Raman Spectroscopy as a diagnostic tool for traditional and ammonia combustion

Riccardo Dal Moro*, Fabio Melison*, Lorenzo Cocola*, Luca Poletto*
riccardo.dalmoro@pd.ifn.cnr.it
*National Research Council – Institute for Photonics and Nanotechnologies (CNR-IFN),
via Trasea 7, 35131 Padova, Italy

Abstract
This paper presents a high sampling rate, low-cost diagnostic method based on Raman scattering analysis. Although gas analysis using this physical phenomenon is not yet an industry standard, it is rapidly gaining interest for in-line applications. Compared to other laser diagnostic techniques, Raman spectroscopy enables straightforward detection of molecules such as N_2 and H_2, which are either undetectable or difficult to measure using absorption-based spectroscopic techniques in industrial processes. The proposed system supports both qualitative and quantitative analysis of all Raman-active species. It has been specifically characterized for the detection of nitrogen oxides (NO, NO_2) as well as major species commonly present in conventional combustion environments, including O_2, H_2, N_2, CO_2, CO, CH_4, SO_2, H_2O, and H_2S. The system achieves limits of detection (LODs) ranging from 70 to 2600 ppm under operating conditions of 1-second integration time at 1 bar. Additionally, the system is applicable to ammonia (NH_3) combustion diagnostics, which features several Raman-active bands, including a strong signal at $\nu = 3334\ cm^{-1}$.

Introduction
In recent years, combustion research has increasingly focused on enhancing efficiency and exploring innovative solutions to support the decarbonization of industrial processes. As novel combustion strategies involving fuels such as hydrogen and ammonia emerge, there is a growing need for advanced diagnostic systems capable of providing deeper insight into these complex processes.

Optical diagnostic techniques require no sample preparation and offer high sampling rates, enabling excellent temporal resolution of dynamic processes. Leading laser-based spectroscopic methods, such as Fourier Transform Infrared (FTIR) spectroscopy and Tunable Diode Laser Absorption Spectroscopy (TDLAS), rely on molecular absorption at specific wavelengths. Other techniques, including Laser-Induced Fluorescence (LIF) and chemiluminescence analysis, are based on light emission from excited molecular species. These methods provide high sensitivity (ppm-level detection), but a key limitation is their inability to simultaneously detect all species of interest with a single instrument. Furthermore, important species such as H_2 and N_2 are generally not detectable using absorption-based techniques.

Raman spectroscopy is based on one principle of light scattering, where the interaction of a laser source with sample molecules produces scattered light, a small portion of which is shifted in wavelength according to the unique vibrational modes of the molecules. This wavelength-shifted signal provides a molecular fingerprint that enables species identification. The use of monochromatic pump radiation allows the detection of multiple gases using a single light source.

Materials and methods

The experimental setup used in this study has been previously described in detail [1]. Briefly, a continuous-wave (CW) Nd:YAG laser operating at 532 nm with an optical power of 1 W is focused onto the sample through a multi-pass reflection system to enhance the interaction length. The scattered signal is collected and analyzed using a dispersive spectrometer, with detection performed by a standard uncooled industrial CMOS detector. The instrument has been characterized under operating pressures ranging from 0.7 to 7.5 bar.

Quantitative analysis of the gas samples is carried out by comparing the measured spectra with reference calibration spectra. A fitting algorithm minimizes the difference between the measured spectrum and a synthetic one to determine the chemical composition of the sample. The spectral fitting is performed on data normalized with respect to the laser intensity and the pressure inside the measurement cell, giving as output the partial pressures of the individual chemical species in the gas mixture assuming that all relevant species are detected.

Results and discussion

As previously mentioned, the instrument was characterized under operating pressures ranging from 0.7 to 7.5 bar, with signal integration times varying from 0.15 to 10 seconds per acquisition. The Raman shifts [2] and detection limits (LODs) based on measurements performed with an integration time of 1 second at a pressure of 1 bar inside the measurement cell are as follows (wavenumber, LOD): CO_2 (1388 cm^{-1}, 609 ppm), N_2 (2331 cm^{-1}, 1253 ppm), O_2 (1555 cm^{-1}, 712 ppm), H_2 (4156 cm^{-1}, 801 ppm), CH_4 (2914 cm^{-1}, 179 ppm), CO (2143 cm^{-1}, 757 ppm), NO (1877 cm^{-1}, 2611 ppm), NO_2 (750 cm^{-1}, 69 ppm), SO_2 (1151 cm^{-1}, 238 ppm), H_2S (2611 cm^{-1}, 215 ppm), H_2O (3657 cm^{-1}, 1467 ppm).

The analysis of NOx species is complicated by fluorescence interference, particularly from NO_2, which emits across the spectrum toward longer wavelengths. As long as the fluorescence signal does not saturate the detector, it is still possible to extract quantitative information from the Raman emissions. An illustrative case is the high-temperature combustion of urea ($CO(NH_2)_2$). The combustion was carried out in a furnace at 1350 °C in an atmosphere of pure oxygen (100% O_2). Raman measurements were performed with an integration time of 0.5 seconds at a pressure

of 1.2 bar. Figure 1 shows a comparison between a spectrum acquired during combustion (continuous line) and one obtained from a reference gas mixture (dotted line) containing 1000 ppm of NO_2, 79% N_2, and 20.9% O_2.

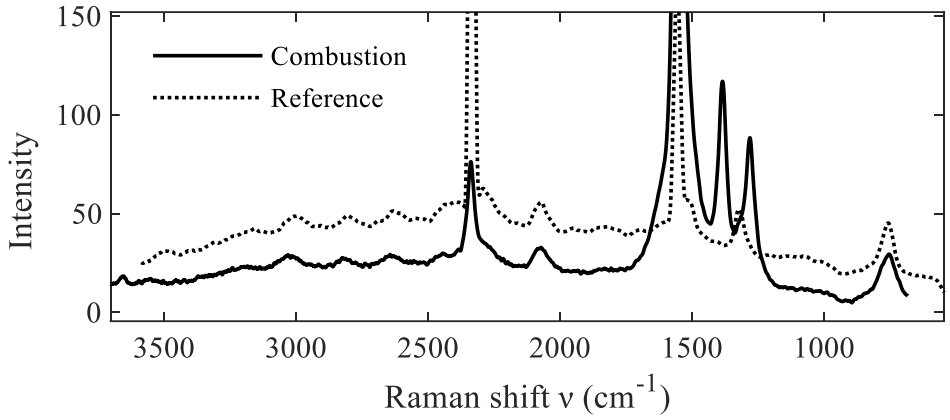

Figure 1. Comparison between the spectrum acquired during combustion (continuous line) and a spectrum obtained from a certified cylinder (dotted line) containing 1000 ppm of NO_2, 79% N_2, and 20.9% O_2.

Results and discussion

This study presents a Raman based gas analyzer performance for combustion diagnostics, with acquisition times as short as 0.15 s at 0.7 bar. The system operates between 0.15 and 10 s integration times and 0.7 to 7.5 bar pressures. At 1 s and 1 bar, the instrument achieves LODs from 70 to 2600 ppm, detecting key combustion species (O_2, H_2, N_2, CO_2, CO, CH_4, NO, NO_2, SO_2, H_2O, H_2S). Future improvements will focus on alignment stability, device miniaturization, and streamlined setup.

References

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