STANDOFF STACK EMISSIONS MONITORING USING SHORT RANGE LIDAR
Jean-Francois Y. Gravel, Francois Babin*, Martin Allard
INO Québec, QC, G1P 4S4, Canada.*Email: francois.babin@ino.ca

ABSTRACT
There are well documented methods for stack emissions monitoring. These are all based on stack sampling through sampling ports in well defined conditions. Once sampled, the molecules are quantified in instruments that often use optical techniques. Unfortunately sampling ports are not found on all stacks/ducts or the use of the sampling ports cannot be planned efficiently because of operational constraints or the emissions monitoring equipment cannot be driven to a remote stack/duct. Emissions monitoring using many of the same optical techniques, but at a standoff distance, through the atmosphere, using short range high spatial resolution lidar techniques was thus attempted. Standoff absorption and Raman will be discussed and results from a field campaign will be presented along with short descriptions of the apparatus. In the first phase of these tests, the molecules that were targeted were NO and O2. Spatially resolved optical measurements allow for standoff identification and quantification of molecules, much like the standardized methods, except for the fact that it is not done using in stack sampling, but directly in the plume formed by the emissions from the stack.

1. INTRODUCTION
The standoff monitoring for NOx , SOx, COx, particulates and O2 emissions from compressor stations is of great interest for pipeline operators. New regulations for more testing is a strong motivator behind this work.

The well documented methods for stack emissions monitoring are all based on stack sampling through sampling ports in well defined conditions. Once sampled, the exhaust gases are analyzed by the usual laboratory instruments that are often based on optical techniques. Following a first test phase on a TransCanada compression station where NO, CO2 and O2 were successfully measured, the work presented here mainly focuses on standoff absorption and Raman for NO and O2 measurements. Results obtained from intermediate scale simulated stacks will be presented along with description of the apparatus and procedures. Spatially resolved optical measurements allow for standoff identification and quantification of molecules, much like the standardized methods. However this it is not done using in stack sampling, but directly in the plume formed by the emissions from the stack.

2. METHODOLOGY
To evaluate the potential of the approach in a simple but controlled way, two different systems were used, one using a propane burner, the other one a PVC tube. A versatile spectroscopic LiDAR breadboard system based on a pulsed tunable laser source is used for the measurements. Installed in a mobile laboratory located about 45 m away from the mock-up stacks, measurements are performed outdoors in a parking lot.

The first mock-up stack is based on a propane gas burner commonly used for heating. The high temperature exhaust generated by this burner is of particular interest because it creates a depleted oxygen region. Oxygen analysis is then performed by UV-Raman LiDAR.

The other system is based on a 4 inches PVC tube connected to a commercial blower. This represents the smallest stack size expected to be encountered on a compression station plant. The blower is used to create a high velocity gas output at one end of the tube. An injection port is also added between the blower and the PVC tube exit. A controlled NO gas mixture can therefore be introduced within the flowing air simulating a NO emission source. Nitric oxide analysis is then performed using an absorption method close to UV-DiAL.

In both cases, the probing laser is aimed directly over the mock-up stack exit.
For Raman measurements, the 355 nm output of the Nd:YAG source is used for excitation.

For absorption measurements, the third harmonic of the Nd:YAG laser is used as the pumping source for a tunable Optical Parametric Oscillator which is then frequency doubled to generate deep UV light in the 225-230 nm range. The wavelength is precisely selected to match an absorption feature of NO molecule.

Signal collection is achieved through a 20 cm aperture telescope routed either to a filter based 2 channel wavelength selector with PMTs or to a compact monochromator also equipped with a PMT. Both options allow for full waveform measurements of the LiDAR returns.

**Absorption measurements**

By opposition to traditional DiAL methods that require high stability of the wavelength output, the wavelength of the laser is not alternated between ON and OFF transition wavelengths. Making the hypothesis that the NO emission in the stack exhaust is approximately constant within a few minutes required for the measurement, the wavelength is slowly scanned across an absorption feature. The absorption cross section of NO is at the same time monitored thanks to a laser pick up that goes through a NO reference cell followed by a photodetector.

All the LiDAR curves obtained at each wavelength are normalized to a reference wavelength lidar 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 of the lidar curve. For each LiDAR return curve (for each wavelength), the ratio of the averaged values after the stack over the averaged values before the stack 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. 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 used as inputs for the DOASIS software.

**Raman measurements**

For the analysis of O$_2$ in the propane burner exhaust, Raman returns for oxygen and nitrogen (for normalization) are collected. Ratio of O$_2$ signal over N$_2$ signal, indicates the variation in O$_2$ concentration as N$_2$ is expected to be constant within the atmosphere as well as within the exhaust gas.

3. RESULTS

A portion of the NO absorption features can be found in Figure 1. This spectrum has been measured in the NO reference cell. The absorption is measured throughout all of the experiments which means that at any wavelength used within a scan, the absorption cross-section is known.

Figure 1. NO absorption spectrum as measured with the INO UV-DiAL platform in a reference cell uncorrected for baseline effects.

Scanning the laser wavelength across the absorption feature results in LiDAR traces used to build an absorption spectrum that reflects the presence of NO. In the case of Figure 2, it is obvious that the blue dotted line is returned by a wavelength that is closer to an absorption maximum than the wavelength represented by the orange line. It is also clear that the absorbing region (stack simulator) is located approximately 46 m from the LiDAR.
Eleven different wavelengths were used for scanning of the absorption line from the stack plume. Using the reference cell for cross-section evaluation, the results were inputted to the DOASIS software which computed the best fit to retrieve a concentration in the stack output plume. Figure 3 shows the absorption results computed for both the reference cell and the exhaust stack.

Tests were performed at 3 different nitric oxide concentrations and 3 replicates. Detailed results are expressed in Table 1.

It is to note that there is a large uncertainty in the expected values that is related to the velocity measurements and blower stability. More experiments need to be done to properly evaluate the accuracy and repeatability of the approach. However, a rough estimate of the limit of detection can be made using the standard deviation of the measurements times 3 thus giving 11 ppm-m for a 3min40s measurement.

For Raman measurements of oxygen, the propane burner exhaust was used. Full waveform return of both O$_2$ and N$_2$ signals analysis showed a clear decrease in signal at approximately 44 m. This dip is mostly related to the lower density of the hot exhaust gases; around 600°C (see Figure 4).

Taking each point of the O$_2$ curve and normalizing it by N$_2$ curve allow to determine the relative decrease in oxygen concentration related to the combustion process of the burner. Even at lower air density, N$_2$ concentration should remain constant.
In this case, the drop in concentration is ~ 9% of the normal 20.9% O₂ in air which correspond to about 19% in air. Here again using the 3 standard deviation approximation to estimate the limit of detection gives 0.4% O₂ within a 13 minutes measurement.

4. CONCLUSIONS

It is not easy to simulate real stack exhaust conditions at a small but representative scale. However two different approaches were proposed and two different spectroscopic LiDAR approach for monitoring of the NO emission and determination of O₂ concentration were tested. It has been demonstrated that it is possible to achieve stack emission monitoring from a distance using spectroscopic LiDAR to analyze the exhaust gases. The quantitative potential of the approaches have been demonstrated and limit of detection for NO was estimated to 11 ppm-m for 3 min 40 s measurement time. For O₂, it was determined that the lowest variation in concentration that could be detected would be roughly 0.4% on a 13 min basis. Parts of the mock-up would need to be improved to allow better evaluation of the accuracy and precision of the methods used above. An important hardware limitation of the approaches was related to the lack of spatial resolution that would be needed for very small diameter stacks. For example, the 6 ns pulse length laser would need to be replaced by a shorter one to get better spatial resolution.

Although this work is already interesting from a scientific point of view, it is important that the approaches be accepted by the industry and even more so by regulators. For this, at least two major aspects need to be addressed. First, the measurement is done in the plume just above the stack. This way of doing a measurement has not been yet documented in the standard monitoring methods, although there is a German standard for lidar plume monitoring. A clear assessment that the open path sampling through exhaust gases just above the stack is equivalent to an upstream sampling done from a port located inside the stack needs to be made. Second, it is clear that the concentration value found in the plume needs to be related to a mass emission rate. To achieve this, one needs the size and aspect of the stack as well as the velocity of output gases. The accepted method asked for the velocity to be measured directly in the stack. However, it is clear that it makes no sense to do remote monitoring if someone still need to access the sampling ports of the stack to measure velocity. A project is ongoing for evaluating possible approaches to do this measurement by another standoff method.