

REPORT

LiDAR Based NOx Measurements from Exhaust Stacks

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1 EXECUTIVE SUMMARY

Following the development of a standoff LiDAR for the measurement of NO emissions from compressor station exhaust stacks in collaboration with TransCanada Pipelines, INO performed an assessment of the existing LiDAR for the measurement of NO₂. The proposed activities were:

- Adapt simulated stack for NO₂ measurements
- Perform laboratory absorption measurements on reference cells
- Perform concentration measurements on NO₂
- Perform concentration measurements of NO and NO₂ in a single laser wavelength scan
- Analyze data - Determine Limit of detection and interferences
- Report and publicize results

All of these were done, or at the very least attempted. The stated goal of this project was to demonstrate the use of a UV-DIAL prototype for the stand-off measurement of NO_x from exhaust stacks. The measurement campaign was done at INO on an instrumented mock-up stack in realistic Canadian weather conditions. This gave insight into the use of the technique for mass emission rate measurements of NO_x from pipeline compressor station exhaust stacks.

It was determined that:

- 1) It is possible to measure NO and NO₂ from a stand-off distance directly at the output of an exhaust stack by the UV-DIAL technique;
- 2) It is possible to measure NO and NO₂ in a combined sequence of UV laser wavelength scanning;
- 3) Optimizing the measurements implies selecting a subset of wavelengths that enhances the uniqueness of the signature for both NO and NO₂;
- 4) NO₂ has a chemical behavior that is troublesome near typical ambient outdoors temperature, especially under 22°C (thus a good part of the year in Canada), an hindrance for the UV-DIAL technique as used and for the referee measurement of NO₂ in the exhaust stack mock-up;
- 5) The stability of the NO₂ reference concentration is difficult to ascertain when the reference cell and ancillary control equipment is not temperature regulated.
- 6) Designing, producing and using a stable optical NO₂ reference cell will be a challenge for field use;
- 7) A reference cell with a constant flow of gas from a calibrated cylinder was required;
- 8) Using a reference measurement on a mock-up stack that uses combustion of natural gas in possible addition to the gas from a calibrated cylinder would be preferable;
- 9) Sensitivity was, in part, limited by sub-optimal control of the laser pointing;
- 10) Calibrating the LiDAR overlap functions with respect to wavelength before the concentration measurements and adapting the data processing mitigates part of the problems;

- 11) Slow mechanical wavelength scanning, as done here, is not the most appropriate form of measurement because of the instability in LIDAR return and in the NO_x concentration-length product;
- 12) The instabilities in LIDAR return and in concentration along with the slow wavelength scanning will ultimately limit the prototype sensitivity;
- 13) Detecting and removing outliers caused by instabilities in the particle concentration along the beam path mitigates some of the instabilities;
- 14) Single shot whole spectrum measurements would be the best LIDAR approach;

The points above summarize our conclusions and best practices. Although INO was able to measure NO, the prototype is far from optimal. There are two major drawbacks/hindrances.

- The first is the speed at which the laser wavelength is scanned. The laser wavelength must be scanned across the entire set of wavelengths within a fraction of a second in order to minimize the effect of instabilities in LIDAR return or in the NO_x concentration along the laser beam path. This is not trivial. INO is working on a faster version of the measurement, in order to “freeze” the measurement in as short a measurement time as possible.
- The second is the reference cell for NO₂. In order to have a good reference, the concentration of NO₂ in the reference cell must be stable. INO found it was helpful to continuously flow a small amount of calibrated gas in the cell. This will be a problem for a fieldable system. The reference cell and the reference cell control system (cylinder, flowmeters, tubing, pressure gages ...) will need to be controlled in temperature. This will make for a much more complex system than anticipated. Another type of wavelength reference, one that would be more stable with temperature and more amenable to field use is required.

It was not possible to obtain a flow of measurable NO₂ from the mock-up stack. So no ambient temperature mock-up exhaust stack measurement of the concentration of NO₂ could be performed.

Using the measurements, it was determined that for a reasonable 1% absorption of the laser beam in the exhaust plume, the sensitivities would be 0.75 ppm-m and 25 ppm-m for NO and NO₂ respectively. This would require measurement times longer than those used here. The limit of detection of NO₂ is not sufficient and would require major enhancements in the UV LiDAR platform if we keep using the same approach. A different analytical strategy will need to be used for the sensitivity to reach the adequate level. One way would be to reduce the number of wavelengths used and to improve the laser repetition rate. Finally, as the measured LOD depends on the stability of the emission source, it will be necessary to add a reference instrument to the mock-up system in a future implementation.

2 INTRODUCTION

For the oil and gas industry, monitoring of pollutants such as NO_x is a need. Today's stack monitoring technologies rely on in-situ measurements (in-stack). The in-situ technologies measure directly in the stack (across-stack measurements) or by sampling in the stack. There are clear promulgated methods for measuring and sampling. However, it is difficult to sample some stacks because of the absence of sampling ports, or because they are located in remote areas where access is difficult.

Institut National d'Optique (INO) in collaboration with TransCanada Pipelines have an ongoing collaboration for the development of a standoff capability for the measurement of stack emissions of natural gas pipeline compressor stations. The aim is to propose a portable instrument capable of measuring pollutants from a safe distance of about 50 m without needing any sampling port nor any special site access authorization (from outside the fence).

In this specific phase of the development INO has been funded by Petroleum Technology Alliance Canada (PTAC) to pursue the development on its standoff platform. The work being funded here is related to NO_x detection capabilities using the INO UV-DiAL platform.

In this work, INO proposed to adapt a stack simulator for NO₂ measurements and to perform laboratory and in simulator quantitative measurements for NO and NO₂. INO also proposed to determine detection limits and to discuss the possible interferences for a real application. This report summarizes the project results and presents a discussion on interferences and their impact on the wavelength range selected for operation.

INO is aware that the level of knowledge required to fully understand the implications of every technical parameter and/or setting is high and that part of the discussion may be confusing for non-experts in optical detection. INO did its best to present a clear picture of all the work done and also tried to clearly explain the reasons behind every decision or conclusion.

In this report, a very brief introduction on the DiAL approach is first presented. In a following section, the measurement system and stack simulator are presented. A heated version of a mock-up stack was built and tested to allow controlled flow of NO, NO₂ or both into the main gas flow even at low ambient temperatures. Any other gas could eventually be inputted to the main air flow, such as SO₂. The goal was to have a concentration measurement from the LiDAR that was in line with the concentration determined by the flowmeters and the gas velocity and representative of a realistic case. The measurement concept is also detailed and a brief explanation of the algorithm used for data analysis is included. Detailed results and discussion are finally presented.

3 UV-DIAL, HOW IT WORKS

Differential Absorption LiDAR (DiAL) is an optical spectroscopic technique that allows for spatially resolved remote optical absorption measurement for concentration measurements of a molecule of interest. Simply put, when laser light illuminates a molecule at a feature wavelength, the molecule absorbs the laser light. This absorption feature is a unique molecular signature. In the present case, a tunable laser is scanned in wavelength across pre-determined wavelength values. Some wavelengths correspond to wavelengths of low absorption for NO or NO₂, others correspond to strong absorption. Using the backscattering return generated from the particles present in air along the beam propagation path, it is possible to “see” highly absorbing regions or high NO or NO₂ concentration zones. A decrease in signal strength (backscatter) determines amounts of NO or NO₂ in the atmospheric volume being sampled. This is possible if the measurement is calibrated, which means the absorption cross-sections or the propensity to absorb is quantified at each wavelength used for the scan. This is achieved in our case using a NO or NO₂ reference cell with a known concentration. A simple ratio between the energy that goes through the cell vs the energy before the cell allows for pure gas absorption cross-section determination. This reference spectrum is used in a software to extract the same signature from the measurements on the exhaust stack. The spectral signature is unique to NO or NO₂ (see Figure 1). The return signals are very strong in the UV and although there could be significant optical loss from propagation in the atmosphere, the distances being short this is not a problem.

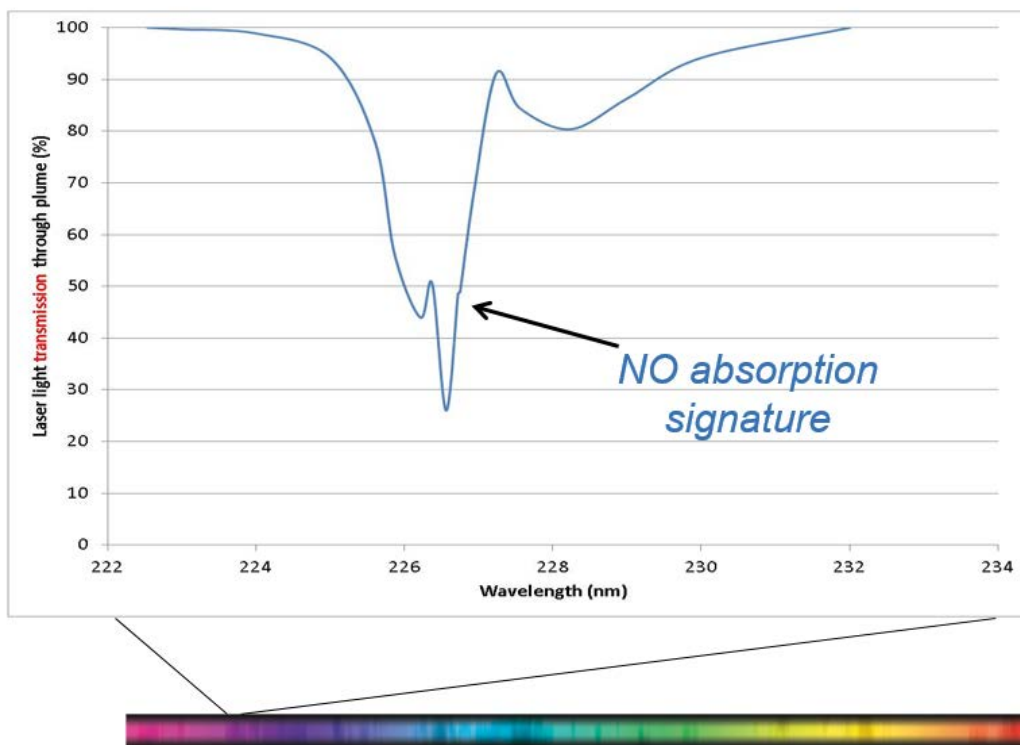


Figure 1. UV LiDAR – Absorption feature of NO in the deep UV.

4 MEASUREMENT SET-UP

This section should be skipped if only the results are of interest. This section is an in depth description of apparatus and how it was modified and used in this project. The breadboard/prototype used in the project is the result of many prior projects using UV lasers, at a fixed wavelength or using a tunable wavelength for LiDAR measurements of many different molecules and particulates.

4.1 UV spatially resolved absorption

In Germany, there is a Guideline for the use of LiDAR for atmospheric pollutant measurement [1]. There is no such guideline or standard in North America. However, UV-DIAL (Ultraviolet Differential Absorption LiDAR) is an interesting alternative to other promulgated methods and should be studied in the mid to long term. For UV-DIAL, it is necessary to have a tunable optical source or at least two wavelength stable laser sources. In these tests, the tunable laser is a pulsed 355 nm laser followed by an OPO (Optical Parametric Oscillator) tunable in the visible spectral range. This light must then be frequency doubled to reach the UV range (second harmonic generation). Tuning is done by rotating crystals in synchronicity. For these tests, changing the wavelengths was done with calibrated motorized actuators and a power optimization algorithm. The laser light from the tunable laser was monochromatic (a single well defined wavelength), but with a finite linewidth on the order of 0.017 nm. In order to get an absorption profile, the laser wavelength needs to be scanned, which takes time. The particulates that are used for generating the return have ample time to change in density or size distribution (gusts of wind, changes in weather, etc.).

The goal is to have and demonstrate as simple a system as possible. Classical fast alternate stabilized two wavelengths approach is for ultimate sensitivity and selectivity, but this is not always necessary. This depends on the absorption features' spectral width and also on the density of the features, as will be seen in the results and analysis section. The density of spectral features in NO and NO₂ and the spectral width of the resolvable absorption features did not warrant these complex sub-systems in INO's view.

In order to enhance selectivity, INO adopted a measurement scheme that required multiple wavelengths. So the laser wavelength was scanned to cover multiple wavelengths. The choice of wavelengths is important and are to be chosen in part by trial and error while considering possible interferences. This does add complexity to the system, but this was deemed more useful than using a wavelength stabilization scheme. This use of multiple wavelengths is such that the measurement is more like a differential optical absorption spectroscopy (DOAS) than like the conventional DiAL. Consequently, INO will be using techniques and software developed for DOAS measurements, in particular the use of reference spectra measured simultaneously in reference gas cells with the same system and the use of the software DOASIS. This allows INO to measure multiple gases with the same platform and reduce interference from molecules having absorption at the same wavelengths as those used for the quantification of NO and NO₂ and eventually SO₂.

It must also be mentioned that detecting NO₂ at wavelengths above 400 nm is possible and requires a simpler laser system. But this requires more modifications to the system and since there is absorption by NO₂ in the deep UV, it was decided to test at these lower wavelengths, since the deep UV wavelengths are necessary for NO detection. Also, there is no interference from ambient light in this spectral region and normalized backscattering by molecules and particulates is stronger. This might be required for efficient signal detection on very short integrated paths, even though the laser light is weaker at these deep UV wavelengths. There should also be less difficulty in using these deep UV wavelengths, because the stronger absorption in the atmosphere implies less propagation distance thus potentially reducing security risks.

The laser pulse energy is only ~1 mJ at these UV wavelengths, and the laser is pulsing at 10 Hz, for an average optical power of ~10 mW, depending on the exact wavelength. The pulse length is approximately 6 ns, meaning the LiDAR's spatial resolution is limited to about 1 m in length providing the electronic detection bandwidth is sufficient. The bandwidth is 350 MHz and the sampling rate is 400 MS/s (a point every 2.5 ns or every ~ 0.375 m). This is more than sufficient to resolve the 6 ns pulse from the laser.

The breadboard is shown in Figure 2. The laser system cannot be seen, being in the bottom box (black box on table). The emitting optics is inside the box. The laser beam is expanded and routed out of the box. The emitted laser beam strikes a folding mirror in front of the receiver telescope. The cylindrical form on the top is the receiver telescope with a parabolic collection mirror 20 cm in diameter. Both the emitted beam and the return signal are on the same optical axis. The output laser light can be tuned in the UV from 210 nm to 260 nm at <10 mW for UV-DIAL. Tunable light in the blue-green region is also possible. The telescope optics is coated with aluminum for use in the deep UV. The light is collected by a non-solarizing optical fiber and routed to an optical setup that couples the return light to a grating monochromator and a photomultiplier tube (PMT) for measuring the return signal. The monochromator bandpass is approximately 4.4 nm when there is an output slit (600µm), and > 20 nm when the output slit is removed. Optical filtering is necessary for isolating the return from the ambient light, but also to isolate the light from the generated fluorescence. There is a mismatch in numerical aperture between the grating monochromator and the receiver telescope. This should be corrected in the future for optimum signal recovery.

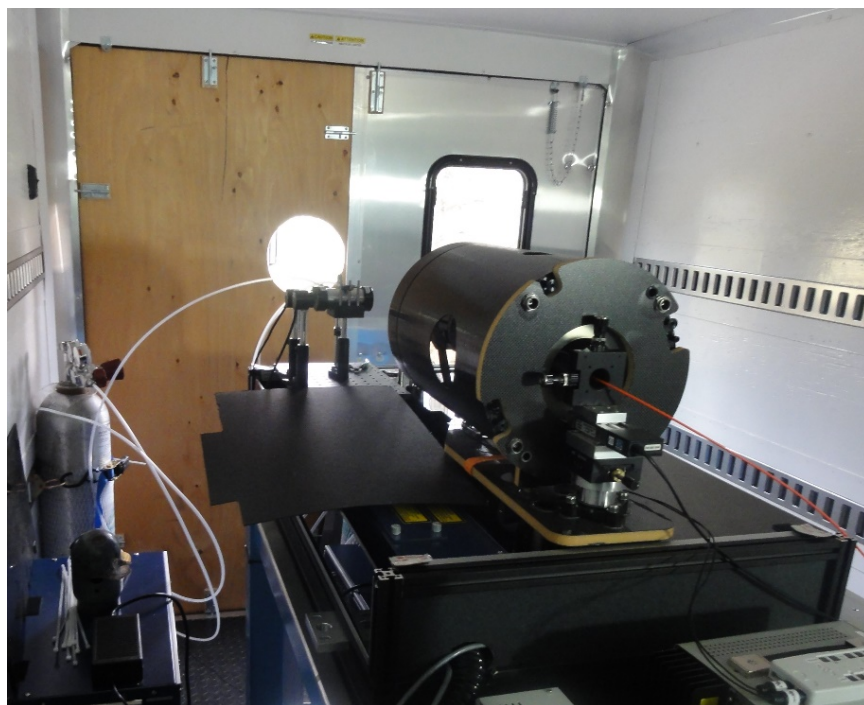


Figure 2. UV-DIAL breadboard prototype in mobile laboratory.

The incoming light on the PMT generates a signal that is digitized at 400 MS/s. The PMT amplifies the signal generated by the return photons to a level such that the digitization circuit is not a significant contributor to measurement noise. Not seen on the photo are the laser controller and the grating monochromator with PMT.

Other components that are seen on the photograph are a calibrated gas cylinder, gas routing hardware and a reference gas cell. Figure 3 is a drawing of the UV-Dial setup. The laser output is routed to the exterior using multiple folding mirrors. After the last folding mirror there are two glass wedges that pick up part of the laser beam. A first deflected beam goes through the reference gas cell to a high speed Si photodiode detector and a second deflected beam goes directly to another Si photodiode detector. The exact configuration is irrelevant since components can be moved around for the best work performance.

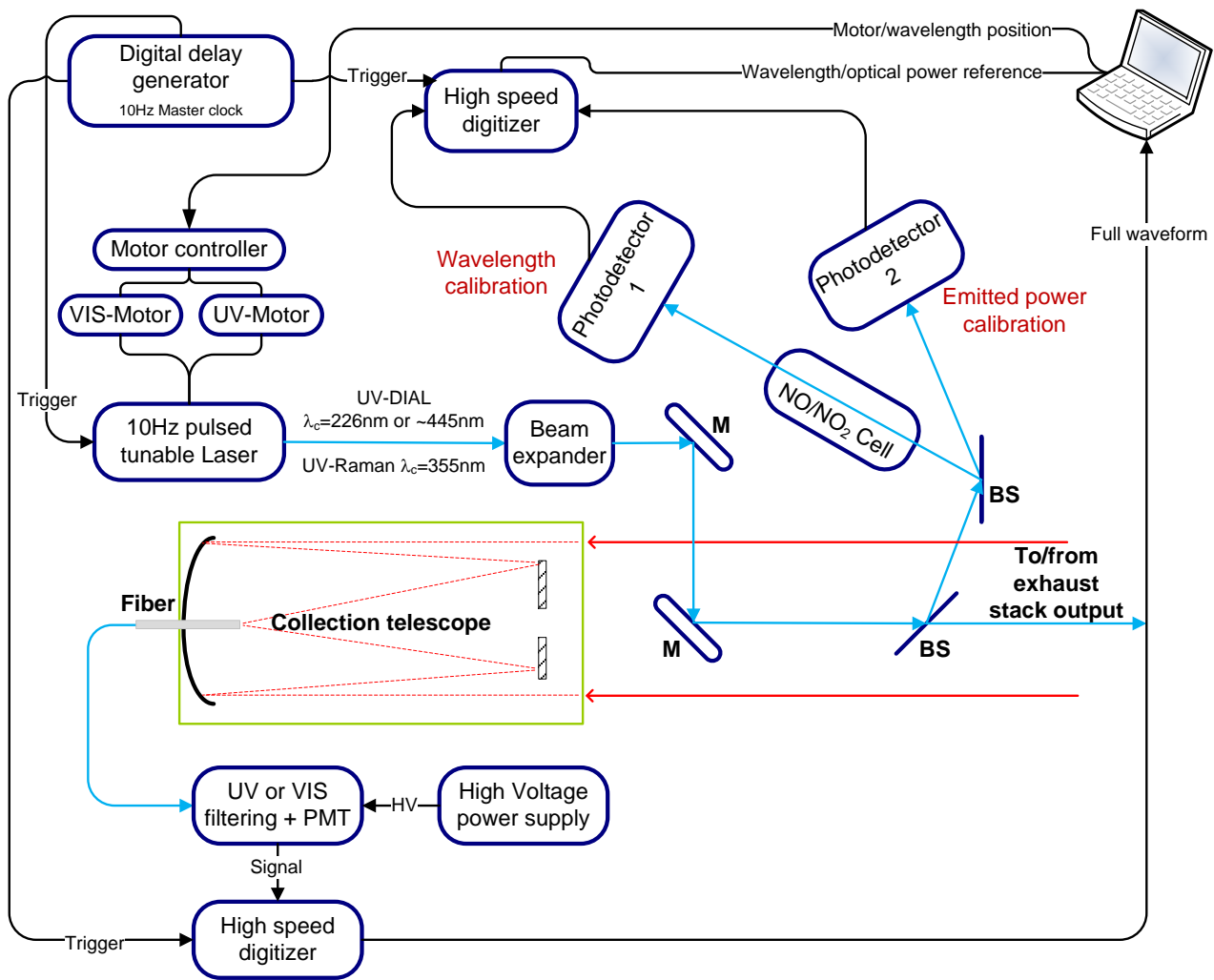


Figure 3. Drawing of the UV-DIAL measurement set-up. M is for mirror, BS is for beam sampler (wedge).

4.2 Mock-up exhaust stack

The mock-up stack operates at near ambient temperature. This was done in order to control more closely the NO and NO₂ concentrations in the gas flow, which cannot be done if naturally produced using a gas burner. The amount of NO₂ in high temperature gases is usually fairly low, to the point of not being measurable. A mock-up stack was designed and built that allowed for a controlled flow of NO, NO₂ or both into the main gas flow. Any other gas could eventually be inputted to the main air flow, such as SO₂ and particulates. The goal was to have a concentration measurement from the LiDAR that was in line with the concentration determined by the flowmeters and the gas velocity at the stack output. Another feature of the mock-up stack is that it has only 10 cm (4 inches) of diameter, the lower limit for the diameter of monitored exhaust stacks. This has a major influence on the results and shows both the limits and the potential of the INO breadboard as modified.

The near ambient temperature mock-up stack uses an unregulated and unfiltered air blower that pushes air through the bottom of a 10 cm diameter ABS tube. The air has been previously heated to around 25°C using a 1500 W portable electrical heater. This precaution is needed to avoid N₂O₄ formation which occurs naturally when the NO₂ temperature goes below 21°C. The NO₂ cylinder is also heated using a heating strap and insulation foil. However, in spite of these precautions, NO₂ turned to N₂O₄ at least partially during our experiments. We will discuss this situation later in the results section.

Directly after the blower input there is an ABS Tee. In one of the arms of the Tee there are gas connectors for inputting the different gases to be controlled and measured. The gases are from certified high pressure gas cylinders of NO and NO₂ diluted in nitrogen (5% NO, 10% NO₂). The amount of NO_x introduced in the mock-up stack is regulated using a mass flow controller.

The exhaust gas exit speed is controlled by varying the speed of the air blower. A future upgrade to the mock-up stack is a regulated and controlled air blower. The exhaust speed is measured using a hot wire anemometer.



Figure 4. Photo of the ambient temperature mock-up exhaust stack and gas cylinders.

A similar setup was used in a previous campaign and fumes and a camera were used to image the stack output. It was possible to analyze the images to gather information on exhaust plume behavior with respect to exhaust gas velocity and wind velocity and direction. This in turn allowed the INO team to optimize measurements with the platforms/breadboards. Figure 5 clearly shows that the exhaust gas stream is stable and well contained for at least half an exhaust stack diameter downstream of the output for an exhaust speed of ~ 5 m/s and very little wind. It is in this part of the exhaust stream that the laser beam is probing.



Figure 5. Fumes outputted from the mock-up stack at ~5 m/s.

5 CONCEPT OF MEASUREMENT

5.1 Procedures

From previous discussions with compressor station operators, expected NO concentration coming out of compressor stacks is between a few tens of ppm and 150 ppm. NO₂ is the balance of the total NO_x measurement (NO_x-NO) normally achieved using chemiluminescence measurement. It is expected to be in the low ppm to ppb range for high temperature exhaust like those considered here. Because of this lower concentration, the NO₂ is much more difficult to measure from a distance. It must be remembered that the UV-DIAL measures a concentration-length product, this means an absolute number of molecules. The concentration is deduced using the known length over which the measurement is done, which is considered to be the stack diameter in this phase of the work. The longer the length, the stronger the signal for a given concentration. Larger stacks are therefore easier to measure than very small stacks. The concentrations used in the mock-up stack are very high in order to reproduce concentration-length products found in larger exhaust stacks.

For the test campaign, the goal is to measure NO and NO₂ and to evaluate a limit of detection for the prototype. The objective of the project is to show the potential of the approach for quasi-simultaneous measurement of both NO and NO₂ using the same platform and analytical strategy for both.

Figure 6 shows the concept of the measurement approach. Light from the INO platform inside a mobile laboratory interact with molecules and particulates in and around the exhaust stack plume. The return signal comes from elastic scattering on particles and molecules and allow for spatially resolved absorption measurement. From these measurements, concentration of NO_x in the exhaust plume can be deduced.

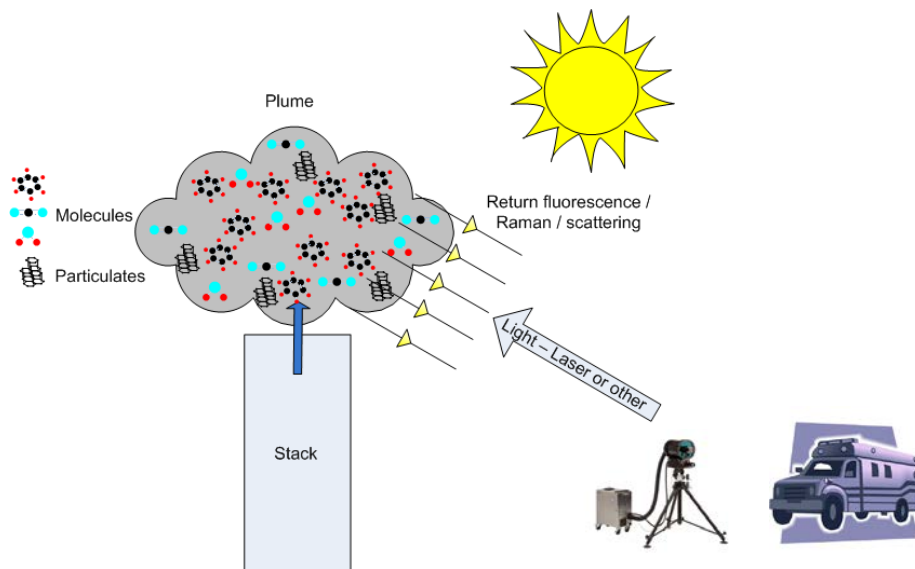


Figure 6. Concept of measurement.

The UV beam from the laser in the INO platform is routed towards a folding mirror that sends the UV beam across the stack plume, very close to the stack output itself. The scattering generated by the UV laser returns to the receiver telescope via the folding mirror (laser and return signal have the same optical path). Ideally, the volume resolved by the INO platform would be adjusted to be equal or smaller than the stack width projected along the line of sight of the UV laser beam. In the present case, the mock-up stack is only 10 cm in diameter. The INO LiDAR platform used in these tests cannot resolve a volume with such a small length. The wavelength used for absorption of NO is ~226 nm and between 240 – 246 nm for NO₂ although wavelengths between 221 and 240 nm were also tested. The power out of the INO platform is approximately 10 mW.

UV-DIAL measurements require particles and molecules to scatter the UV light from the laser. To some extent, the more particles in the air, the better the measurement, as long as the particulate matter loading is homogeneous throughout the laser beam measurement path. Of course, the air must be clean enough for the laser light to get to the exhaust stream and back. For concentration retrieval, back-scattering measurements must be made before the stack output and after so we can

deduce the in-stack absorption from which a concentration can be calculated. Details of the procedure will be explained in the results and analysis section.

In order to get the mass emission rate, the exhaust speed also needs to be known. INO does not have a remote instrument that measures exhaust speed. This could eventually be done by an infrared camera, but this needs to be well proven and referenced. INO is currently working on this issue.

If there are strong winds, the exhaust plume could extend along the propagation axis of the optical beams and fluctuate with time. This is to be avoided in order to get the concentration value of the mock-up exhaust stack only, because of the inability to resolve the 10 cm diameter of the stack. Nevertheless, an appreciable amount of NO or NO₂ could end up in the atmosphere between the mobile laboratory and the exhaust stack. INO tried to do with this situation.

5.2 Mobile laboratory

INO had a closed trailer manufactured for the transport of the platforms/breadboards to anywhere they are needed. The trailer was fitted with an optical table onto which the platform/breadboard for the UV-DIAL is fixed. When on site, the trailer is lifted onto four jack stands to stabilize the optical setups and to have stable exhaust stack pointing.

All the required equipment is hauled with the mobile laboratory (ML) and pick-up truck that pulls the ML. It is fitted with the necessary computers and ancillary equipment and temperature control (heating or cooling, season dependent). The optical beams are routed towards the exhaust plume with 12" diameter folding mirrors (motorized or not).

Figure 7 is a photo of the mobile laboratory in which is mounted the UV-DIAL system and of the settings of the INO test campaign. The campaign was done in a reserved part of one of INO's parking lots. The pointing stability of the laser beam was ascertained. The stability of the beams, for the purposes of the campaign, is thus not a worry.



Figure 7. Site installation of INO mobile laboratory (folding mirror in front of open doors).



Figure 8. Mock-up stack with gas bottles at the end of the stand-off path.

5.3 Test site security

There are multiple aspects to security. There is the security of INO personnel on the site, then there is the security of the INO platforms for all personnel and for possible citizens or other workers in the optical beam paths, if any. These security issues are related to optical hazards from lasers and lamps, on the eyes and skin, and from optical explosive hazards if any. The use of noxious gases is also an issue, in particular NO_2 . These were analyzed and summarized below.

5.3.1 Eye and skin optical radiation safety issues

When a laser is pointed towards the sky, Transport Canada must be advised and permission obtained. INO checked with Transport Canada in the past for the Concepts of Measurement it was envisioning, and if a large enough target is installed or if the optical beams are horizontal, then no permission is needed. There was a large enough target behind the mock-up exhaust stack (behind with respect to the optical beam direction), that no permission was required.

If the installation on eventual other test sites was such that the optical beams were horizontal, then a target/stop panel would also be required, unless the beam was at more than 3 or 4 m in height all along its path at close range (<1 km) and the path end would be a building wall, bushes or the like. At great distances, there is no optical hazard. The safety analysis for each platform/breadboard will give the nominal hazard distances.

5.3.2 Explosion safety analysis

Unfortunately, the IEC 60079-28 standard for use of optical radiation in explosive environments only covers wavelengths from 380 to 10 000 nm. INO's UV standoff sensor uses laser light under 380 nm. INO does not know of a specific standard for light of any kind, under 380 nm, in an explosive environment. For the tests in this phase of the work, there were no explosion risks. It is however interesting to think about potential risks. Because this approach is to be used in gas compression stations, this point is of great interest. Here is an abstract of standard IEC 60079-28:

“This standard contains requirements for optical radiation in the wavelength range from 380 nm to 10 µm. It covers the following ignition mechanisms:

- Optical radiation is absorbed by surfaces or particles, causing them to heat up and, under certain circumstances, this may allow them to attain a temperature which will ignite a surrounding explosive atmosphere;*
- Direct laser induced breakdown of the gas at the focus of a strong beam, producing plasma and a shock wave both eventually acting as the ignition source. These processes can be supported by a solid material close to the breakdown point.”*

This standard does not apply for 355 nm (or lower in wavelength) light that is not focused. This is the case of the laser light in the UV platform. INO will need to insure that the laser light is never focused anywhere along its path, except inside specially designed enclosures. The optical beams will all travel from the inside of the mobile laboratory (or close to) to the exhaust plume through the outdoor atmosphere.

It is clear when reading the standard, that powers in excess of multiple watts or pulse energies in excess of tens of mJ will not ignite an explosive atmosphere unless a very strong absorber is present and/or if the optical radiation is focused.

In light of this analysis and the reduced optical powers and densities used in the INO platforms, there are no explosion risks whatever the measurements site.

5.3.3 Security measures for laser and other forms of light

Basic security measures were planned for this campaign. A security perimeter was delimited inside which goggles were required at all time the flashing exterior red/orange light was indicating the emission of laser light.

5.3.4 Toxicity Analysis

Using the references [2] and [3], a toxicity analysis was completed to ensure that the mock-up stack operator and people at test site proximity do not take any health safety risk. Considering a Threshold Limit Value-Short Term Exposition Level of 5 ppm for NO₂, an in stack concentration of 600 ppm, a 2 m stack height and average wind levels in Québec City for November, it was determined that dilution is sufficiently high at a distance of 20 m or more that no risk is present for a 15 min exposition duration. A security perimeter was therefore installed around the stack during the experiment. A mask was used for the stack operator when needed.

6 RESULTS

The following sections describe the results obtained during this test campaign and include some previously obtained results to help the reader have a better understanding of the process. There is raw and processed data. The goal is to prove that a reasonable amount of signal returns to the platform thus enabling absorption measurements, and that the sensitivity is in the low ppm range for the UV-DIAL of NO_x. Some conclusions and recommendations are included in these results sections.

6.1 UV-DIAL (UV multi-wavelength absorption)

A series of UV-DIAL measurements were done. UV-DIAL is a known technique that can lead to concentration retrieval. The scanning capabilities of the DiAL system were tested in the past by scanning a gas cell filled with NO and a buffer gas (nitrogen). This gave rise to the spectrum shown in Figure 9. This spectrum was done using a ~0.005 nm step for the laser wavelength scan. The very sharp absorption features of NO in this region are such that the laser wavelength scanning mechanism is not sufficiently precise and repeatable from one scan to another for accurate absorption measurements without a reference cell. The spectrum shows the important features of the NO absorption spectrum as measured by the INO UV-DIAL system. Knowing the exact NO concentration in the gas cell, absorption cross-sections can be computed with respect to wavelength. No effort was done to precisely calibrate the wavelengths, as this is not absolutely necessary at this stage.

Literature gives an absorption line pressure broadening of ~0.172 GHz/kPa, which comes to approximately 0.003 nm of full width at half maximum for isolated spectral lines, confirmed by the results published by Edner et al. [4]. It is also possible to simulate the NO spectrum with a software called LIFBASE Spectroscopy Tool from SRI International. Using these simulations it is concluded that the laser linewidth is close to 0.017 nm, the spectral absorption linewidth being only 0.003 to 0.005 nm. This is in line with the type of laser used, a non-injection locked frequency doubled OPO. This will be discussed in more detail.

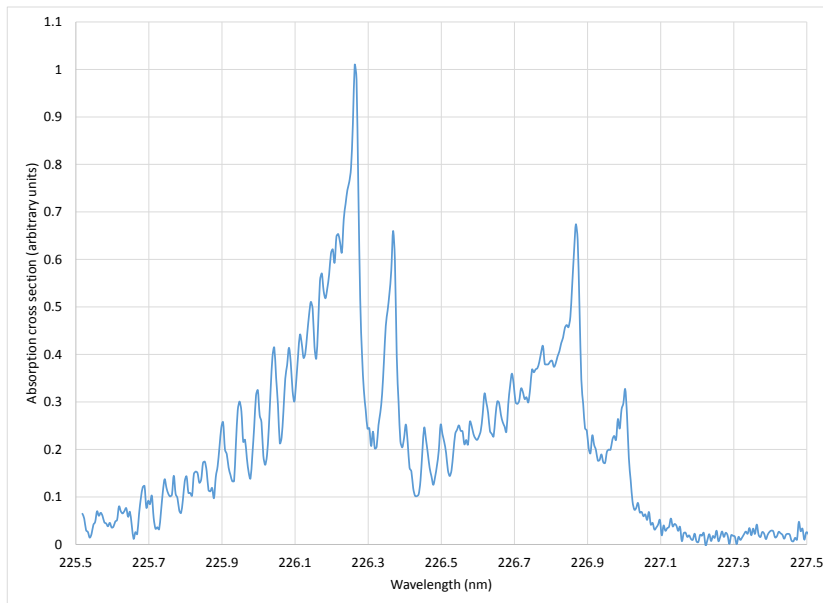


Figure 9. Absorption profile and cross sections of NO from reference cell. 0.005 nm wavelengths steps are used in the scan.

Because of the nature of the measurement and the design of the UV-DIAL breadboard, the measurement of UV absorption is a lengthy process. As such, the NO concentration could change while the measurement is ongoing and while the wavelengths are scanned serially. The particulate matter concentration, on which the measurement is based for generating the return, can also change in front and behind the plume from one measurement point to the other. This is not the case in classical two wavelength DiAL experiment with very fast switching time between the “ON” and “OFF” wavelengths. Part of this work is to evaluate the limitations of the relatively slow scanning approach for quantitative measurements.

The DiAL technique requires at least two wavelengths, in order to get the extinction coefficient used in the retrieval of concentration in a pure DiAL approach. In these tests for NO, the idea was to scan the laser wavelength around 226 nm and to measure an absorption cross section with the reference cell at the same time as the measurement is done in the plume. The NO (or NO₂) concentration in the cell being precisely known. This does not make for the most sensitive measurement if the laser wavelength is not exactly at absorption peak or minimum, but it does make for a much simpler system which is an important aspect of this demonstration. In addition, the absorption in the cell is a measure of the quality of the overall measurement, the peak and minimum absorption being known a priori. The data is analyzed in light of this last approach.

Although only two wavelengths are necessary when measuring a pure substance, more wavelengths are required when there is cross-interference with other molecular species. This is the case between NO and NO₂ and other atmospheric species and pollutants. The analysis will thus use more than two wavelengths. The exact number of wavelengths will be determined by careful analysis of the absorption spectra of the molecules of interest and of potential interfering molecules.

The relation between absorption and concentration can be non-linear, because of strong absorption at the spectral line center, when the laser linewidth is larger than the absorption linewidth. This is to be

avoided. Calibration curves should be built in order to ascertain that the measurements are done in the linear part of the signal vs concentration curve. The concentration and the absorption are related by the following equation;

$$n = -\frac{1}{\epsilon_{\lambda}} \left\{ \frac{1}{2L} \ln \left(\frac{I_{after} O_0}{I_0 O_{after}} \right) + \sigma_{ext} \right\}$$

Where n is the molar concentration, ϵ_{λ} is the molar absorptivity at wavelength λ , L is the length of interaction between the laser and the plume, I_0 is the intensity just prior to the plume, I_{after} is that of the return of the laser after the exhaust plume, O_0 and O_{after} are overlap functions describing the instrument response with distance and σ_{ext} is an extinction coefficient (loss not do to absorption by the molecule of interest). Theoretically, one would need to add the instrument's response as a function of wavelength. Also, the interaction length is twice the plume width, as the absorbed light goes twice across the plume. There are different ways to go about retrieving concentration without measuring the overlap function or the extinction coefficient.

One of them is to normalize the return signal at all wavelength by the return signal at a reference wavelength. This also cancels out all the variables except the molar absorptivity, the interaction length and the concentration **if the hypothesis is made that there is no NO or NO₂ elsewhere in the atmosphere**. Then, a ratio is taken of the spectra after the exhaust plume over the spectra before the exhaust plume. An average is made over a number of spatial points. The average can be a weighted average or not.

$$n = -\frac{1}{2(\epsilon_{\lambda} - \epsilon_{\lambda_0})L} \left\{ \ln \left(\frac{I_{after}}{I_0} \right)_{\lambda} - \ln \left(\frac{I_{after}}{I_0} \right)_{\lambda_0} \right\}$$

The steps that follow depend on the number of wavelengths used.

One of the problems of the technique is that the NO or NO₂ can diffuse into the atmosphere and have a non-uniform distribution. So when computing the ratio of ratios as described in the previous paragraphs, there will be an impact from this non-uniformly distributed and non-stationary gas plume. When there is wind, the extra NO or NO₂ is carried away, and it is preferable not to have the laser beam pointing in the same direction as the wind. In practice, and in the future, it will be necessary to have a spatial resolution such that averaging is done just at the edges of the plume at the output of the exhaust stack. This was not possible here, the laser pulsewidth being ~6 ns or 0.9 m compared to the 0.1 m diameter of the mock-up exhaust stack.

6.1.1 NO

Figure 10 shows the absorption cross sections for NO in the wavelength range of interest. This first graph is what would be obtained by scanning a very small linewidth laser in this wavelength range. There are multiple absorption lines having the ~0.003 nm expected linewidth. This spectrum is a simulation generated by the software LIFBASE. The absolute cross section values are from the thesis

of Houchem Trad [5]. When, in the simulation, the laser linewidth of 0.017 nm is added, the spectrum of Figure 11 is obtained. This resembles what is obtained with the INO system (see Figure 9). The simulation was done with a Voigt profile, whereas the laser has a more Gaussian profile, but the general idea is clear from the graphs.

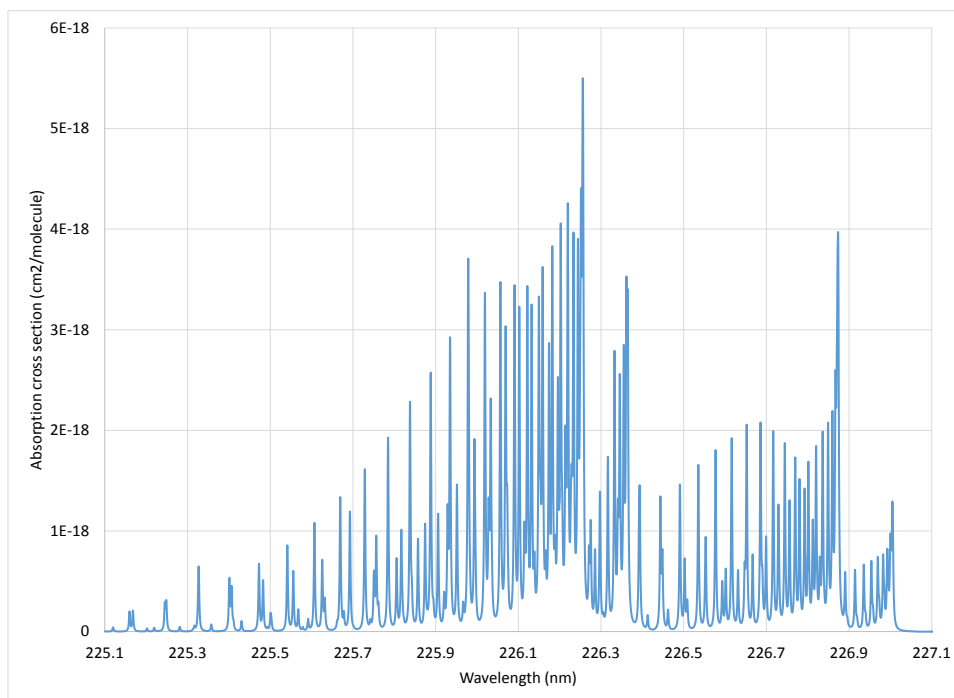


Figure 10. NO absorption spectrum from LIFBASE at high optical resolution.

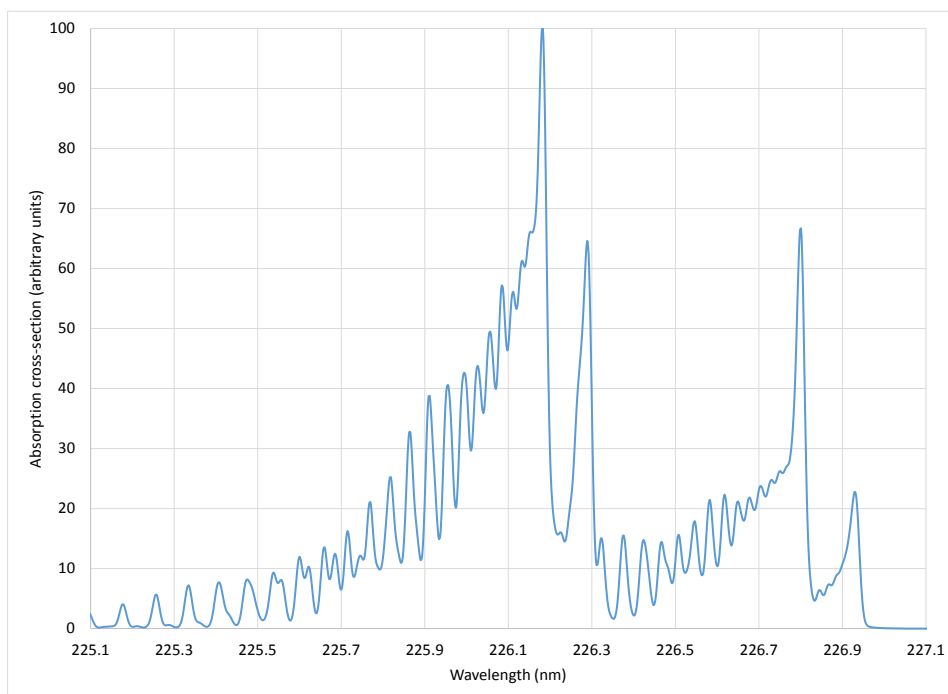


Figure 11. NO absorption spectrum from LIFBASE with 0.017 nm of optical resolution.

Unfortunately, there are many more molecular species in the air in and around the exhaust stack. Not the least being NO_2 , since it is one of the molecules that can be found in large quantity in the exhaust stack of some reciprocating engines. There are other molecules that absorb at these wavelengths, such as O_2 , O_3 (ozone), SO_2 . An analysis of the possible interference from NO_2 , SO_2 , O_2 and O_3 , indicate that using multiple wavelengths would be preferable. When there is another molecular specie, more than one wavelength is required, unless the other molecule has a constant absorption coefficient (including zero) at all wavelengths used for the measurement of NO , in which case it is included in the extinction coefficient and disappears in the computations. As seen in Figure 15, NO_2 has an absorption cross section that varies by less than 1.2 % from 226.1 to 226.5 nm. The absorption spectrum of O_3 , O_2 and SO_2 are shown in Figure 12, Figure 13 and Figure 14 respectively. O_2 absorbs very little, but does so all along the laser beam path, but there is no absorption feature, it is the Herzberg continuum. O_3 absorbs more than O_2 and is also in a continuum (the Hartley band) and is the major cause of laser power loss along the laser beam path. O_2 and O_3 have absorption cross sections that do not vary by more than 1.5% between 226.1 and 226.5 nm. SO_2 has features, but slowly varying features compared to NO , it would be the molecular specie that would interfere the most with a two wavelength measurement. The absorption cross sections are compared in Figure 16. O_2 is in the graph, but since it is 5 orders of magnitude smaller in absorption cross section, it appears in the graph as a line along the wavelength axis at the zero mark. All these spectra should be used in the retrieval of the NO concentration, although it is not done here.

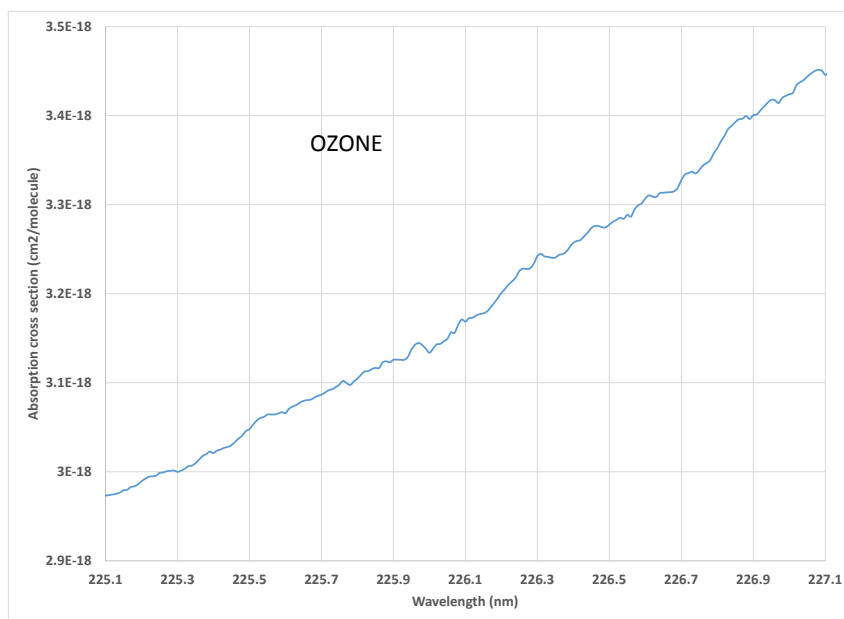


Figure 12. Absorption spectrum of ozone around 226 nm.

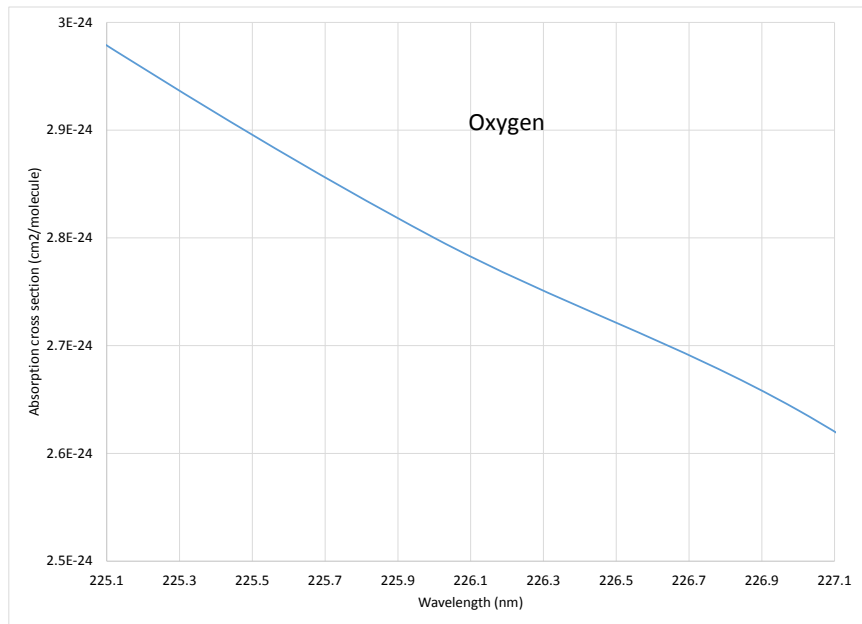


Figure 13. Absorption spectrum of oxygen around 226 nm.

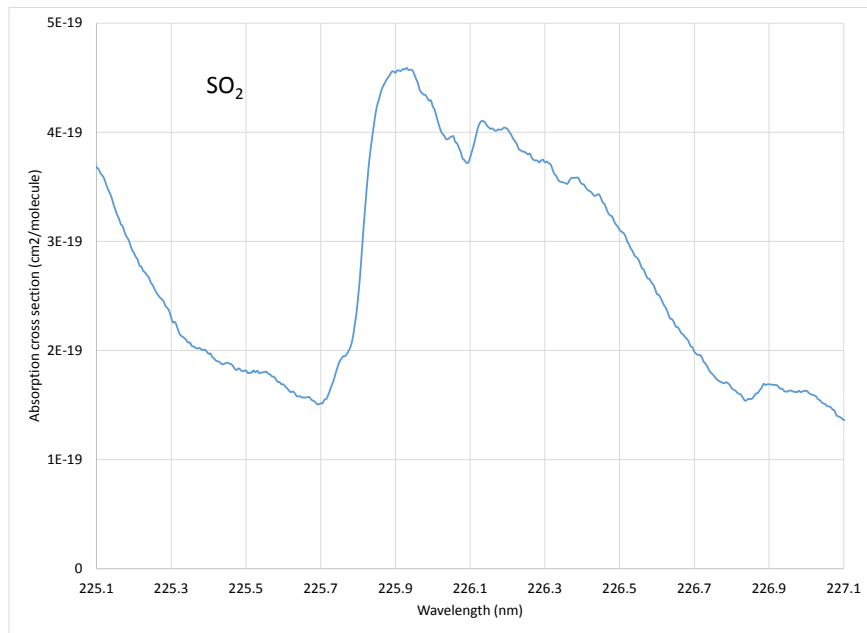


Figure 14. Absorption spectrum of SO₂ around 226 nm.

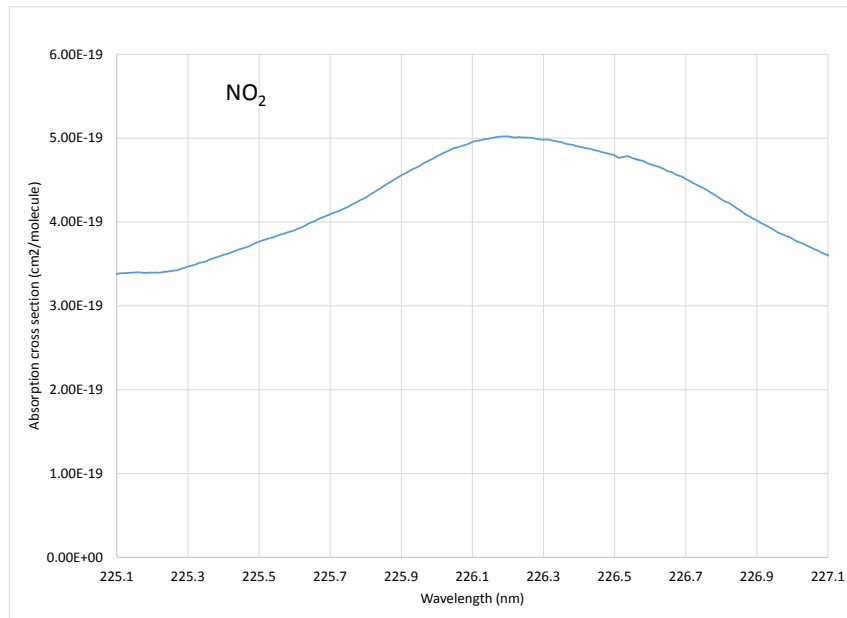


Figure 15. Absorption spectrum of NO₂ around 226 nm.

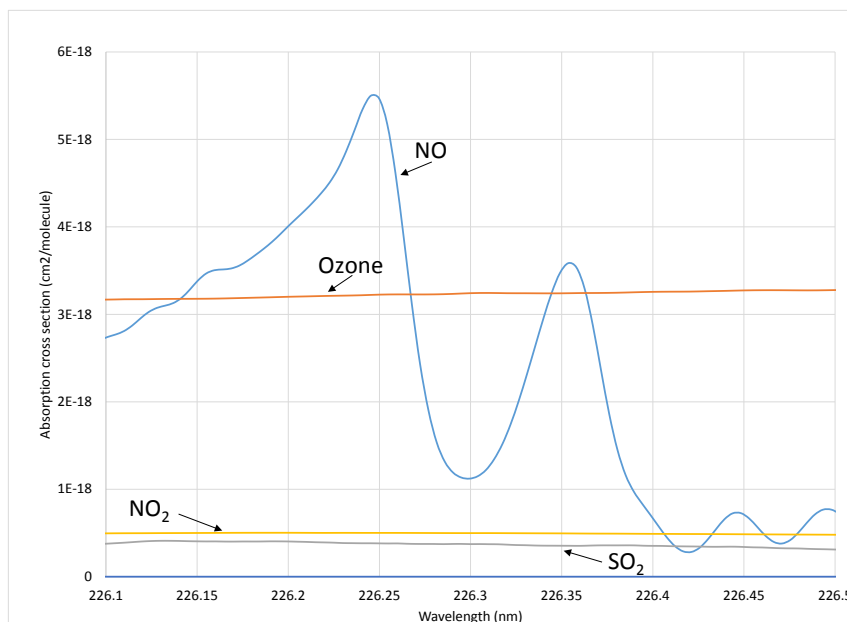


Figure 16. Absorption spectra of NO, ozone, oxygen (not seen because orders of magnitude lower), NO₂ and SO₂ around 226 nm.

The maximum cross section for NO is taken to be $5.5 \times 10^{-18} \text{ cm}^2/\text{molecule}$ at 0.017 nm of optical resolution. This is a rough estimate. The exact value is measured with the reference cell. Although the other mentioned molecular species do not vary significantly in absorption cross section, they have a differential cross section and, depending on their relative concentration, can have an important impact on the concentration retrieval of NO. For this reason, multiple wavelengths are used and the results are inputted to a software called DOASIS that retrieves the concentration from the measurements at these multiple wavelengths. The multiple wavelengths are chosen in the 226.415 to 226.8 nm range

at wavelengths to be determined but such that at least one laser wavelength is close to the maximum and at least another is close to the minimum in absorption cross section when scanned.

Figure 17 shows transmission spectra measured through the reference cell with 0.5% NO in nitrogen at atmospheric pressure. The scans are not all started or ended at the same wavelength. These spectra show some of the limitations of the scanning mechanism of the INO UV-DIAL platform. Although the wavelength that are “asked” of the motorized scanning system are the same, the results vary. This is clear considering the fact that when the concentration does not change, the transmission should not change either, which is not the case for the “asked” wavelengths in the figure. This is not a major problem, since this exact measurement is used as a reference measurement in the analysis process. The concentration in the cell is known, since a calibrated gas cylinder is used in flow mode.

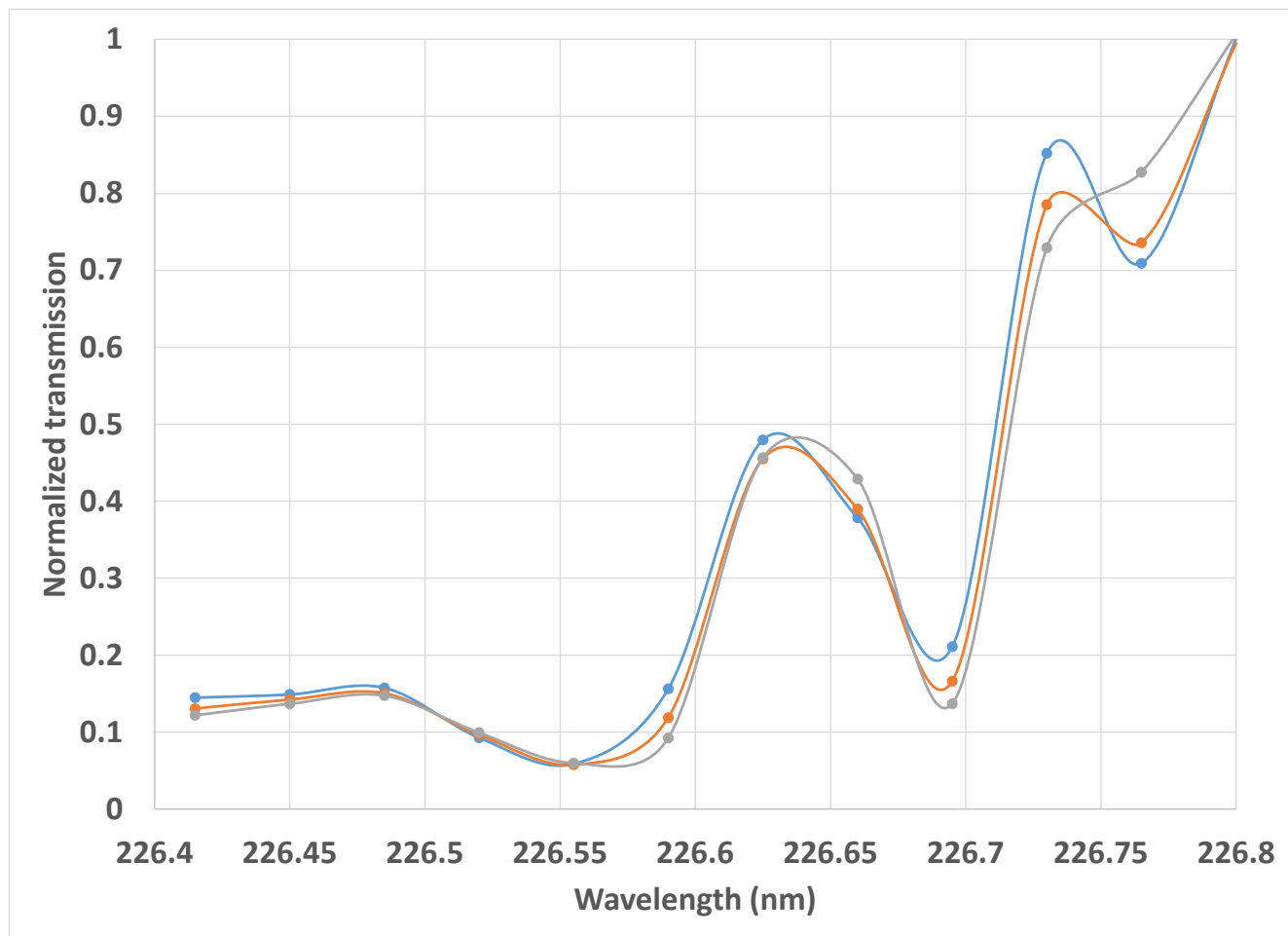


Figure 17. Transmission spectra of NO in reference cell.

The peaks and valleys of the transmission spectra are inverted with respect to the absorption cross section graphs previously shown. The transmission is what is used in the DOASIS software.

The reference spectra have a high signal to noise ratio. They are measured with an appreciable amount of laser energy. The fact that they are not repeatable is not a major concern, since they are measured at each scan and used to calibrate the LiDAR returns and the measurements in the exhaust stack scan by scan. Before inputting the spectra to DOASIS, each of them is normalized to

1 using the highest transmission point. The wavelength axis is indicative only (and should be shifted slightly to lower wavelengths).

It is known that there is an equilibrium between NO and NO₂ in presence of oxygen. However, in this case, the reference gas used to fill the reference cell is free of oxygen and hypothesis is made that the NO concentration in the cylinder is stable and that the presence of NO₂ negligible in terms of concentration.

The reference cell allows for concentration calibration and correction of any and all inaccuracies in the wavelength of the laser. The next step is the measurement of the LiDAR return. Figure 18 shows a typical LiDAR return averaged over 200 pulses (20 seconds), when there is practically no absorption by NO in the exhaust stack. It is an indication of the overlap function, the $1/r^2$ LiDAR response and the decay due to the extinction coefficient. The LiDAR system is essentially blind up to 15 to 20 m. The system sensitivity rises to a maximum at ~ 35 m and then falls off with distance. The system's receiver optics was set so as to have an optimal signal when at ~44 m.

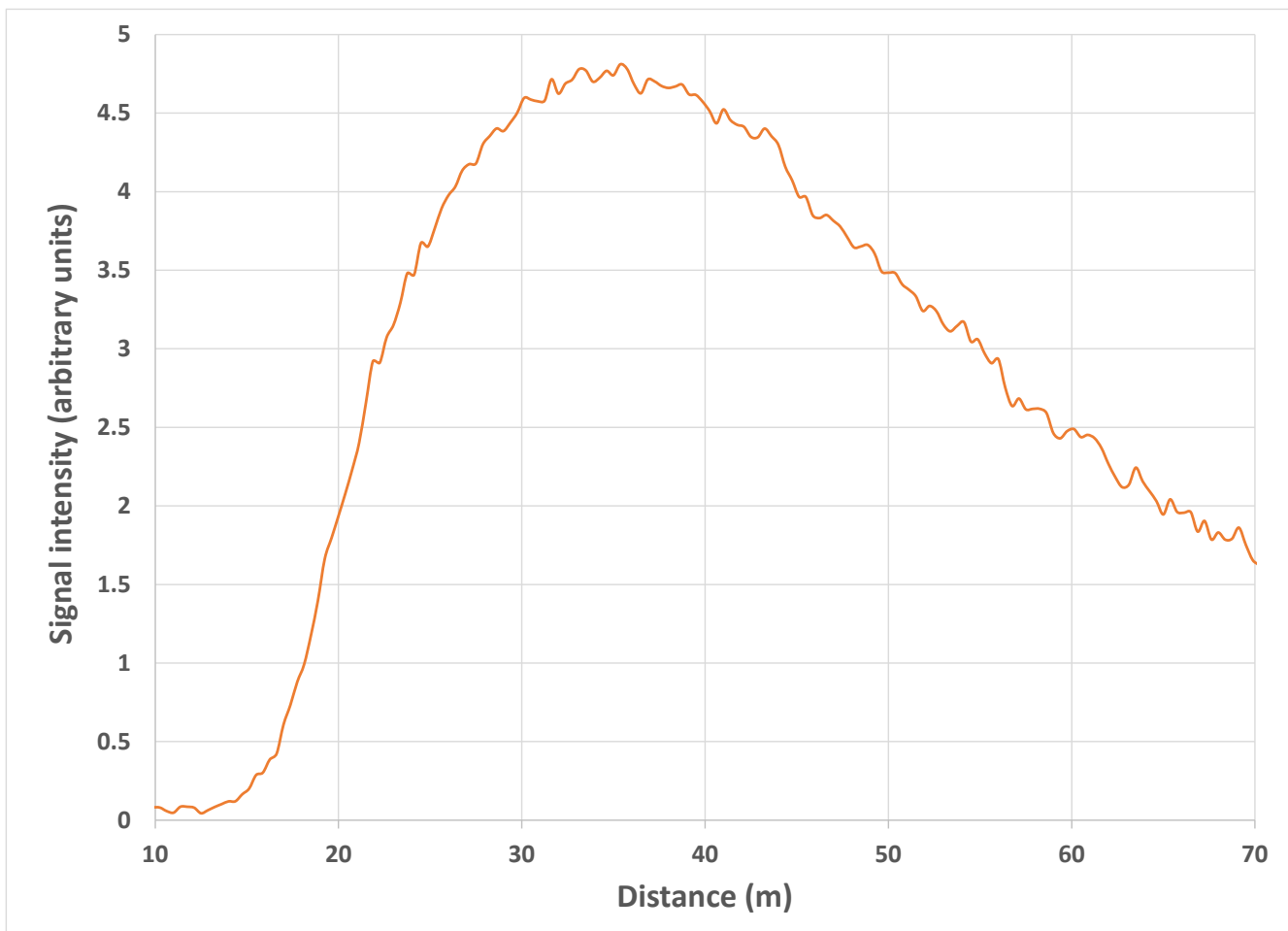


Figure 18. LiDAR return curve from exhaust stack with practically no absorption.

The next graph (Figure 19) shows the same measurement but with absorption by NO in the exhaust stack. There are two comments on this second LiDAR return; 1) there is a peak at the position of the exhaust stack. This is due to NO fluorescence, the optical filtering not being sufficient to filter out all of the fluorescence; 2) the drop in power is clearly seen after the exhaust stack position, indicating the absorption by the NO in the stack.

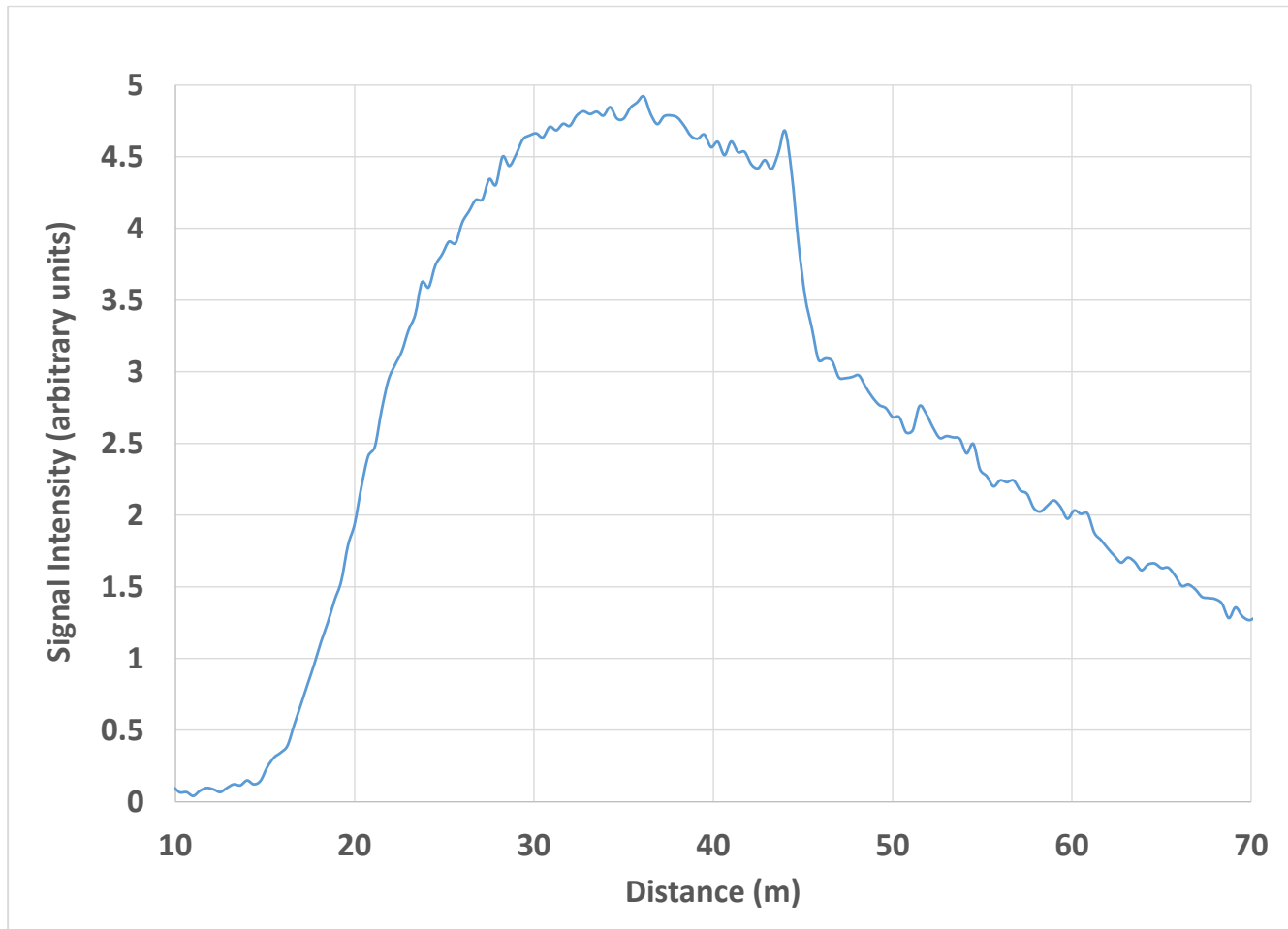


Figure 19. LiDAR return curve with distance. With fluorescence and significant absorption by NO.

Figure 18 is a curve for which there is practically no absorption in the exhaust stack and Figure 19 is a curve for which the absorption is significant. This can be clearly seen from the break in the curve. The absorption is seen in the difference between the first curve and the second curve after the stack (~ 44 m). The rate of change becomes the same after the exhaust stack. The curves are very similar before the stack. It takes a distance of ~ 2 m for the curve to no longer be affected by the drop caused by the exhaust stack. This is due to the laser pulse length, the electronic detection bandwidth and the shape of the laser pulse. The absorption is easily detectable at the concentration used in this example.

The computations use the curve from each individual wavelength in the laser wavelength scan. All the curves are normalized to a reference wavelength curve, the wavelength being the one for which there is minimum absorption in the reference cell. Once these normalized curves have been obtained, an average is made over a pre-determined number of points. For example all the points after the stack,

from 50 to 55 meters are averaged. The same is done for points before the stack, for example from 35 to 40 meters. For each normalized LiDAR return curve (for each wavelength), the ratio of the averaged values after over the averaged values before is computed. Finally, the resulting spectrum is re-normalize with respect to the highest transmission point in the spectrum, in order to have only transmissions lower than 1, including noise. Figure 20 is an example of the results for three transmission spectra measurements across the stack taken in succession, each wavelength being the average of 200 laser pulses (20 seconds measurement time). The reference transmission spectrum from the reference cell is also re-normalized to 1, and these two spectra, along with the concentration in the reference cell, are the inputs to the DOASIS software.

The spectra of Figure 20 have more noise than the reference spectra of Figure 17. This is to be expected, the LiDAR return is weak. Even in the presence of noise, the absorption signature of NO is clearly visible. Moreover, some of the variations are not noise, since they appear both in the spectra from the stack and from the reference cell. This is probably due to a non repeatable wavelength scan. This legitimizes the approach taken of measuring in the reference cell and inputting this reference spectrum in the DOASIS software.

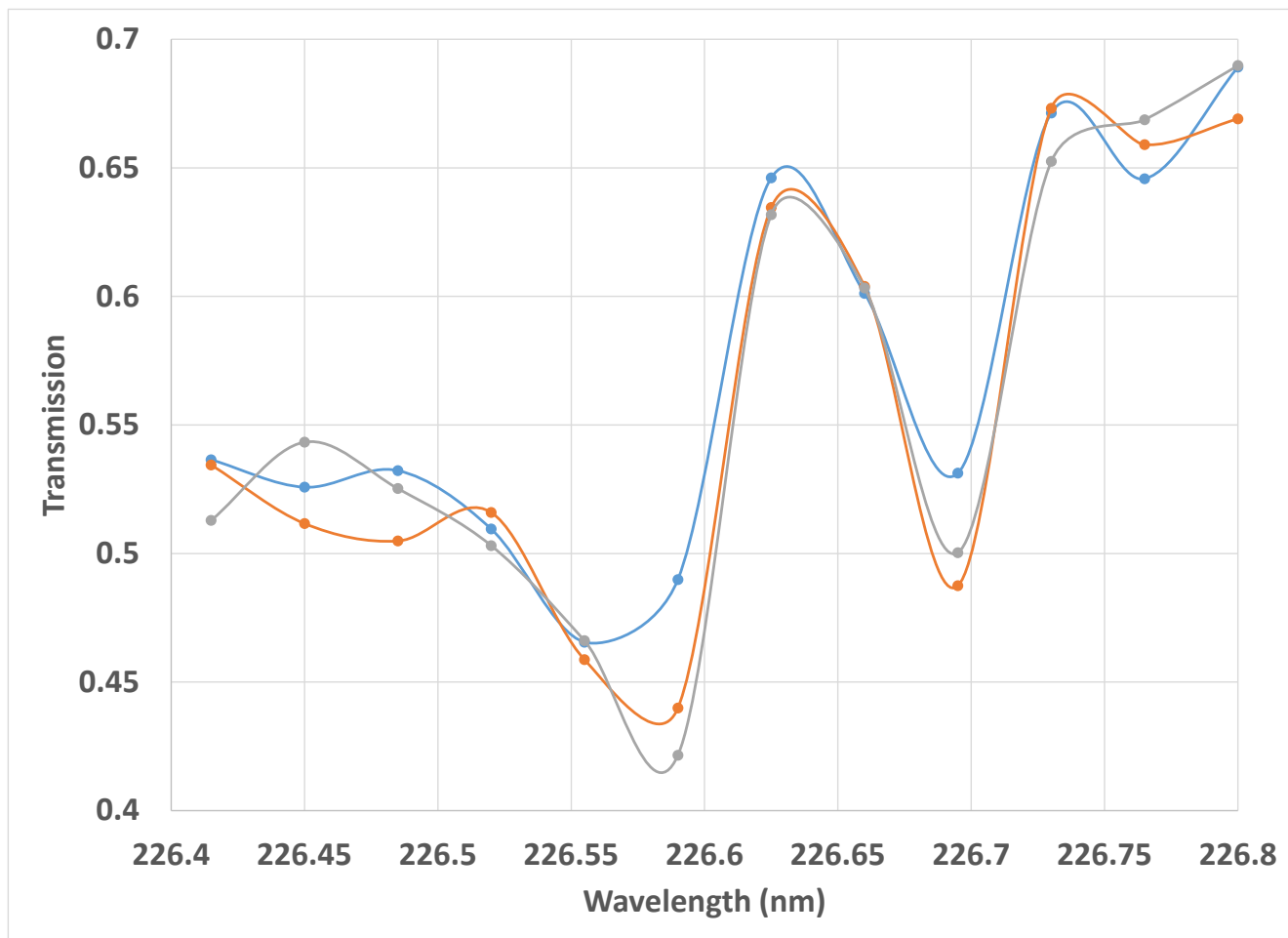


Figure 20. Transmission scans of NO at ~64 ppm-m in the exhaust stack (200 pulses per point).

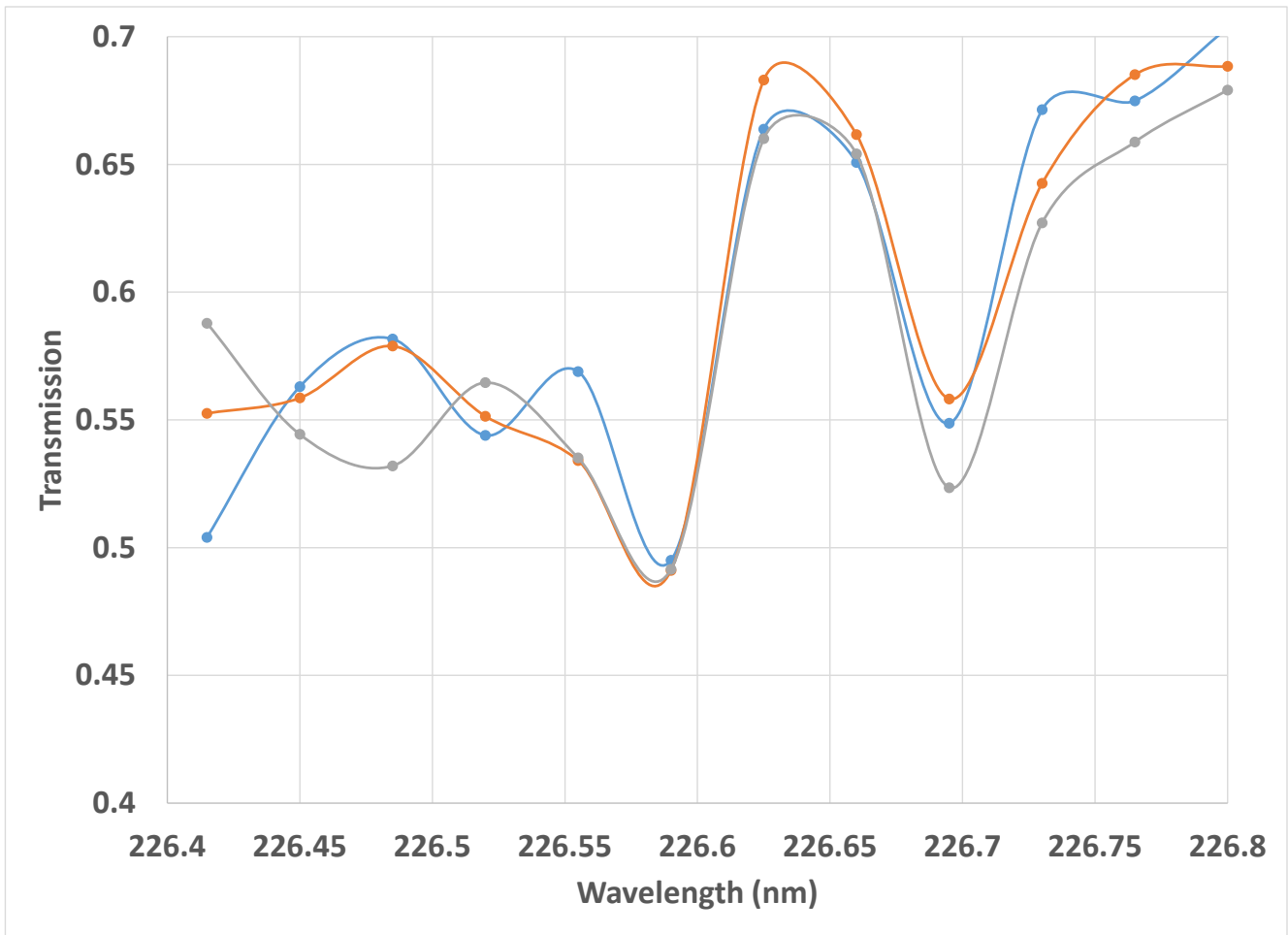


Figure 21. Transmission scans of NO at ~42 ppm-m in the exhaust stack (200 pulses per point).

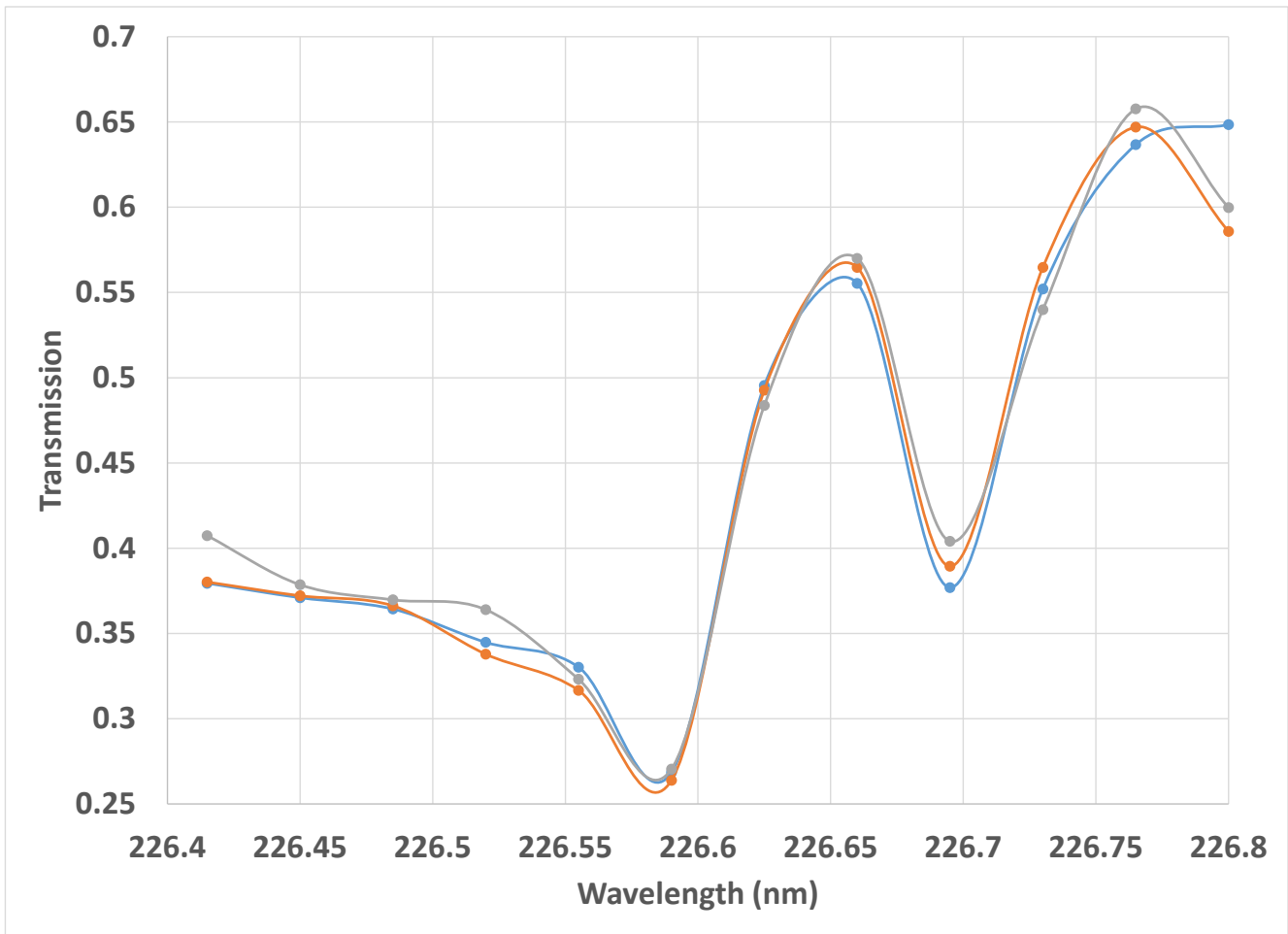


Figure 22. Transmission scans of NO at ~127 ppm-m in the exhaust stack (200 pulses per point).

Figure 21 and Figure 22 are spectra at different concentration length products in the stack exhaust. These show the repeatability of the measurement and the rise in noise with lowering of the concentration.

Accuracy and repeatability are difficult to assess in an outdoor environment like this one. Accuracy and repeatability of the measurements depend on the signal to noise ratio of the UV-DIAL measurements but also depend on the accuracy of the flow speed measurement in the mock-up exhaust stack, on the stability of the exhaust flow (which changes the concentration of NO during the measurement), on the stability of the flow across the flowmeter used for NO monitoring, and on a varying level of NO elsewhere along the laser beam path than in the stack plume. A thermo-anemometer is used to monitor blower speed stability. The absolute reading depends on where in the exhaust plume the wire is placed. Flow speed is continuously logged. It varies substantially in the course of the measurements. If the flow speed measurement is incorrect because of a bad placement in the exhaust flow, it cannot be corrected for. A scale factor should also be added to take into account the spatial distribution of speeds across the exhaust stack diameter. This would raise the average flow speed by values of 10% or more. Good accuracy and repeatability assessments are difficult in these conditions. Accuracy will depend on the referee measurement. *No referee measurement was attempted for this phase of the work.* As a matter of fact, INO has more confidence

in the numbers from the UV-DIAL measurements than from the concentration deduced from the anemometer and flowmeter readings.

The approach used clearly underestimates the concentration-length product as measured by the UV-DIAL approach. The UV-DIAL measurement accuracy also depends on the accurate evaluation of NO in the reference cell.

The measurements show a limiting aspect of scanned UV-DIAL. The concentration must remain stable during a scan. Thus having multiple rapid scans that are then averaged would be better than a slow scan with averaging at every wavelength. But then there is the problem of the repeatability of the wavelength scans. This will be analyzed further at a later date.

Measurements in the mock-up exhaust stack were done at three different concentration, down to an estimated 42 ppm-m (or ~14 ppm in a 3 m diameter stack). Table 1 shows the results for three series of three measurements at the different concentrations. Bear in mind the instability of the exhaust stream. Figure 23 shows the results in graphical format. It is clear that the scale factor between the expected and the computed is off by 10% (slope). An estimated 2% error was added over the 10% scale factor.

Table 1. Results from three sets of scans at different concentrations.

	Expected (ppm-m)	Measured average (ppm-m)	Standard deviation
Concentration 1	127	159	7.3
Concentration 2	61	87	6.9
Concentration 3	42	65	4.3

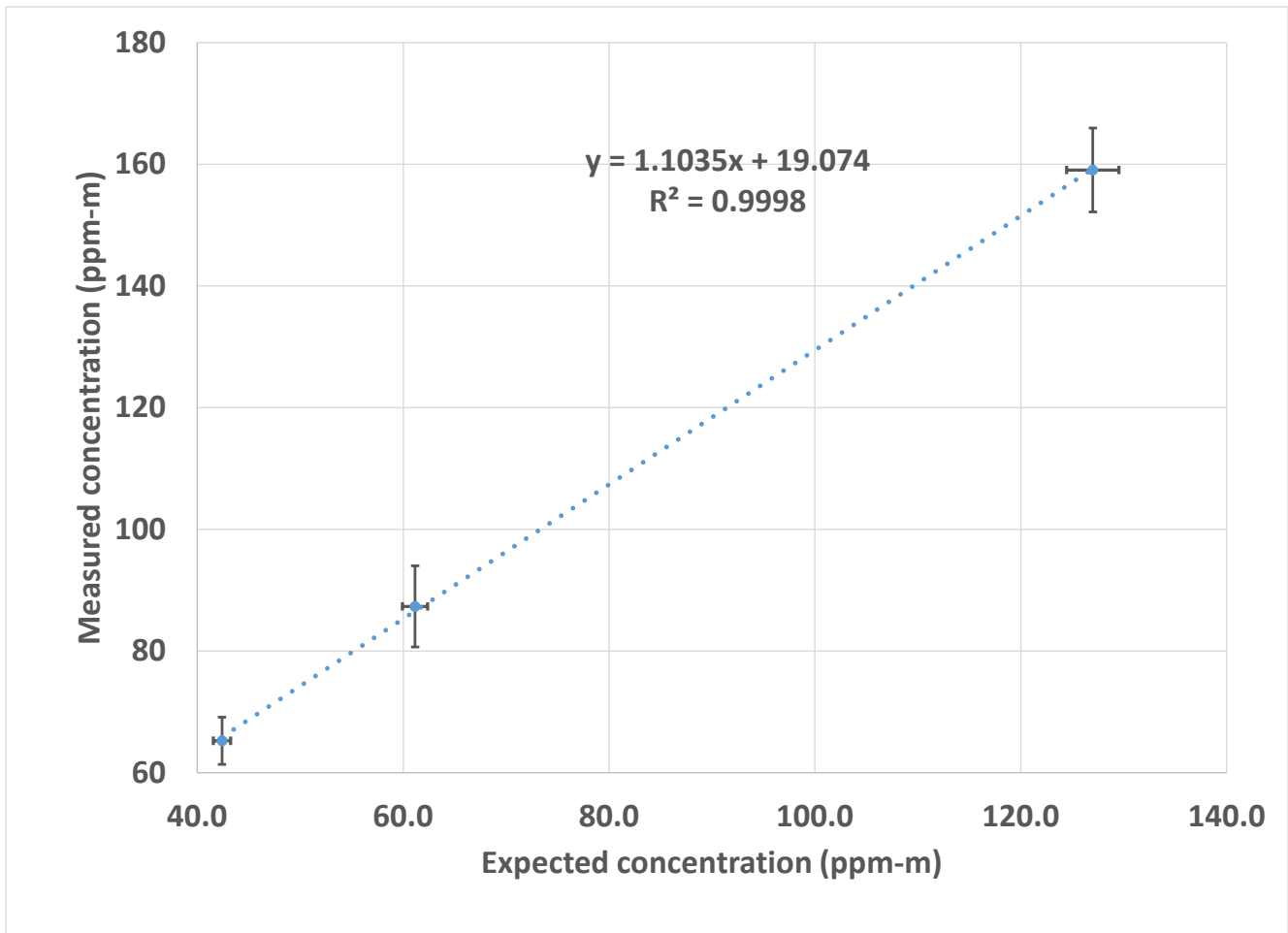


Figure 23. Expected versus measured concentration-length product in mock-up exhaust stack.

Repeatability might need to be enhanced. INO is fairly confident of the accuracy of the DOAS LiDAR approach at ambient temperature. The scans used in this set of measurements take 240 seconds (4 minutes). This is probably too short a measurement time, especially at the lower end of the concentration range. The limit of detection cannot be extrapolated using simple signal to noise ratios since the data is passed through a fitting software. Nonetheless, the standard deviation diminishes with falling concentration. In order to get a limit of detection, an estimate of the minimum detectable absorption is necessary (absorption is not linear with concentration, it is an exponential function). 1% measurable absorption is a reasonable goal. At this absorption level a 0.75 ppm-m concentration-length product is measurable for NO if the 5.5×10^{-18} cm²/molecule cross-section is correct.

Taking multiple scans and averaging the transmission before inputting to the fitting software would enhance the repeatability and accuracy. In order to have a repeatable measurement at 3 ppm-m (1 ppm in a 3 m diameter stack) measurement time needs to be increased and above all scanning rapidly over the selected wavelengths and averaging a series of transmission spectra. Using the 21 minutes measurement time required by USEPA Method 20, the LOD would be much better. It would be in fact very close to the 3 ppm-m LOD required for a 1 ppm LOD in a 3 m diameter stack.

The idea was to show that UV-DIAL at 226 nm was sufficiently sensitive with the available laser power. The proof is there.

6.1.2 NO₂

Figure 24 shows the absorption cross sections for NO₂ in the wavelength range of interest. This first graph is what would be obtained by scanning a very small linewidth laser in this wavelength range, although, contrary to the NO case, the NO₂ linewidths are large and laser linewidth has much less of an influence, except for the last series of lines between 245 and 252 nm (Figure 25). This resembles what is obtained with the INO system. For selectivity, the lines between 245 and 252 nm are preferable, but not for sensitivity.

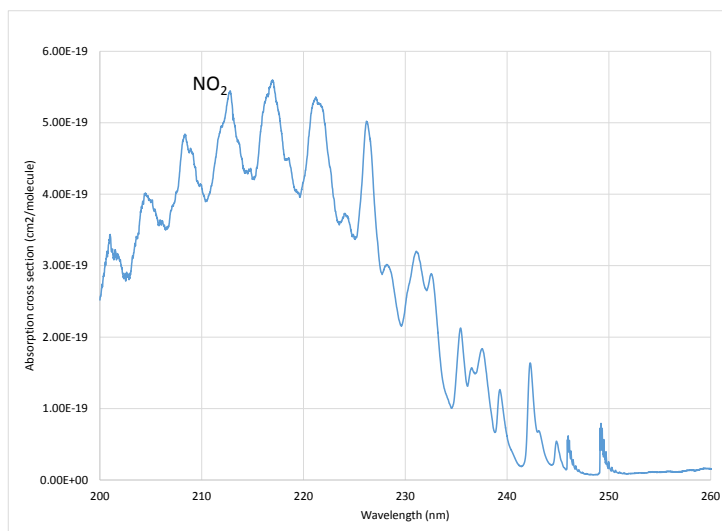


Figure 24. Absorption spectrum of NO₂ from 200 to 260 nm. (taken from reference [6])

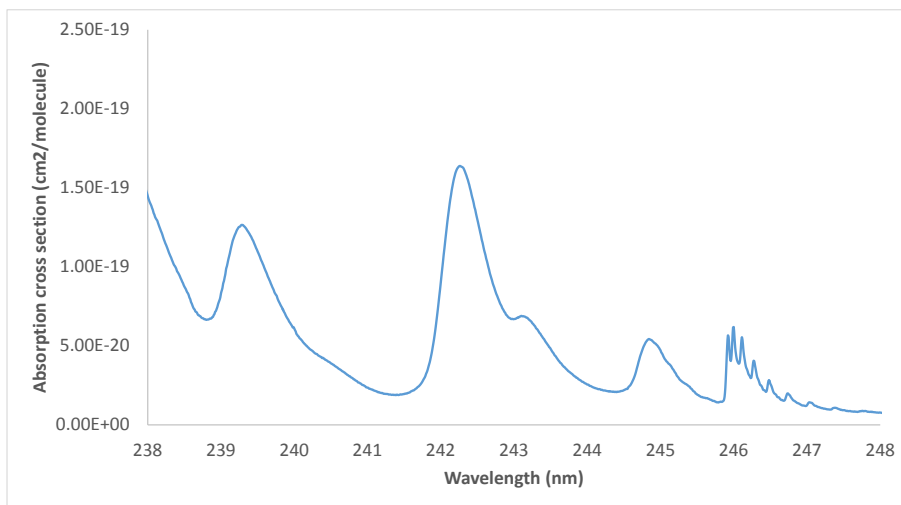


Figure 25. Absorption spectrum of NO₂ from 240 to 252 nm (taken from reference [6]).

The UV-DIAL approach has been described and characterized with NO. The methods described in the NO section will be applied to the measurement of NO₂.

As with NO, the presence of interfering molecular species in and around the stack was investigated. SO₂ and NO₂ have similar types of absorption spectra. Using decimation to measure only at peak and valleys in the NO₂ spectrum would not differentiate it sufficiently from SO₂ at wavelengths below 230 nm. At the more specific wavelengths between 245 and 252, there could be interference from O₂ in the air. Unfortunately INO does not have the high resolution spectra of O₂ necessary to conclude. This leaves the 230 – 245 nm interval. The absorption spectra of SO₂, O₂ and O₃ are shown in Figure 26. O₂ absorbs very little, but does so all along the laser beam path, but there is no absorption feature between 232 and 242 nm, it is the Herzberg continuum. O₃ absorbs more than O₂ and is also in a continuum (the Hartley band) and is the major cause of laser power loss along the laser beam path, and starts to show features at ~242 nm also. O₂ and O₃ have absorption cross sections that vary substantially between 232 and 242.5 nm. SO₂ has features, less intense than NO₂, and it would be the molecular specie that would interfere the most with a multi-wavelength measurement. The absorption cross section for O₂ is enhanced by five order of magnitude and that of ozone is reduced by one order of magnitude to fit on the same graph.

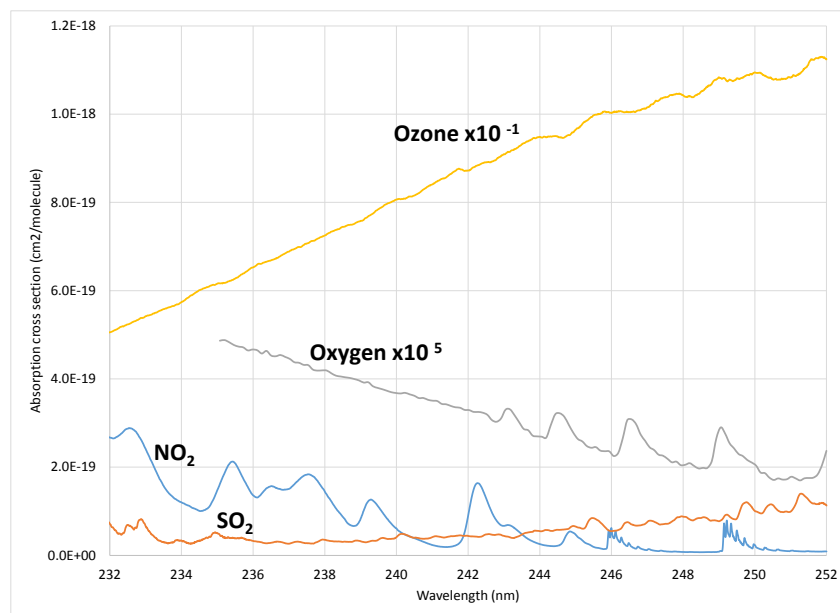


Figure 26. Absorption spectra of NO₂, SO₂, O₂ and O₃ between 232 and 252 nm.

In Figure 25, the maximum cross section for NO₂ is $\sim 1.6 \times 10^{-19} \text{ cm}^2/\text{molecule}$. As explained in the NO section, the differentials in cross-section are the important parameter. The maximum differentials of $\sim 3 \times 10^{-19} \text{ cm}^2/\text{molecule}$ for NO₂ in less than 5 nm (226 – 230 nm) are not that huge. The differential is almost as large in the 240 to 246 nm interval, although the absolute absorption will be much different. This is where the measurements will be performed. The correct value is measured with the reference cell. The other mentioned molecular species do vary significantly in absorption cross section, and can have an important impact on the concentration retrieval of NO₂. For this reason, multiple wavelengths are used and the measurement results are inputted to the DOASIS software that retrieves the concentration from the exhaust stack measurements at these multiple wavelengths. The multiple wavelengths are chosen in the 240 to 246 nm range at an interval such that the laser wavelength is close to the maximum and minimum in absorption cross section when scanned. The interval over

which the scan is made cannot be too large, the extinction coefficient varies rather rapidly with wavelength in this spectral range.

Figure 27 shows the high resolution spectrum of NO₂ in the reference cell with 1% NO₂ (1000 ppm-m) (average of 100 pulses per point and a wavelength step of 0.05 nm). It is very similar to the spectrum from the literature and the level of absorption is in line with the cross-sections found in the literature.

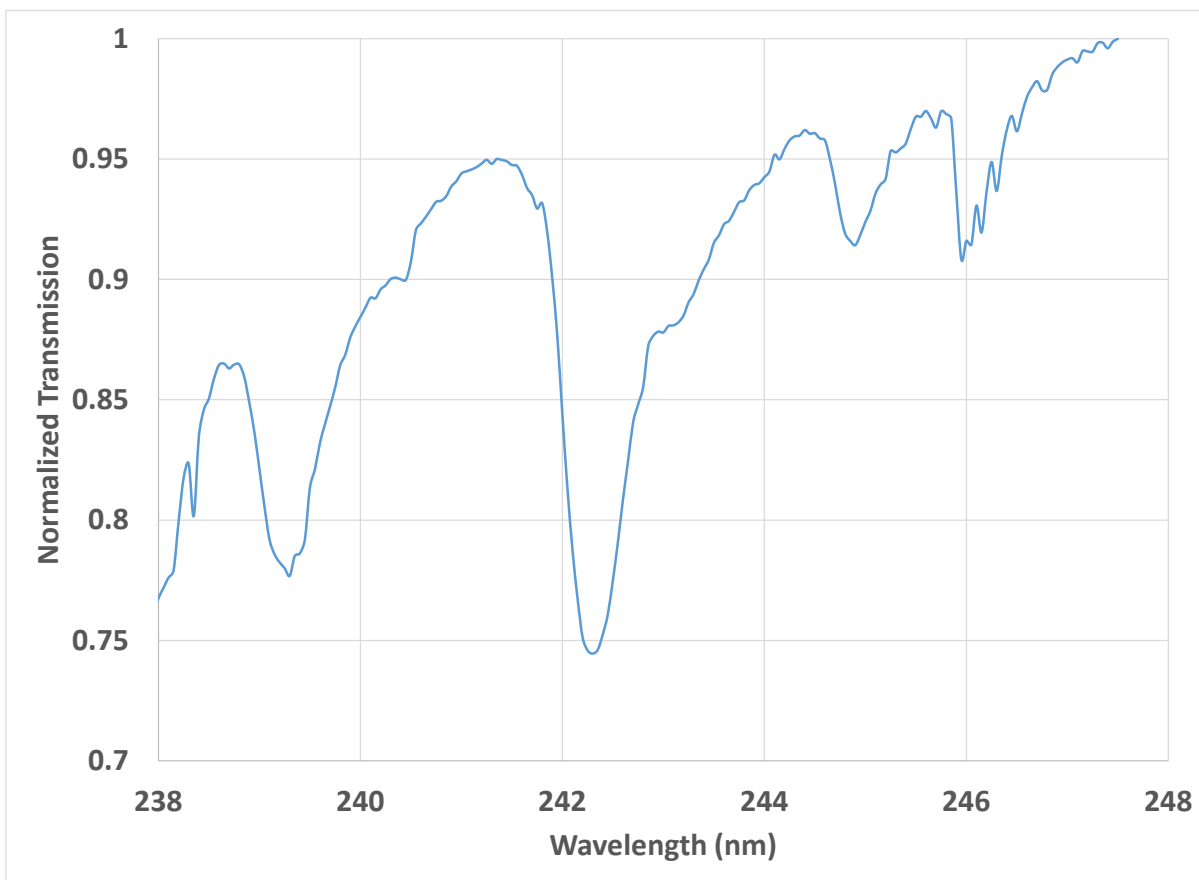


Figure 27. High resolution spectrum of NO₂ in reference cell.

Figure 27 shows spectra measured through the reference cell with 1% NO₂ in nitrogen at atmospheric pressure. The concentration in the cell is known, since a calibrated gas bottle is used in flow mode. This measurements points are averaged over 200 pulses.

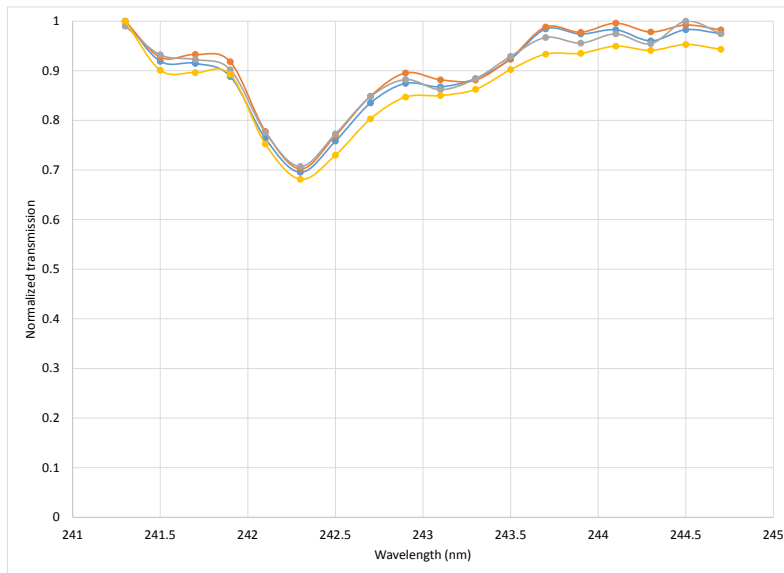


Figure 28. Transmission spectrum in reference cell at 1000 ppm-m.

The wavelength interval over which the measurements are made is large. In this example 3.4 nm is covered. The laser beam pointing direction can shift significantly during the scan. This can explain the lack of repeatability in the reference spectra if the laser beam wanders on the detector surface or even if it happens to partly wander off the detector surface, even slightly. A shift in laser pointing changes the overall system sensitivity, both for the reference cell and the LiDAR return, skewing the spectra differently for the reference and the LiDAR return. This problem was tackled as shown in the high resolution spectra of Figure 27. In the example of Figure 28 it is clear that the spectra are not totally in line with the spectrum found in the literature, the first bump at the lower wavelength end being absent in the literature.

Measurements were attempted in the mock-up stack at ambient temperature. Working with NO_2 is difficult because it is highly reactive and transforms at relatively high ambient temperature. Generating a flow, outdoors, from a calibrated gas cylinder is challenging when the temperature drops. Most of our attempts were made in the fall with temperatures below 10°C . The gas cylinder was heated, as was the air blown through the mock-up exhaust stack. In spite of these precautions, no NO_2 made it through the tubing from the cylinders to the exhaust stack, as measured with the UV-DIAL platform. The platform is less sensitive for NO_2 than it is for NO , but at the expected concentrations, the measurements should have been successful. The ambient temperature mock-up stack was inefficient at generating a flow of measurable NO_2 . It is known that NO_2 molecules tend to combine and to form dimers at low temperature. The resulting N_2O_4 specie has different absorption features and thus cannot be measured using the same reference spectrum. There is thus no sensitivity estimate for NO_2 in the ambient temperature mock-up stack to show for this campaign. INO did perform NO_2 measurements in other campaigns. The measurements in this campaign were to show enhanced sensitivity because of platform enhancements. Sensitivity can be inferred from the measurements in the gas cell and those of NO in the mock-up stack. Moreover, there are lessons learned.

The first lesson learned, clearly, is that generating an outdoors flow of NO₂ is better performed through combustion unless the whole apparatus is heated to a high enough temperature. The second is that a very sensitive and accurate referee measurement, other than measuring the inputted flow rate from a calibrated gas cylinder, is necessary. The third lesson learned is that a spectrum must be measured in a very short time. The number of wavelengths used in a scan must be minimized and multiple rapid scans need to be averaged. The scans must be done within a few seconds or less. Skewed scans, outliers, must be detected and rejected. And lastly, the pointing stability of our platform must be improved or the platform modified. These two last lessons are now explained in more detail, with measurement examples.

The LiDAR returns are similar to those measured in the case of NO, as shown in Figure 29, but there are differences. There is no NO₂ flowing in the exhaust stream here and the normalized return curves differ from wavelength to wavelength. The wavelengths shown cover 10 nm. This can be explained by the pointing stability when laser wavelength is scanned. A change in pointing causes a change in overlap between the laser beam and the receiver field of view. This change in overlap generates a structure very alike a spectrum when the lidar waveforms are processed to generate an absorption spectrum. This unwanted artificial structure skews the results and diminishes the sensitivity. What is seen here is practically no change between 221 nm and 229 nm, only a slight rise in overlap at greater distances. The maxima are at the same distance from the platform. Between 229 and 233 nm, the rise is more significant, indicating a more substantial shift in the overlap function. In the case of the measurement at 231 nm, the laser beam was pointing such that the maximum in the overlap shifted towards the platform (closer range). The processing algorithm works on the hypothesis that the overlap between laser beam and receiver field of view does not change from wavelength to wavelength. If it does, the measured absorption spectra from the exhaust stream will be nowhere near the reference spectra, skewing the results. This could be accounted for by measuring the changes in overlap before an absorption measurement, as was done here. *This is an enhancement developed in this campaign.*

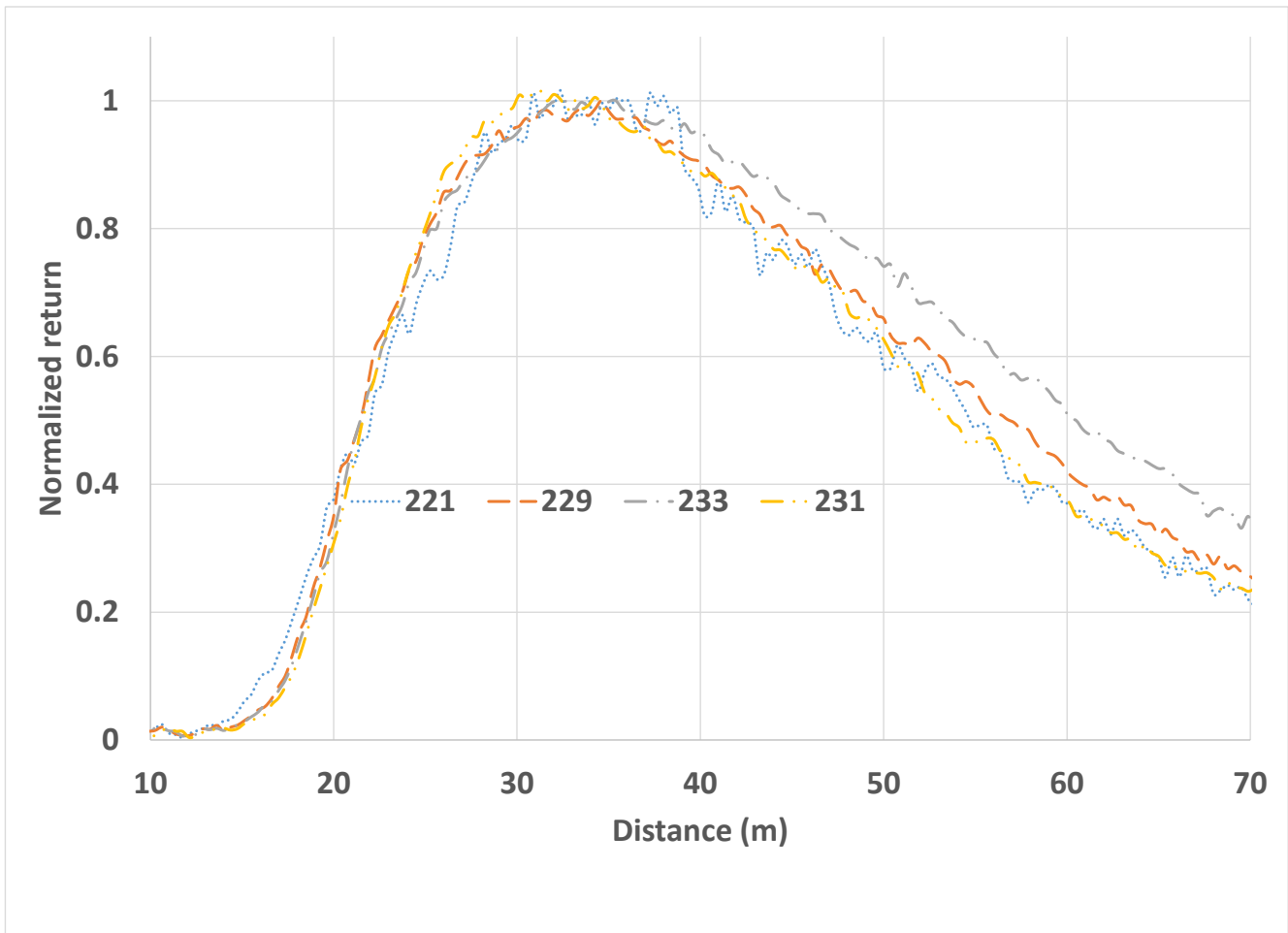


Figure 29. Overlap functions for different wavelengths.

There are instances where artifacts cannot be accounted for. An example is given in Figure 30. In this case, the change in overlap seems extreme. This is a different set of measurements than that of Figure 29. In this case, the curves were normalized through a reflection at the end of the laser beam path (the peak at the end of the curve). The curve at 227 nm shows a very strong peak near 22 or 23 meters from the platform. A peak that does not occur at other wavelengths. This peak is most probably due to a gust of wind transporting a concentration of dust different from the ambient air. A significantly different concentration. The method relies on the fact that the concentration of particles in the air is the same all along the laser beam path or, at the very least, that it is stable with time, so it can be folded into the overlap function. Remember that the measurement is actually an average of 100 or 200 curves measured every 100 ms for 10 to 20 seconds. A change in only one of these curves, at the distances where data is taken for the processing, will skew the measurements. *Detecting these events and removing them from the data is another enhancement.*

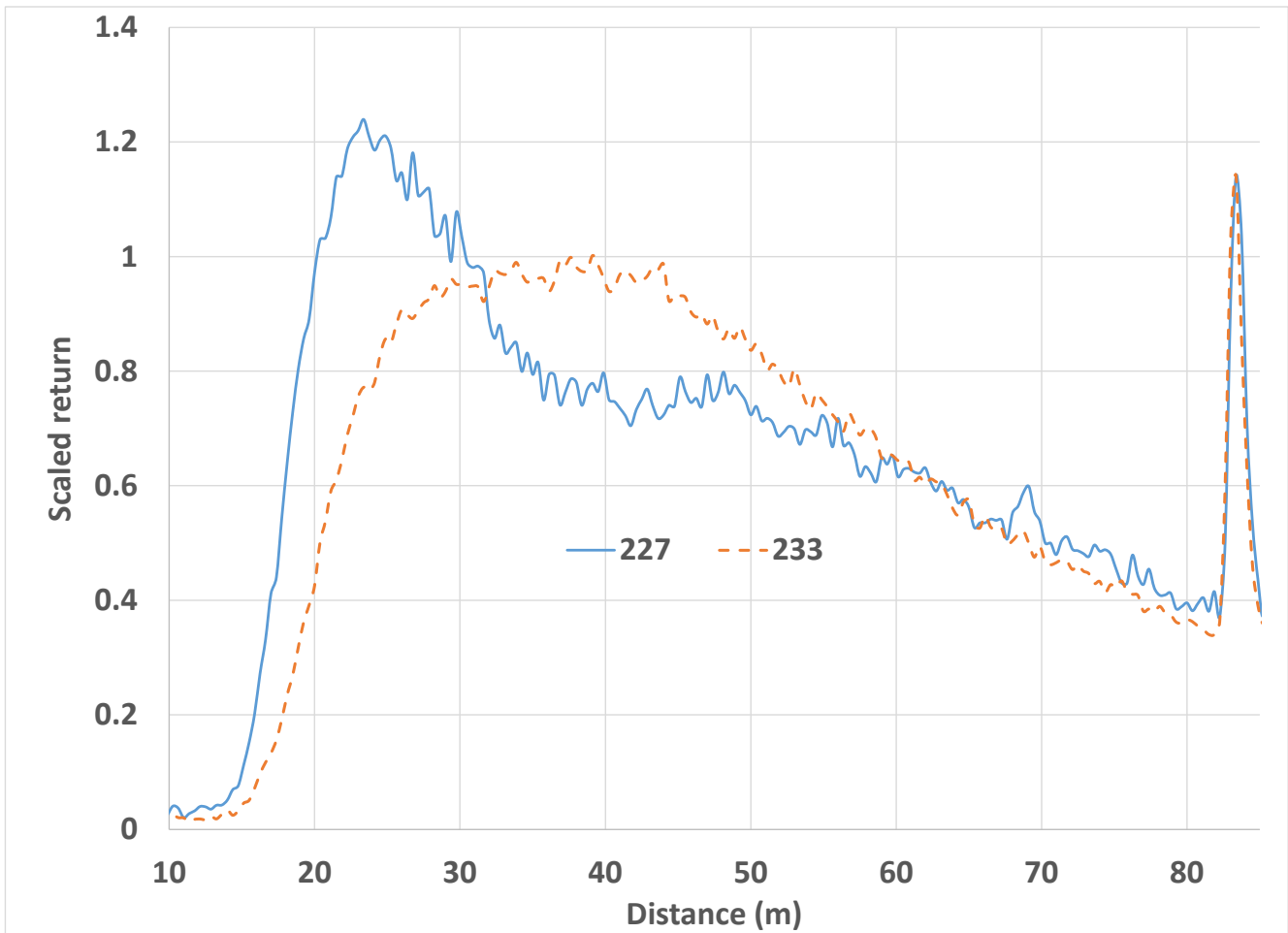


Figure 30. Skewed overlap function.

Considering the results, the quantitative analysis made for NO cannot be repeated here for NO₂. Other measurements are required. It is possible, on the other hand, to estimate the potential sensitivity. If the reasonable hypothesis is made that 1% of absorption is measurable, then 25 ppm-m is the ultimate sensitivity (or a ~8 ppm concentration across a 3 m stack). This seems rather high for detecting NO₂. One would need to go down to 0.1% of absorption to detect 2.5 ppm-m (or ~1 ppm across a 3 m stack) or 0.01% to detect 0.25 ppm-m. This would be extremely challenging with the UV-DIAL platform. Stronger absorption features would be preferable, if they can be found.

7 CONCLUSION / BEST PRACTICES

The stated goal of this project was to demonstrate the use of a UV-DIAL prototype for the measurement of NO_x. The measurement campaign was done at INO on an instrumented mock-up stack in realistic Canadian weather conditions. This gave insight into the use of the technique for concentration measurements of NO_x from pipeline compressor station exhaust stacks. It was determined that:

- 1) NO₂ has a chemical behavior that is troublesome near typical ambient outdoors temperature, especially under 22°C (thus a good part of the year in Canada), an hindrance for the UV-DIAL technique as used and for the referee measurement of NO₂ in the exhaust stack mock-up;
- 2) The stability of the NO₂ reference concentration is difficult to ascertain, the equilibrium between NO, NO₂, N₂O₄ and other compounds in the reference cell and in the mock-up exhaust is often unclear;
- 3) Designing, producing and using a stable optical NO₂ reference cell is a challenge;
- 4) A controlled environment (temperature) is required for the reference measurement of NO₂;
- 5) A reference cell with a constant flow of gas from a calibrated cylinder is required;
- 6) Using a reference measurement on a mock-up stack that uses combustion of natural gas in possible addition to the gas from a calibrated cylinder would be preferable;
- 7) It is possible to measure NO and NO₂ from a stand-off distance directly at the output of an exhaust stack by the UV-DIAL technique;
- 8) It is possible to measure NO and NO₂ in a combined sequence of UV laser wavelength scanning;
- 9) Optimizing the measurements implies selecting a subset of wavelengths that enhances the uniqueness of the signature for both NO and NO₂;
- 10) Sensitivity was, in part, limited by sub-optimal control of the laser pointing;
- 11) Calibrating the LiDAR overlap functions with respect to wavelength before the concentration measurements and adapting the data processing mitigates part of the problems;
- 12) Detecting and removing outliers caused by instabilities in the particle concentration along the beam path mitigates some of the instabilities;
- 13) Slow mechanical wavelength scanning, as done here, is not the most appropriate form of measurement because of the instability in LIDAR return and in the NO_x concentration-length product;
- 14) The instabilities in LIDAR return and in concentration along with the slow wavelength scanning will ultimately limit the prototype sensitivity;
- 15) Single shot whole spectrum measurements would be the best LIDAR approach;

The points above summarize our conclusions. Although INO was able to measure NO and NO₂ (in this last case only in the reference cell in this particular campaign), the prototype is far from optimal. There are three major drawbacks/hindrances. The first is the speed at which the laser wavelength is scanned. The laser wavelength must be scanned across the entire set of wavelengths within a fraction of a second in order to minimize the effect of instabilities in LIDAR return or in the NO_x concentration along the laser beam path. This is not trivial. INO is working on a faster version of the measurement, in order to “freeze” the measurement in as short a measurement time as possible.

The second is the reference cell for NO₂. In order to have a good reference, the concentration of NO₂ in the reference cell must be stable. But multiple parameters affect the stability of the concentration. INO found it was helpful to continuously flow a small amount of calibrated gas in the cell. The parameters that affect the stability are: total dose of UV laser radiation, cell temperature, temperature of the calibrated gas cylinder, temperature of the tubing and flowmeters... This will be a problem for a fieldable system. The reference cell and the reference cell control system (cylinder, flowmeters, tubing, pressure gages ...) will need to be controlled in temperature. This will make for a much more complex system than anticipated. It could be worthwhile to think of another type of wavelength reference, one that would be more stable with temperature and more amenable to field use. This could be an interference filter type sub-system or a temperature stabilized solid etalon. Or a reference cell with a different, more stable gas having an absorption spectrum very similar to that of NO₂.

The third is the mock-up stack used for testing. INO attempts to create flows of known concentration using calibrated gas cylinders and calibrated flow meters along with precise measurement of the main flowrate. Inputting NO_x into an ambient temperature stream is not trivial. The stream needs to minimally be warmer than 22°C. This requires heating of the input stream. But also of the whole chain, from the calibrated gas cylinder to the main flow stream. This is not optimal and does not guarantee that the computed concentration is actually what is coming out of the exhaust of the mock-up stack. A better solution would be to use a natural gas burner. Since this usually does not create a sufficient concentration of NO₂, it could be seeded with additional NO₂. A referee measurement would then measure the amount of NO₂ in the main stream. A referee measurement such as chemiluminescence or across stack absorption using continuous wave UV or IR-DOAS.

In conclusion, it was possible to determine a detection limit for NO₂ but without any actual measurements of exhaust stack NO₂ because of the instability of the mock-up stack set-up and the inadequacy of the NO₂ flow control. It was shown that measuring both NO and NO₂ in a single scan was possible. Using the measurements, it was determined that for a reasonable 1% absorption of the laser beam in the exhaust plume, the sensitivities would be 0.75 ppm-m and 25 ppm-m for NO and NO₂ respectively. This would require measurement times longer than those used here. The limit of detection of NO₂ is not sufficient and would require major enhancements in the UV LiDAR platform if we keep using the same approach. A different analytical strategy will need to be used for the sensitivity to reach the adequate level. One way would be to reduce the number of wavelengths used and to improve the laser repetition rate. Finally, as the measured LOD depends on the stability of the emission source, it will be necessary to add a reference instrument to the mock-up system in a future implementation.

8 EXTENSION PLAN

Results and conclusions generated from this work will be available to the industry through PTAC. In accordance to contract, dissemination of the results will also be completed at a later date during next calendar year (2016), most probably at the PTAC Air Issues Forum event.

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