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A novel lidar system for CH₄ and VOC's detection of fugitive emissions and environmental monitoring

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ABSTRACT

This study presents an overview of the recently results obtained by a novel concept of a lidar to remotely monitor methane and volatile organic compound including aerosols and fugitive gas emissions from pipelines, waste disposal areas and tankages. The system works based on Raman and fluorescence scattering principles by emission of a 355 nm beam (3rd Nd:YAG harmonic) and detection of the wavelengths at 355 nm (elastic), 353 nm (oxygen + nitrogen rotational Raman) and 396 nm (methane vibrational Raman) and alternatively the system can be switched to a fluorescence lidar based on a 32-channel PMT coupled to an spectrometer to be able to observe fluorescence scattering caused by VOC's and aerosols. This paper shows a summary of the results obtained in the preliminary campaigns, which were carried out under different conditions to be adopted as benchmark for the system performance regarding detection limits, calibration capabilities, and time vs range resolution, in order to optimize the system performance.

Keywords: Methane, Fugitive Emissions, Rotational Raman, Fluorescence

1. INTRODUCTION

Fugitive emissions, defined as unintended or irregular leaks of gases and vapors, are an important source of air pollution that is difficult to monitor and control.¹ Within industrial facilities such as oil and gas processing plants, fugitive methane emissions can be a significant source of greenhouse gas emissions^{2,3} and as an important category to take into account when dealing with GHG emission budgets by environmental agencies.⁴ For instance, the most recent estimate from the IPCC indicates that total waste emissions (including landfills and wastewater treatment) constitute anywhere from 35 to 69 Tg CH₄ yr⁻¹, out of a global methane source budget of 500 - 600 Tg CH₄ yr⁻¹.⁵ In Brazil, as in other countries, there are specific regions with high concentration of industrial activities, as well as agribusiness, and showing high population density. These sites, including megacities and industrial sites, are growing in size and economic activity. At the same time, there is a remarkable growth in concerns about the environmental issues associated with these activities. Among the necessary information to be supplied in order to mitigate environmental and health consequences of the economic activities is real time and trustable information on emission rates of air pollutants. Such information constitutes an essential tool for industries and environmental authorities. Detection of fugitive gases is often difficult because the gaseous plumes emanating from individual sources are often intermittent and at low concentrations relative to ambient values of 1.7 ppmv. Some current methods for detection of fugitive emissions, which most often involve using survey teams equipped with handheld vapor analysers or infrared cameras, are generally labor-intensive and necessarily intermittent.⁶ Optical remote sensing techniques as lidar can attend the need for real time and trustable information on fugitive emissions. These techniques are non-intrusive, of relative simple construction, thus demanding less maintenance, and are able to provide data from distant locations with a high spatial resolution, typically up to 20 km from the measuring local, and 3 to 4 m long segments. Besides, information

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on different pollutants can be obtained simultaneously by adequate optical arrangements and data treatment methods. The technique can supply adequate information at lower costs and less effort than other techniques. In this work we present the first results of a new lidar design to detect atmospheric methane and volatile compounds aiming to monitor fugitive emissions at storage and distribution gas arrays, waste disposal areas. The system is based on the detection of the wavelengths at 355 nm (elastic), 353 nm (oxygen + nitrogen rotational Raman) and 396 nm (methane vibrational Raman) and alternatively the system can be switched to a fluorescence lidar based on a 32-channel PMT coupled to an spectrometer to be able to observe fluorescence scattering caused by VOC's and aerosols as well. While in the past pure Raman lidar systems for this purpose were used, the combination with fluorescence is unique.^{7,8}

2. SYSTEM DESCRIPTION

The lidar system was designed to allow the measurements of aerosol, methane and organic compounds. The lidar is based on a tripled Nd:YAG laser with a 20 Hz repetition rate, and pulse energy of 70 mJ at 355 nm. The backscattered light is collected by a 30-cm aperture Newtonian telescope. The optical signal is delivered to the detection module by means of an optical fiber.. The lidar contains two separate detection modules. One is a three - channel module (TCM) for detection of elastic backscatter at 355 nm, rotational Raman backscatter at 353.9 nm and methane vibrational Raman scattering at 396 nm. Another one is a 32-channel spectrometer for the fluorescence measurement. The optical fiber can be switched between the detection modules for specific tasks. The optical signal from the fiber is collimated in the TCM by a silica lens and collimated beam is separated for the spectral components by two dichroic mirrors. The spectral components are isolated by the interference filters and detected by R9880 PMTs. The outputs of the detectors are recorded at 7.5 m range resolution using Licel transient recorders that incorporate both analog and photon-counting electronics. The full geometrical overlap of the laser beam and the telescope field of view (FOV) is achieved at approximately 500 m height for 1.0 mrad the field of view used. The TCM allows both Mie - Raman aerosol⁹ and Raman methane measurements. The interference filter (Alluxa, CA, USA) centered at 393.9 nm of 1 nm FWHM selects the group of rotational Raman lines of oxygen and nitrogen near the isosbestic point, to minimize the temperature dependence of efficient scattering cross section¹⁰ The use of rotational Raman scattering allows to increase the backscattered power to more than factor 10 comparing to vibrational Raman nitrogen component at 387 nm. Moreover, separation of 353/397 nm wavelengths by dichroic mirror is easier than 387/397 nm. Suppression of 354.7 nm elastic scattering by rotational Raman filter is above 10^4 , so two normally installed interference filters were used together to provide more than 8 orders of magnitude of rejection of the elastic signal. The interference filter (Alluxa, CA, USA) in the methane Raman channel was centered at 395.7 nm. The filter bandwidth was 0.3 nm and the peak transmission was above 80%. Suppression of 355 nm radiation was specified by the manufacturer to be above 12 orders. Due to the low methane Raman backscatter the measurements were performed in the night time only. The 32-channel Licel spectrometer uses 32-channel PMT operated in photon-counting mode in combination with grating spectrometer, making possible the measurements in 378 - 555 nm spectral range with 5.5 nm resolution.

3. RESULTS OF TESTS

3.1 System Assembly

Figure 1 shows the present aspect of the complete system, with all components assembled. The laser source consists of a Nd:YAG laser (Q-smart 450 model from Quantel SA) operating at 355 nm, with a fixed repetition rate of 20 Hz and energy per pulse of 400 mJ at the fundamental wavelength. The set up first step was the energy pulse and laser power check. The second step was the signal detection of three photomultiplier tubes (PMT). The PMT Raman detection box was designed with three channels (355, 353 and 396 nm). One channel for detection of elastic scattering, another one for detection of oxygen plus nitrogen rotation Raman, which will serve as a reference signal, and the last one for the detection of the vibrational Raman signal of methane. With the support of a digital phosphor Oscilloscope (Tektronix, TDS 580D), it was possible to confirm that the photo-multipliers signal intensity is adequate for the measurements to be performed. Figure 3 illustrates the primary signal that is obtained in the check procedure, which consisted in injecting methane into the atmosphere

through a cylinder at a distance of approximately 45 m from the system. It can be seen a detected signal in the position the cylinder was located, even though some overlaps issues still need to be carefully corrected.



Figure 1. CH₄-VOC lidar system in operation at IPEN/CNEN-SP, São Paulo, Brazil

3.2 SET UP

3.3 Acquisition Software

The third and fourth steps (spectroscopy and acquisition software, respectively), were carried out simultaneously. For the set up of the spectroscopy and the detector module for the fluorescence detection box, the installation of its acquisition software was necessary. Licel provides a package of software modules for setting up the Licel Multispectral Lidar Detector for network operation, and for operating the Licel Multispectral Lidar Detector. These software modules are written in LabVIEW G language. After appropriate configuration of the software modules, it was possible to acquire the pulse height distributions for either all 32 channels or selected channels of the Licel Multispectral Lidar Detector. The system allows a number of parameters that can be set up during the preliminary acquisition such as operating voltage and range of each specific channel. It is possible to display each one of the 32 channels individually as well as multidimensional contour plot. For individual channels the average count rate is displayed. The range for the integration of the spectral display can also be adjusted during the preliminary acquisition. This may be set by the Channel Display switch either to Index or Wavelength.

3.4 CH₄-VOC Raman system and multispectral 32 channel measurements and preliminary tests.

After pre-established adjustments, concerning the components of the CH₄-VOC system, an intense training of the team was performed for operating the system, including the adjustment of conditions during a measurement campaign, such as the software operation control of primary data acquisition system (acquisition frequency regulation, channel selection, regulation of sensitivity in each range of wavelengths, among others) and interpretation of the data. These practical sessions were essential for establishing the system operating procedure. In order to carry out the first campaign and monitor the performance of the team, a test was carried out at IPEN site. The atmospheric fluorescence measurements were based on measurements made with the system facing the atmosphere, at a fixed angle of 45°, aiming to collect light intensity data from the atmosphere in different conditions (day, night, clean or cloudy weather), for laser emission at wavelength of 355 nm. Figure 2 presents two different primary measurements collected.

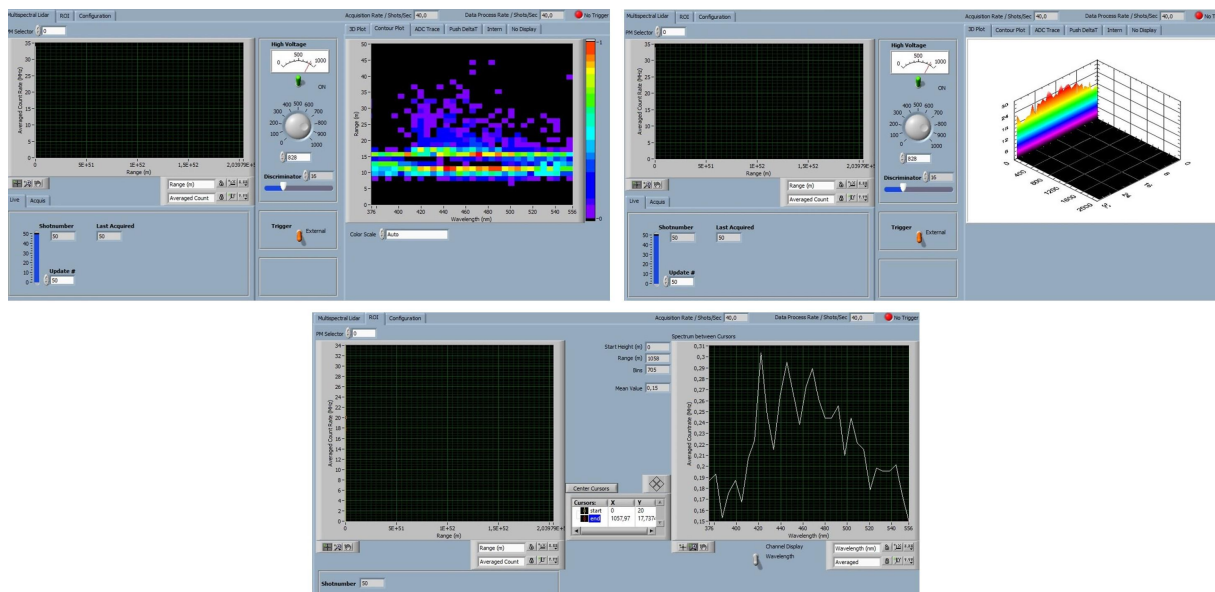


Figure 2. Simulated atmospheric fluorescence measurements.

3.5 Methane air mixtures measurements in a tunnel

Preliminary tests to verify the detection ability for methane in a simulated leak in the atmosphere. Exploratory experiments were carried out in an improvised tunnel, which consisted of an empty corridor with a rectangular section (about 3 by 3 m), in which a methane cylinder was discharged at a small constant rate. The methane concentration at the discharge site was monitored with a calibrated gas chromatograph, with a detection limit of 0.1% (volumetric fraction). The lidar system was positioned at a distance of 45 m from the emission source. Figure 3 shows the results obtained for the signal measured by the system (Raman scattering at 396 nm) as a function of distance from the lidar. The chromatograph, which was 45 m from the LIDAR, did not detect a presence of methane in the air, for volumetric fractions less than 0.1%. However, as shown in Figure 3, the system was able to clearly detect the signal corresponding to methane, which has a standard profile corresponding to the dispersion along the tunnel. The values shown in the graph for distance less than 20 m must be discarded because they are outside the detection limit of the system.

3.6 Methane Retrievals

On July 19th and 23rd 2018 measurements were performed with the Rotational Raman and table 1 presents the features of system used to in this measurement.

Table 1. CH_4 – VOC system acquisition parameters

Date	July 19th 2018	July 23rd 2018
Integration Time (min.)	320	330
Angle of Inclination	30°	
Channels	353 nm (N_2 RR), 355 nm & 396 nm (CH_4 RR)	
Repetition Rate	20 Hz	
Energy/pulse	100 mJ @ 355 nm	
Sampling Rate	2000 shots	
$\Sigma_i(files)$	192	168

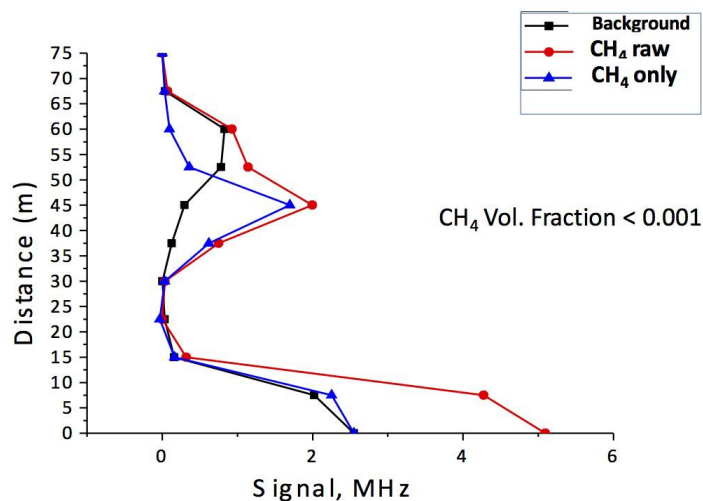


Figure 3. Raman scattering signal (at 396 nm), collected in a tunnel with emission of methane into the atmosphere (emission at 355 nm).

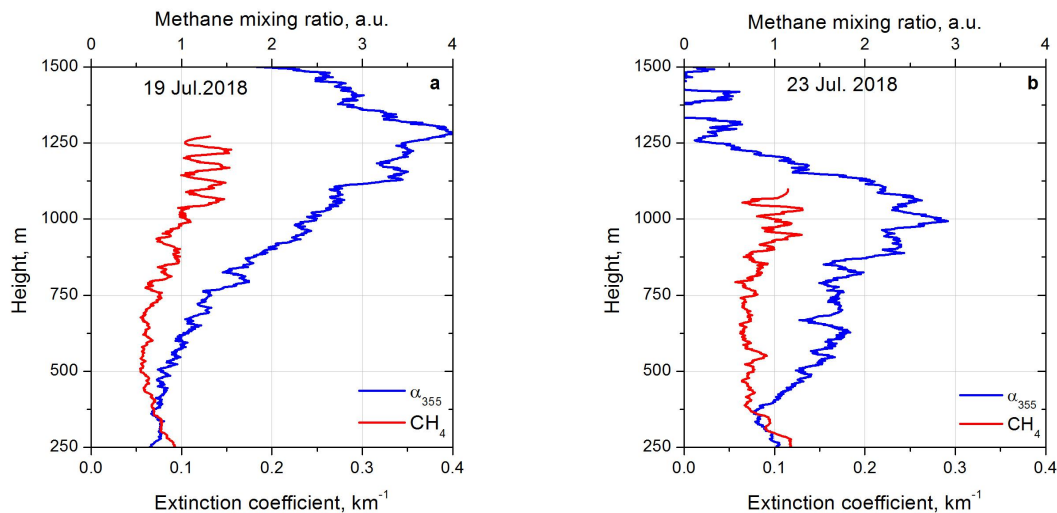


Figure 4. Vertical profiles of the methane mixing ratio and of aerosol extinction coefficient at 355 nm on 19 July, and 23 July. The mixing ratio is uncalibrated and given in arbitrary units. Measurements are averaged over 19:30 - 23:50 UTC temporal interval. Methane mixing ratio is smoothed with 2-nd order polynomial over 30 points.

The results are shown in Figure 4.

The results presented are such we can detect methane concentrations above the background threshold of about 1890 ppb.¹¹ In the plots presented we show also the aerosol extinction at 355 nm which might indicate some of methane results could be an spurious aerosol fluorescence induced by the laser and should be further inspected with the Fluorescent branch of the system in a future experiment.

3.7 Conclusion

A novel lidar design to detect atmospheric methane and volatile compounds was developed based on the detection of the wavelengths at 355 nm (elastic), 353 nm (oxygen + nitrogen rotational Raman) and 396 nm (methane vibrational Raman) and alternatively the system can be switched to a fluorescence lidar based on a 32-channel PMT coupled to an spectrometer to be able to observe fluorescence scattering caused by VOC's and aerosols as

well. We presented the first steps and results of this new concept and present uncalibrated results however above the background threshold of 0.18 ppm for CH_4 . The next phase will involve take measurements in specific sites where methanes emissions are well above this value, such as waste and storage facilities and natural emission as *swampy* or *marshy* locations. Also future deployments for the fluorescence branch should be further inspected.

3.8 Acknowledgments

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