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Measurement of composition of natural gas and hydrogen-enriched natural gas mixtures by industrial-grade Raman spectroscopy

The distribution network of natural gas is evolving rapidly toward more complex mixtures, having also hydrogen-enriched compositions. The sector requires for state-of-the-art industrial-grade instrumentation capable to determine the composition and the related quality (in terms of Heating Value) of the gas mixtures distributed in the networks. The gas parameters (mainly the concentration of methane and heavier hydrocarbons, carbon dioxide, nitrogen and hydrogen) need to be monitored in real time and in a wide range of compositions, since mixtures are found within an extremely variable range depending on the origin of the gas.
A compact, fast and highly sensitive instrument based on spontaneous Raman spectroscopy has been developed with the specific aim to operate directly in-line to measure the gas composition within a broad range of gas mixtures and operating temperatures between -20°C and +50°C. This approach is intrinsically non-invasive, since it requires a laser beam passing through the gas cell to excite the Raman emission, and multi-species sensitive, since the different components of the gas mixture are simultaneously detected, particularly species difficult or impossible to be detected with conventional absorption spectroscopy (such as hydrogen and nitrogen).
The Raman scattering is stimulated by a laser diode centered at 455 nm with multi-mode emission and 1.5 W optical power. The laser is focused on a sealed gas cell where the sample gas to be measured is flowing, the Raman emission is collected by a grating spectrometer and finally acquired on a 2D camera. The measured spectra are fitted with the calibration dataset acquired at room temperature to achieve the mixture composition. The system is able to determine the main components of the natural gas: methane, heavier hydrocarbons, nitrogen, carbon dioxide and hydrogen. The Heating Value is finally calculated using the ISO6976:2016 standard.
Several certified gas mixtures have been tested with the instrument operated at different temperatures in the range from -20°C to 50°C, to prove the capability to operate in a wide temperature range, being anyway capable of giving the correct gas composition within the precision required by the measurement standard. The system can operate at pressures variable between 1 and 6 bars, requiring less than 30 s to provide a complete measurement. The system has been validated also with hydrogen-enriched gas mixtures.
Two prototypes are currently being tested in-line in the Italian distribution network and in a biogas production plant.

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References

[1] F. Melison, L. Cocola, E. Meneghin, D. Rossi and L. Poletto, Natural gas and hydrogen-enriched natural gas composition measurements by industrial-grade Raman spectroscopy, SPIE Proc. 13026, Next-Generation Spectroscopic Technologies XVI, 130260G (2024)