GASRAMAN: a novel Raman-based sensor for combustible gas analysis

L. Cocola[1*], F. Melison[1], N. Scarabottolo[1], G. Tondello[1], D. Banzato[2], E. Barbera[2], A. Bertucco[2] and L. Poletto[1*]

[1]Institute for Photonics and Nanotechnologies, National Research Council (CNR-IFN), Via Trasea 7, 35131 Padova, Italy

[2]Interdepartmental Centre Giorgio Levi Cases for Energy Economics and Technology, University of Padova (UNIPD-CLC), via Marzolo 9, 35131 Padova, Italy

*luca.poletto@cnr.it

ABSTRACT

A simple Raman-based instrument for composition analysis of combustible gas mixtures has been developed and tested. The device is a reliable and low-cost alternative to current analysis methods used at the gas pipelines and biogas/biomethane facilities, able to evaluate both the actual mixture composition and the heating value. With low power consumption and no required consumable supplies, the instrument is also suitable for field operation at remote facilities. The instrument is based on an efficient and low-cost laser diode coupled to the gas cell and a customized high-brightness miniature spectrometer using an industrial-grade camera.

Keywords: Raman gas sensing; natural gas; biogas; biomethane; ISO 6976; heat of combustion; hydrocarbons; laser diode.

1. INTRODUCTION

The purpose of the GASRAMAN project is the development of a compact, light, low-cost Raman instrument prototype with low power consumption for on-line monitoring of natural gas (NG), methane mixtures, biogas and biomethane composition. NG is a key resource for the energy and fuel market of the next decades, since methane has a lower carbon footprint than coal and oil, so it is going to play a fundamental role in the transition to renewables. Furthermore, it can be easily replaced with biomethane, the production of which has greatly increased in the last decade. Both NG and biomethane mixtures are found with an extremely variable range of compositions. This variability poses a problem to user stations as they must deal with different combustion properties and heating value. With GASRAMAN instrument, we intend to address the issue of measuring the gas mixture composition and its heating value in a reliable, fast and cheap way.

The breakthrough innovation foreseen in the project is made possible thanks to novel concepts in both laser source and high efficiency optics, as well to sophisticated signal processing techniques. The instrument that has been developed has the potential to provide a multi-gas, highly stable and long-lasting alternative to current instruments based on gas-chromatography (GC), electrochemical and other indirect methods. The device requires no gas carriers, no periodic replacement of sensors and provide the actual mixture composition rather than just an evaluation of the heating value of a specific mixture. All these features are packed in a small footprint, completely automated for network operation, with low power consumption compatible with battery and solar panel operation.

The instrument uses as the exciting source a simple diode laser of the lightning-grade types at 450 nm. The Raman emission is acquired through a tailored miniature high-luminosity spectrometer that has been developed to match the brightness, resolution and reliability requirements of the source. We developed algorithms able to deal with the typically drifting and wide spectrum emission of the diode to evaluate Raman spectra. A fitting routine has been implemented to calculate the mixture composition and the associated heating value (according to UNI EN ISO 6976:2017). The resulting system was then validated on calibrated sample mixtures including NG, biogas and biomethane. The error in the measurements of the heating values is anyway well below 0.5%.

A unique characteristic of the device is the ability to measure hydrogen, extremely important for photovoltaic electrolysis devices.

2. STATE OF THE ART

Fuel gas quality measurements are required both in the NG and in the biogas industry. About NG this is mostly done through sampling and lab analysis or by gas-chromatographic instruments installed at a few stations.

Measurement needs of biogas plants are different: if the product has to be consumed on-site, measurements are needed to ensure consistent operation of the plant; the requirements become more stringent if the gas has to be upgraded and injected in the grid in order to make sure that the distributor's standards are matched.
Raman techniques have been widely developed for solid and liquid sensing [1], while gas analysis is much less developed because of the extremely weak Raman signal provided by a gas sample [2-4]. Presently, only few companies offer Raman gas sensors but mostly as scientific-grade instruments, based on high-power, narrow spectral band, solid-state lasers and large spectrometers. These instruments are very expensive thereby limiting the use of this technology for widespread applications. Furthermore, many enhancement techniques, e.g. multiple path cells, are often used to improve the signal level. Most real applications, such as the one targeted by GASRAMAN, do not need extreme resolution figures; also, enhancement techniques are of difficult application in a rugged, industrial context.
From the point of view of the fuel gas industry, sensing currently relies on gas-chromatography which is an excellent technique for trace gas detection, but expensive and requiring periodic recalibration. Moreover it requires a constant supply of a carrier gas. There have been some attempts to address the heating value evaluation by sensing a few components or properties with a fusion of different techniques (electrochemical, metal oxide, infrared spectroscopy, thermal measurements). This approach offers lower accuracy and is usually bound to detect only smaller variations over a predefined gas mixture, being unable to detect the actual composition.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The result of the GASRAMAN project has been the realization of a prototype of a Raman multigas analyzer specifically developed for industrial applications in the field of combustible gas diagnostic. The simplicity of the design and use of low-cost and rugged components open a wide market. With reference to the application case of the project, the availability of such an instrument will enable a major step towards the improvement of energy efficiency and the de-carbonization of the NG infrastructure. Biogas is highly promising to increase the renewable fraction of our energy bills, but its full potential is still limited as most of the produced fuel is used on the production site. Being able to upgrade biogas to biomethane and to distribute it across the existing pipeline infrastructure will greatly improve the end-to-end efficiency of the process by making the energy available where it is needed at a very low cost. Combustible gas may become the energy vector of the future as it is already compatible with existing big users such as electric power plants, industrial and domestic heaters, cars, trucks and buses. Moreover, the pipeline will act as a buffer for energy storage. The transition from natural gas to carbon-neutral sources such as biomethane or hydrogen may be just around the corner provided that the new energy producers can match the standards of NG pipeline.
Thanks to its capability of measuring different NG mixtures, biogas, biomethane and hydrogen, as well as other gases as nitrogen, carbon dioxide, oxygen and water vapour that are often found as impurities, the GASRAMAN instrument will greatly help in the implementation of a smart energy network solving the measurement requirements of a multitude of users: producers, consumers and infrastructure administrators. Thanks to the low power consumption, such an instrument could be installed even in unmanned remote locations, being powered by solar panels, and backed up by small batteries.
As a final note, the new sensing instrument can find many more application cases in different fields such as chemical process control, life support and medical gases as a stable and non-contact method which is able to detect nitrogen and hydrogen as well as many other gases.

Tab. 1. Comparison between different gas sensing techniques used in the NG/biogas industry.

Technique	Cost	Pros	Cons
Gas-chromatograph	>20k€	Sensitive to trace contaminants	Expensive, requires supplies and maintenance
GASRAMAN	~5k€	Full composition detection, stable, non-contact method, H_2 detection	Unable to detect trace gases
Electro-chemical	<1k€	Inexpensive	Different sensors for each component, needs periodic replacement
Infrared	>2k€	Stable, non-contact method	Different sensors for each component. Nitrogen and hydrogen not detected
Indirect methods	<1k€	Inexpensive heat value detection	Unable to identify components

4. PROJECT RESULTS

The core development has been on three main topics:
- implementation of a low-cost laser source for Raman excitation;

- definition and manufacturing of a dedicated cell and spectrometer assembly;
- performance tests on gas samples.

Implementation of a laser diode as exciting source

A blue (447nm) laser diode was chosen as our candidate source due to the short wavelength (optimal for efficient Raman generation), low-cost, high power efficiency and relatively narrow spectrum. Although the available optical power can reach over 3.5 W, the laser is typically operated at 1 W to reduce heat dissipation and energy consumption and maximizing laser life.
Differently from diode-pumped solid-state lasers, the diode does not need to be operated at a fixed controlled temperature, therefore it works without any thermoelectric cooling module. This simplifies the optoelectronic design and lowers the energy consumption. The main drawback of using the diode laser at variable temperatures is found in the temperature dependence of the power, wavelength and spectral width of the emission. Those issues have been taken care of by a customized calibration and a dedicated compensation algorithm.

Development of the spectrometer

Due to the relatively wide diode emission, the collected Raman signal inherits some spectral broadening which makes it unnecessary the use of a high-resolution spectrometer. The Raman source has been de-magnified both in the relay optics (coupling the source to the spectrometer) as well as in the spectrometer itself to minimize the spatial broadening. The design uses optical triplets and C-mount machine-vision grade lenses to minimize aberrations while keeping a high brightness of f/2.8. A slitless design was found to improve immunity to mechanical misalignments and instabilities without any reduction in efficiency.
The gas interaction cell is designed to reduce and trap fluorescence and scattered light from the optics and the cell body itself.
The spectrometer is coupled to an industrial-grade, low-cost uncooled camera using a highly sensitive back-illuminated CMOS sensor.

Performance tests on gas samples

The hardware package and the developed software have been tested on natural gas, biogas and biomethane samples on a testbench to prove the effectiveness of the compensation strategies against a drifting source. Tests were performed with the laser diode operated at different temperatures in a range from 30 to 70 °C.
The spectra processing software has been proved able to reach the required accuracy performances (detection of the higher heating value of natural gas samples within 0.5% deviation from certified analysis) over the whole temperature range.

The device was tested with successful results on:
- several certified natural gas blends (mainly methane, ethane, propane, butanes, carbon dioxide, nitrogen);
- certified biogas samples collected from agricultural and municipal waste (mainly methane, carbon dioxide, nitrogen, water vapour, oxygen, hydrogen);
- upgraded biomethane (biogas after removal of carbon dioxide and minor contaminants in order to match grid injection specifications).

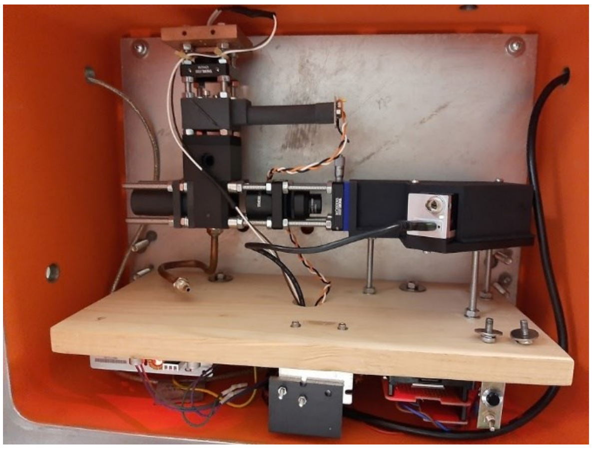

Fig. 1. Prototype of the complete Raman instrument, with control boards and ATEX enclosure.

GASRAMAN **project results** can be summarized as:
1. Realization of the prototype of the Raman instrument for gas analysis.
2. Development of the software package to operate the instrument, including compensation of the spectral broadening and shift of the laser wavelength with the temperature, validation of the deconvolution and fit to extract the gas concentration.
3. Test of the instrument on calibrated mixtures of natural gas, biogas and biomethane. Mixture components are measured with 0.2% precision, heating value within 0.5%, in few-seconds measuring time.
4. Comparison of the new technology with existing products on the market, to highlight its environmental and economic benefits.
5. European Patent PCT filed.

To introduce the future project vision, it is convenient to finally resume the instrument characteristics.
- The requirements are fulfilled, since the tests demonstrate the capability to measure composition and heating value on combustible gases according to BS EN ISO 6976:2016 (0.5% max error in the measurement of the heating value, few seconds measuring time);
- The system is compact, lightweight, and low-cost;
- The instrument has low power consumption and is IoT (Internet of Things) ready. It is suitable for

unmanned remote locations, being powered by solar panels and backed up by small batteries, with a processing unit based on a network-ready, single-board computer.
- System at TRL4: lab validation.

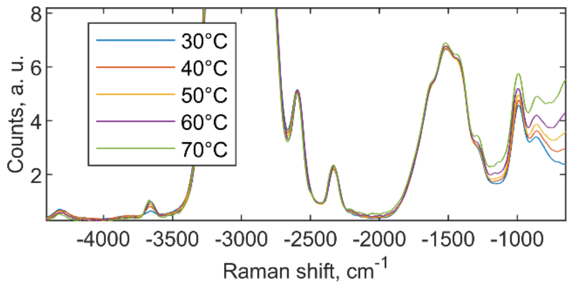

Fig. 2. Raman signals obtained from a certified natural gas sample at different laser source temperature.

5. FUTURE PROJECT VISION

We aim to bring the system to TRL7 and TRL8 with the final goal of TRL9.

5.1. Technology Scaling

The main steps to have an industrial product are:
- **on-field validation** from TRL4 to TRL7. Extensive tests are required to validate and demonstrate the technique in an operational environment, with attention to extremely variable on-field conditions (e.g., the temperature)
- **instrument calibration**. The standardization of the calibration procedures is essential for a fast, reliable, robust instrument setup.
- **optical, mechanical and software engineering**. The design of the instrument must be upgraded to an industrial scale, i.e., standardization of optical, mechanical and software design procedures.

5.2. Project Synergies and Outreach

The consortium for Phase 1 includes 1) research institution and 2) university.
In case of Phase 2, the consortium is going to be enlarged to include in addition to a possible further research, industrial partners of which at least one active in the field of manufacturing equipment for oil and gas stream with a distribution chain internationally operated. Such a partner is of primary importance for the industrialization and future marketing of the system and has already been identified.
Furthermore, interest in biomethane is growing in Europe, and natural gas networks are going to be exploited at both local and national levels. The instrument developed may be an attracting investment for all those companies that make the connections between the biogas upgrading plants and the gas network, as well as for the companies engaged in natural gas distribution. Furthermore industrial partners active in general gas production for both scientific and industrial use could benefit having a low cost easy to use general gas sensor in there supply chain. Some of these companies will be contacted and offered to join the consortium.
Dissemination activities during Phase 1 have been strongly limited by the COVID-19 pandemic. The only public event that we have been able to organize (scheduled for 15/09/2020) is a conference in Padova (Italy) on "Toward a circular economy: technologies for renewable resources".
For Phase 2, we envisage the participation to scientific conferences (1-2 per year), the publication of scientific papers (1 per year), the participation to national and international industrial fairs (2-4 per year), the organization of public events, as conferences and workshops (1 per year), and the preparation of a dedicated project website.

5.3. Technology application and demonstration cases

The present application of the GASRAMAN system is for accurate fuel gas value metering in smart energy networks. The huge existing pipeline infrastructure currently used for natural gas has an embedded potential to support sustainable energy delivery and storage. By accurately monitoring actual energy flows, the technique will enable interaction between the many actors involved in this scenario: different types of biogas/biomethane plants, hydrogen generators from the excess energy produced by solar fields and conventional natural gas suppliers.
The technology demonstration cases bring concrete benefit to:
- *Secure, clean and efficient energy;*
- *Climate action, environment, resource efficiency and raw materials.*

Moreover, not being limited to fuel gas, the technique can provide a multi-gas analytical instrument required in other fields, such as the implementation and finalization of a medical-grade gas analyser, life-support breath analysis, and more generally for on-line gas analysis in industrial process control of petrochemical production plants. The exploitation of demonstration cases others than for fuel gas will be a task of the research partners for Phase 2.

5.4. Technology commercialization

The technology is protected by a patent, that has been filed in Italy and recently extended to Europe. We have already received interest in the technology from a large company manufacturing equipment for oil and gas stream. We have already started a join collaboration to demonstrate the technology in a test facility. The availability of a partner with international marketing experience is of primary importance since it gives a wider visibility of the technology and opens huge marketing possibilities. We envisage to commercialize the technology for fuel gas through this project partner.

5.5. Envisioned risks

The core risks that we envisage in a potential Phase 2 project are:

- ***Technical risks***. The main technical risk is related to the very wide operating temperature range of the instrument for on-site applications (from –20°C to 70°C).
  Mitigation strategy. In case of some serious degradation of the performances due to thermal effects, the mechanical design of the instrument will be revised.
- ***Market acceptance.*** One of the tasks of Phase 2 will be the analysis of market acceptance of the GASRAMAN technology. We strongly believe that the added value of the technology on the field of fuel gas is strong, however some resistance from the market actors vs. the application of a new technique could be experienced.
  Mitigation strategy. The dissemination activities will be reinforced, particularly those vs. the industrial field (e.g., fairs, demo training sessions).

Liaison with Student Teams and Socio-Economic Study

If funded in Phase 2, we will collaborate with MSc. Level student teams, who will be asked to provide ideas and prototypes inspired by the technology for addressing Societal Challenges. A scientist from the staff of the project leader (CNR-IFN), already expert in outreach activities, will be in charge to provide MSc. level explanation materials of the technology. He/she can provide, e.g., online lectures on the technology, face-to-face meetings with classes, technical/scientific material.
Phase 2 will undertake an expert-driven socio-economic study. We will provide information to this study (e.g. interviews, technology impact references, possibility of on-site visits).

6. ACKNOWLEDGEMENT

Authors thank the R&D team of the company Pietro Fiorentini spa which provided the calibrated mixtures representative of different compositions for natural gas. The company already demonstrated a high interest in participating to the possible ATTRACT Phase 2 proposal.

This project has received funding from the ATTRACT project funded by the EC under Grant Agreement 777222.

7. REFERENCES

[1] Paul, R., Safa, G. & Dina, G., 2016. Raman Spectroscopy Review, Int. J. Eng. Tech. Res. 6: pp. 50-64.
[2] Buldakov, M. A. et al, 2013. Analyzing natural gas by spontaneous Raman scattering spectroscopy, J. Opt. Technol. 80: pp. 426-430.
[3] Sieburg, A. et al, 2018. Monitoring of gas composition in a laboratory biogas plant using cavity enhanced Raman spectroscopy, Analyst 143: pp. 1358-1366.
[4] Hippler, M., 2015. Cavity-Enhanced Raman Spectroscopy of Natural Gas with Optical Feedback cw-Diode Lasers, Anal. Chem. 87: pp. 7803-7809.