount of ammonia injected into the exhaust could not be accurately controlled, and the valve on the ammonia cylinder was turned by quarter turn, and the ammonia flow from the cylinder into the exhaust was an approximate value. All the heated samples line from analysers are fitted probes downstream of the SCR after-treatments, see for the schematic of the experiment. The heated sample line material is PTFE material. The experimental were divided into three test.

- In test A, the engine was set to 1000 rpm and 50Nm and the ammonia cylinder needle valve was opened a quarter turn at a time until fully open and closed in an identical manner.
- In test B, the ammonia cylinder valve was fully close, both FTIRs were calibrated using 100% nitrogen in order to clean inside the sample cell in the analyser, not the CLD.
- In test C, the engine speeds were altered to be 1000, 2000, 2200, 1600 and 1300 and then returned to 1000 rpm; at same time, the engine loads were set at 50, 100, 200, 300 and 200 and then returned to 100 N.m (see Fig 1), the ammonia cylinder needle valve was opened a quarter turn at a time and closed in an identical manner to achieve desired ammonia

concentrations.

Table 1. FTIR Specification

Specification	FTIR One	FTIR Two	CLD
Heated Line Temperature (°C)	191±6	113±6	191±6
Recording Frequency (Hz)	5	1	10
Gas Flow Rate (l/m)	10	4±0.5	15
Sample Gas Pressure (kPa)	90 to 300	-5 to 30	25±1.5
T10 to T90 response time	1 sec	5 sec	1.5 sec
Filter Arrangement	Pre-filter	No Pre-filter	Pre-filter
NH_3 Range (ppm)	0-1000	0-1000	
N_2O Range (ppm)	0-1000	0-200	0-10000 (NO_x)

Table 2. Engine Specification

Engine Name	Perkins Tier 4 Final Twin Turbo
Number of Cylinders	4
Displacement	4.4 litres
Combustion System	Direct Injection
Engine Power	130 KW

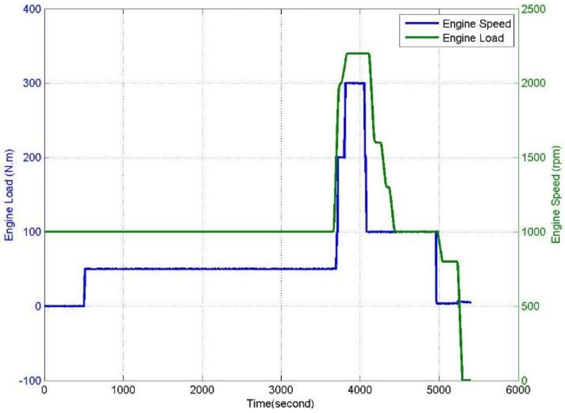

Fig 1. Engine Conditions

III. RESULTS AND DISCUSSION

Fig 2 and Fig 10 represent the ammonia concentration from the gas analysers for the test A and test C. When the needle valve was opened quarter by quarter, both FTIRs showed same the response to the increasing ammonia, and reducing the ammonia inside the exhaust as the needle valves were closed quarter by quarter. The graphs show that FTIR two has a lower reading compared to the FTIR one and similarity through the rest of the testing. At test A (Fig 2), initial spike due to sudden over turn the valve.

There are three possibilities causing the differences, which are FTIR Two has a slower flow rate, a lower response time and temperature lower heated sample line compared to FTIR One (as show in Table 1), which leads to ammonia sticking to all sample line wall. Authors, such as [3], [4], [14] have also mentioned that heated sample line temperature has an effect on ammonia readings.

According to [14], a shorter and straight sample line can reduce ammonia storage in the wall; moreover, [14], [15] believe that a pre-filter can also affect the ammonia reading due to its large surface area for absorption and also reduce the flow rate and ammonia can also stick on particulate matter in the filter, however none of the authors has evidence numerical related to pre-filter effects. In this experiment, the FTIR one contains a pre-filter and a longer sample line than the FTIR two; however, the FTIR one consistently showed a higher ammonia reading than the FTIR two for similar reasons, which are higher response time, as well as higher flow rate and temperature. This means that heated filter and longer heated sample line tube has no effect on ammonia reading as long as the flow rate is great enough.

According to [3], [4], [13], [14], the flow rate and temperature needed for measuring ammonia is 10 l/m to 15 l/m and 190 °C. The FTIR two flow rate is not suitable for measuring ammonia because it only has 4±0.5 l/m, below then recommended by author. The FTIR one also has a higher recording frequency than the FTIR two, which causes the FTIR one to be less smooth compared to the FTIR two. According to [3], a higher acquisition frequency means that it registers fast changes of concentration that result from sharp engine accelerations.

Test B is there calibration as show in Fig 6, Fig 7, Fig 8 and Fig 9. The main objective of the calibration is to use nitrogen to clean out all the gasses inside the detection cell and then set the span gas similar to maximum value of gas being inserted. The reason for this is that all analysers use nitrogen as a reference zero gas when measuring other gasses. The calibration only been done on the two FTIR, not the CLD, the engine continually running which cause the CLD continually measure NO_x (NO and NO_2).

After the calibration, test C graph on Fig 10 shows the gap in the ammonia readings from both FTIRs to be closer, which means proper calibration improves the accuracy of the FTIRs, [13] also has similar finding.

On NO_x measurement, the results show that the NO and NO_2 concentrations depend on the engine load and speed, also the amount of ammonia present inside the SCR. The CLD was used to measure NO_x and to compare with both FTIRs. The NO readings in Fig 3 and Fig 11 show very similar results for all 3 instruments. During the test C, the FTIR two was showing an error message, which led to lower readings for NO_2 and NO_x, as shown in Fig 12 and Fig 13, the cause of error massage is unknown. The error message started from test B. A similar statement also mentioned in the previous study by [13].

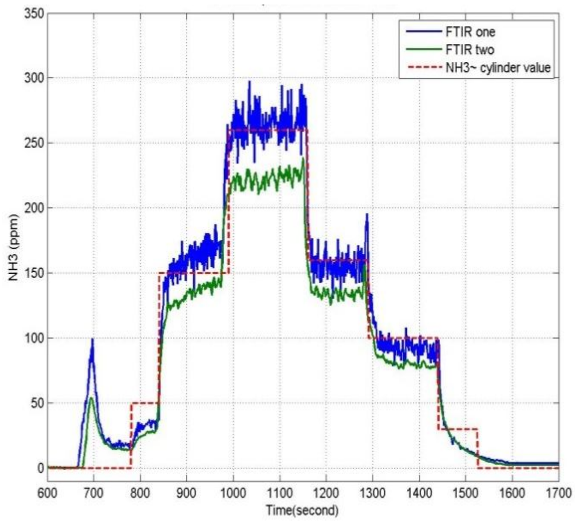

Fig 2. Test A NH_3 Comparison

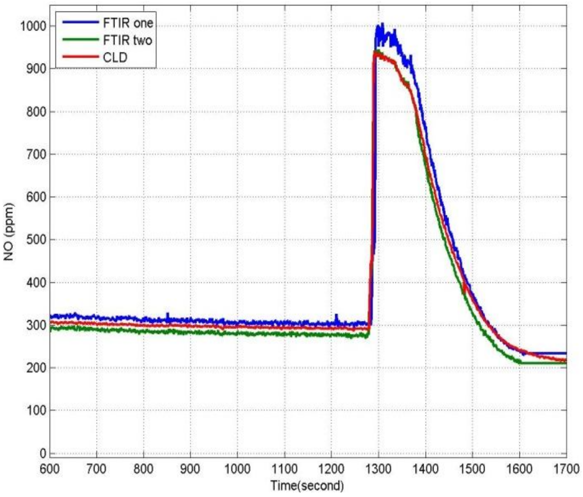

Fig 3. Test A NO Comparison

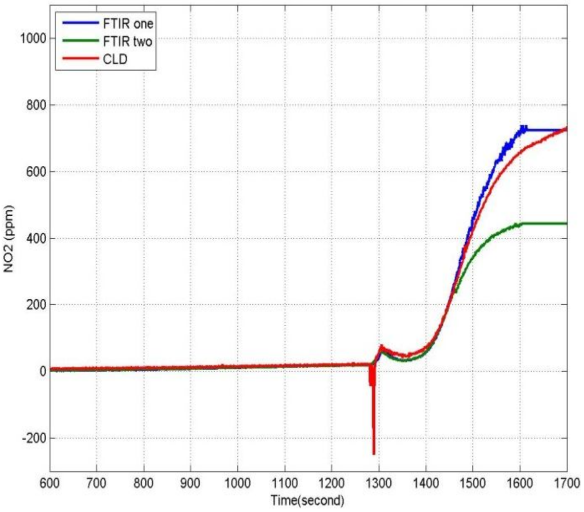

Fig 4. Test A NO_2 Comparison

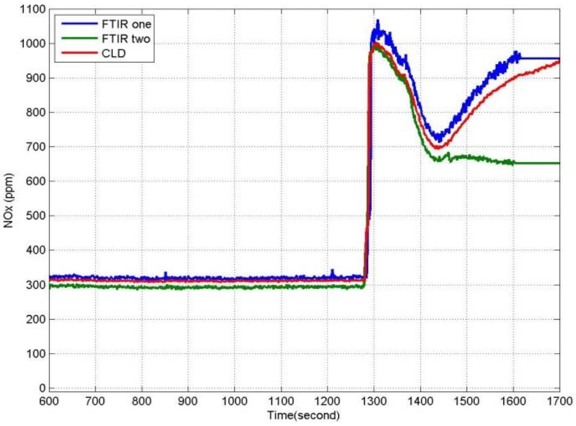

Fig 5. Test A NO_x Comparison

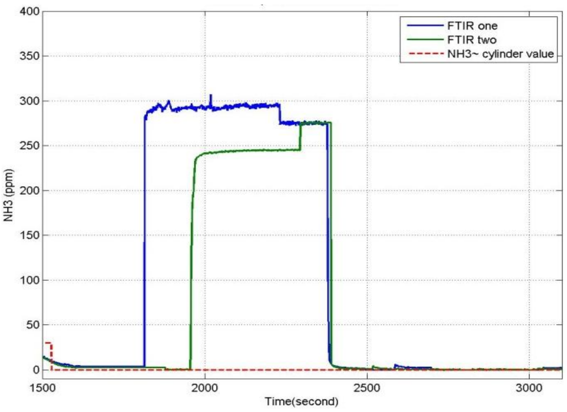

Fig 6. Test B NH_3 Comparison

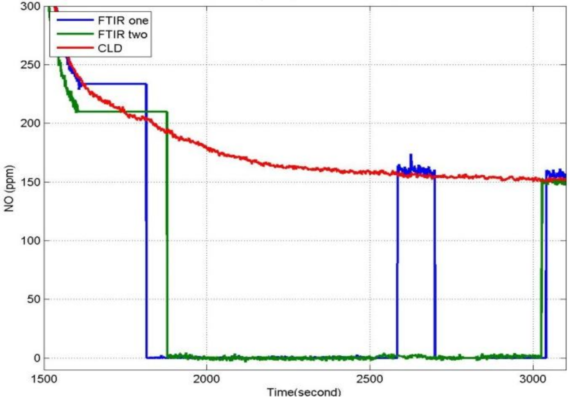

Fig 7. Test B NO Comparison

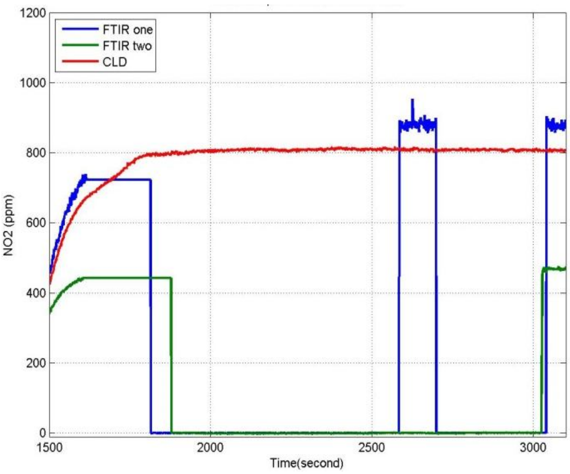

Fig 8. Test B NO_2 Comparison

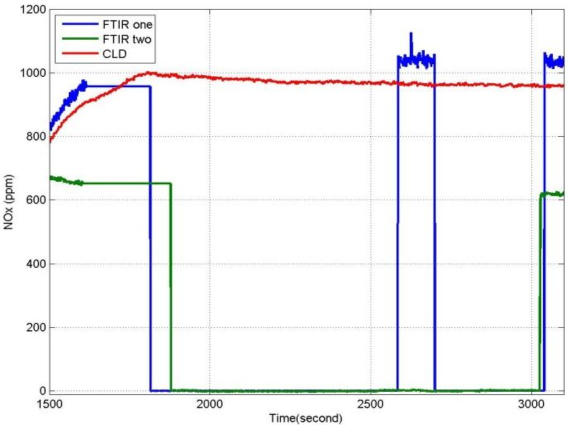

Fig 9. Test B NO_x Comparison

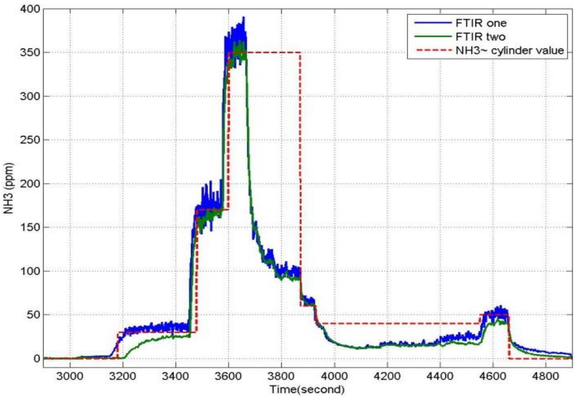

Fig 10. Test C NH_3 Comparison

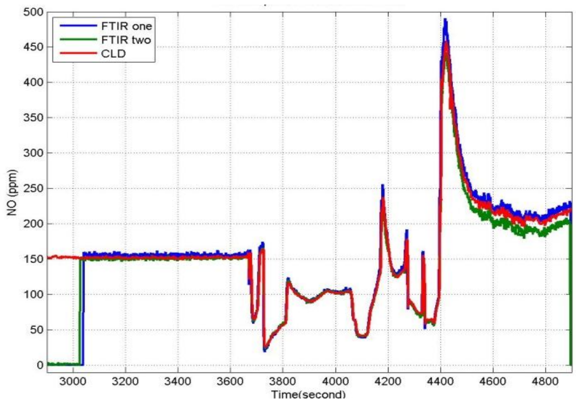

Fig 11. Test C NO Comparison

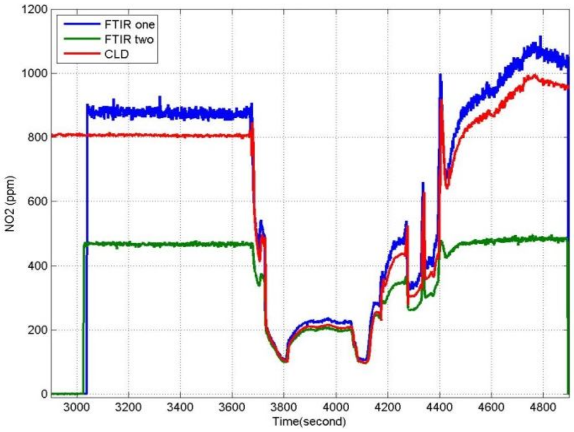

Fig 12. Test C NO_2 Comparison

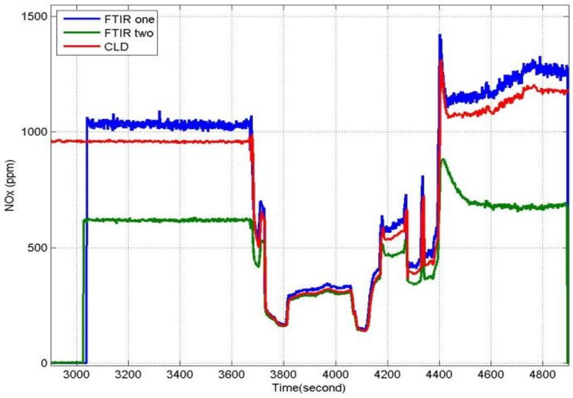

Fig 13. Test C NO_x Comparison

CONCLUSION

FTIR one was more responsive and produces higher ammonia readings compared to the FTIR two, due number of operation aspect such as:

- FTIR two has a lower flow rate than the FTIR one
- FTIR two also has a slower response time than the FTIR one, however both shown very close maximum reading on ammonia.
- FTIR two has a lower temperature sample line than the FTIR one

There are other aspects that can possibly affect the correlation of both FTIRs' analysis, there are:

- Sample line is not straight,
- Location of the probes for both FTIRs are different
- The heated sample line has been used a number of times previously and not cleaned properly, it could affect the soot and ammonia build-up inside [14].

Overall, if proper calibration improves the accuracy of the FTIRs.

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