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Consiglio Nazionale
delle Ricerche

Il progetto Europeo PIPE 4.0: risultati e prospettive

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Biometano: presente e futuro del settore. Potenzialità e limiti allo sviluppo

Agripolis- Aula Magna PENTAGONO - Viale dell'Università, 16

Legnaro (PD)

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Biogas, biomethane: composition

- ▶ Biogas
- ▶ A mixture of different gases produced by the breakdown of organic matter in the absence of oxygen
- ▶ Produced from:
 - ▶ agricultural waste
 - ▶ manure
 - ▶ municipal waste
 - ▶ plant material
 - ▶ sewage
 - ▶ green waste
 - ▶ food waste
- ▶ Biogas is a renewable energy source
- ▶ Different from NG

Compound	Vol. % (typ.)
Methane	50 to 75
Carbon dioxide	25 to 50
Nitrogen	0 to 10
Hydrogen	0 to 1
Hydrogen sulfide	0.1 to 0.5
Oxygen	0 to 0.5

Heating value

- ▶ Heating Value
- ▶ The quantity known as higher heating value (HHV) (or gross energy or upper heating value or gross calorific value (GCV) or higher calorific value (HCV)) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced.
- ▶ A function of chemical composition, described in ISO6976:2016
- ▶ Main fuel gas families, typical HHV in MJ/Nm³:
 - ▶ 1 Town gas: 22.5 to 30.0
 - ▶ 2 Natural gas: 39.0 to 45.0
 - ▶ 3 LPG: 72.0 to 87
- ▶ For an efficient use, biogas must be upgraded to match similar heating value standards as natural gas. Using the distribution network to deliver gas to the end-user improves overall efficiency.
- ▶ Corrosive contaminants (as H₂S) and water vapour must be removed to avoid damage to the infrastructure.

Composition of natural gas

- ▶ Raw natural gas typically consists primarily of methane (CH₄), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of:
 - ▶ Heavier gaseous hydrocarbons: ethane (C₂H₆), propane (C₃H₈), normal butane (n-C₄H₁₀), isobutane (i-C₄H₁₀), pentanes and even higher molecular weight hydrocarbons. When processed and purified into finished by-products, all of these are collectively referred to as Natural Gas Liquids or NGL.
 - ▶ Acid gases: carbon dioxide (CO₂), hydrogen sulfide (H₂S) and mercaptans such as methanethiol (CH₃SH) and ethanethiol (C₂H₅SH).
 - ▶ Other gases: nitrogen (N₂) and helium (He).
 - ▶ Water: water vapor and liquid water. Also dissolved salts and dissolved gases (acids).
 - ▶ Liquid hydrocarbons: perhaps some natural-gas condensate (also referred to as casinghead gasoline or natural gasoline) and/or crude oil.
 - ▶ Mercury: very small amounts of mercury primarily in elemental form, but chlorides and other species are possibly present.
 - ▶ Naturally occurring radioactive material (NORM).
- ▶ Hydrogen is being added in the gas distribution network in significant and increasing amounts as a way to store excess energy production from photovoltaic farms.

Composition of natural gas

Region	CH ₄ %	C ₂ H ₆ %	Other HC %	CO ₂ %	N ₂ %	Other gas %	HHV [MJ/m ³]
Italy	99.53	0.06	0.03	0.03	0.35	-	37.7
Russia	97.50	1.06	0.45	0.15	0.83	0.01	38.0
Northern EU	90.32	4.62	1.33	1.37	2.33	0.03	38.6
Algeria	87.92	6.95	1.77	0.97	2.29	0.10	39.7
Libya	85.98	6.80	2.95	1.44	3.42	0.11	39.9
Regassified	90.05	7.82	1.24	-	0.84	0.05	40.4
Pure methane	100.00	-	-	-	-	-	37.7

State of the art instruments for gas analysis

Calorimetric: measurement of small variations over a predefined gas composition

- ▶ Combustion based; unable to resolve contaminants; for clean NG.
- ▶ Measurement of slight Wobbe Index variations, suitable for energy billing purposes.

Electrochemical/NDIR/sensor fusion: measurement of single components through individual sensors

- ▶ Some of the used techniques are sensitive to contamination or require frequent recalibration; unable to sense nitrogen; good for trace-level contaminant detection in biogas.
- ▶ Measurement of ammonia and hydrogen sulfide levels for process control.

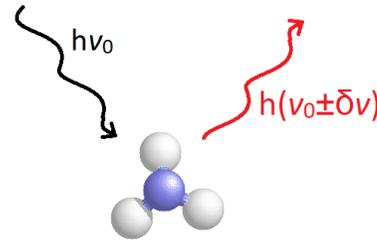
Gaschromatographic: complete gas analysis

- ▶ Resolution of ppm-range contaminants; requires periodic maintenance and carrier gas (e.g. He) supply.
- ▶ Measurement of complete gas composition and contaminant detection, more expensive, often done remotely after sampling

OIML R140 recommendation defines the performance of the measuring systems for gaseous fuels. The maximum permitted errors, relative errors, performance and endurance test methods are specified in the document for different instrument classes.

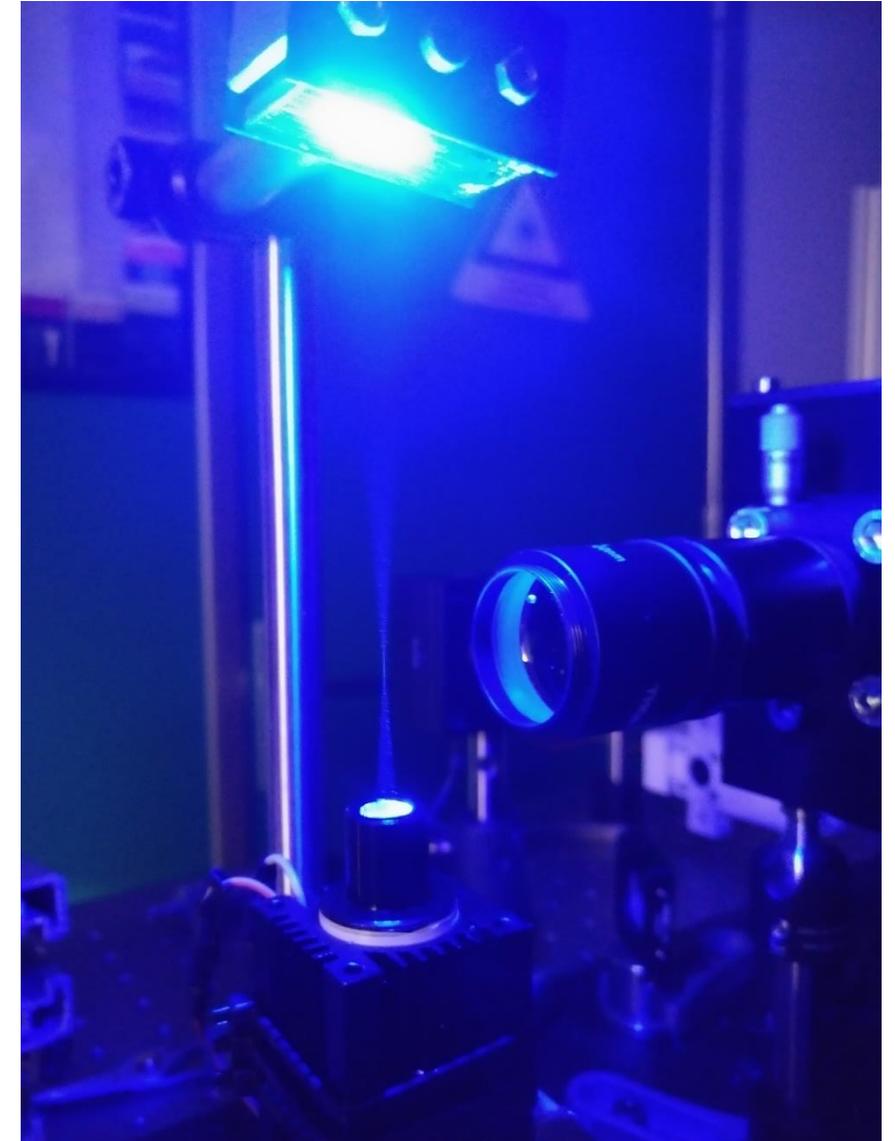
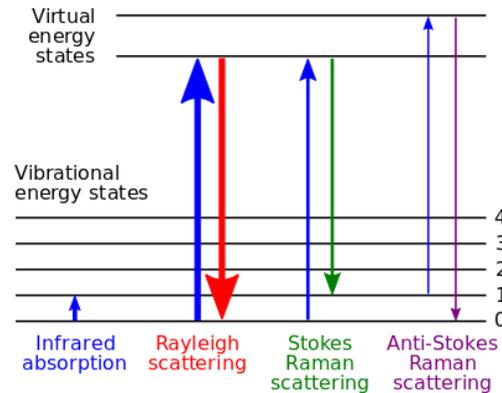
Raman spectroscopy

- ▶ A candidate for composition analysis of an arbitrary gas mixture is Raman spectroscopy, which provides an output analysis similar to gas chromatography
- ▶ Non-contact (only optical access to gas sample required)
- ▶ Sensitive to diatomic gases (H_2 , N_2)
- ▶ Weak signals (need for efficient and powerful laser sources), not suitable for trace detection



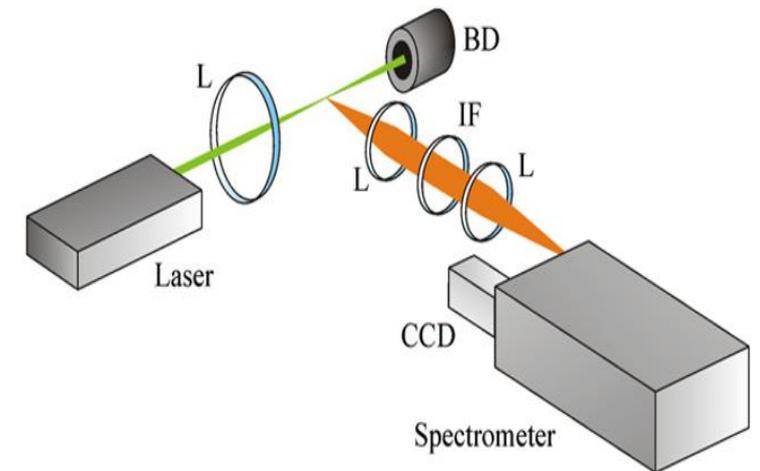
- ▶ Anelastic photon scattering:
 - Interaction leaves the molecule in a different rotovibrational state. Differently from Rayleigh scattering, the emitted photon has a different wavelength (energy) from incident radiation.
 - Energy difference between incident and Raman scattered radiation is a property of a given molecule.

- ▶ Raman emission is proportional to:
 - Intensity of incident (pump) radiation
 - $1/\lambda^4$ (pump wavelength)
 - Intrinsic molecule properties (cross section)
 - Density



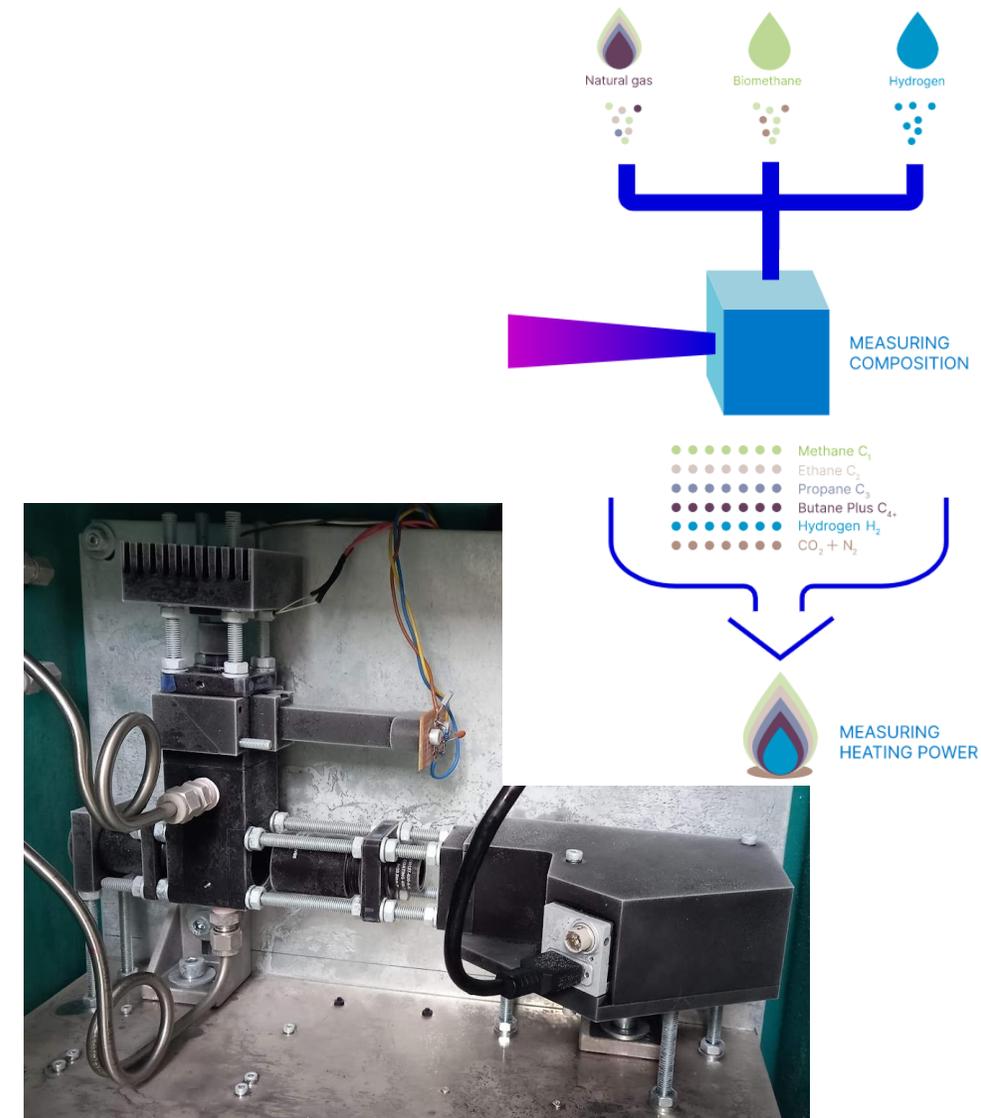
Raman spectrometer

- ▶ CW radiation from a pump laser is focused on a gas sample in order to maximize power density in a given region.
 - ▶ Diffused radiation is collected in the direction orthogonal to both the pump propagation and its electric field. An achromatic optical system couples diffused radiation to a spectrometer input slit.
 - ▶ The strong undesired elastic component at the pump wavelength is rejected with an interferometric filter (IF).
 - ▶ Residual scattered signal is analyzed spectrally and measured by an image sensor.
-
- ▶ Raman signal is very weak compared to the total scattered signal (mostly coming from Rayleigh elastic scattering). The total scattered signal is also a very small portion of the pump laser emission.
 - ▶ The small Raman signal must compete with:
 - Sensor readout and integration noise
 - Residual Rayleigh scattering not completely attenuated from the filter
 - Raman and fluorescence signals from interaction between pump and the optical components of the instrument, stray lights.



ATTRACT first prototype analyzer

- ▶ The prototype is based on a blue laser diode – low cost and low power.
- ▶ Pump laser light interacts with gas sample in a custom made flow cell operating at network pressure (low or medium pressure). The cell is provided with filters to avoid contamination.
- ▶ Analysis of the Raman signal is performed by a custom imaging spectrometer coupled to an industrial grade CMOS camera.
- ▶ An embedded computer takes care of instrument control, data processing, fitting of the spectra and measurement readout.
- ▶ The prototype is provided with ATEX explosion-proof enclosure.

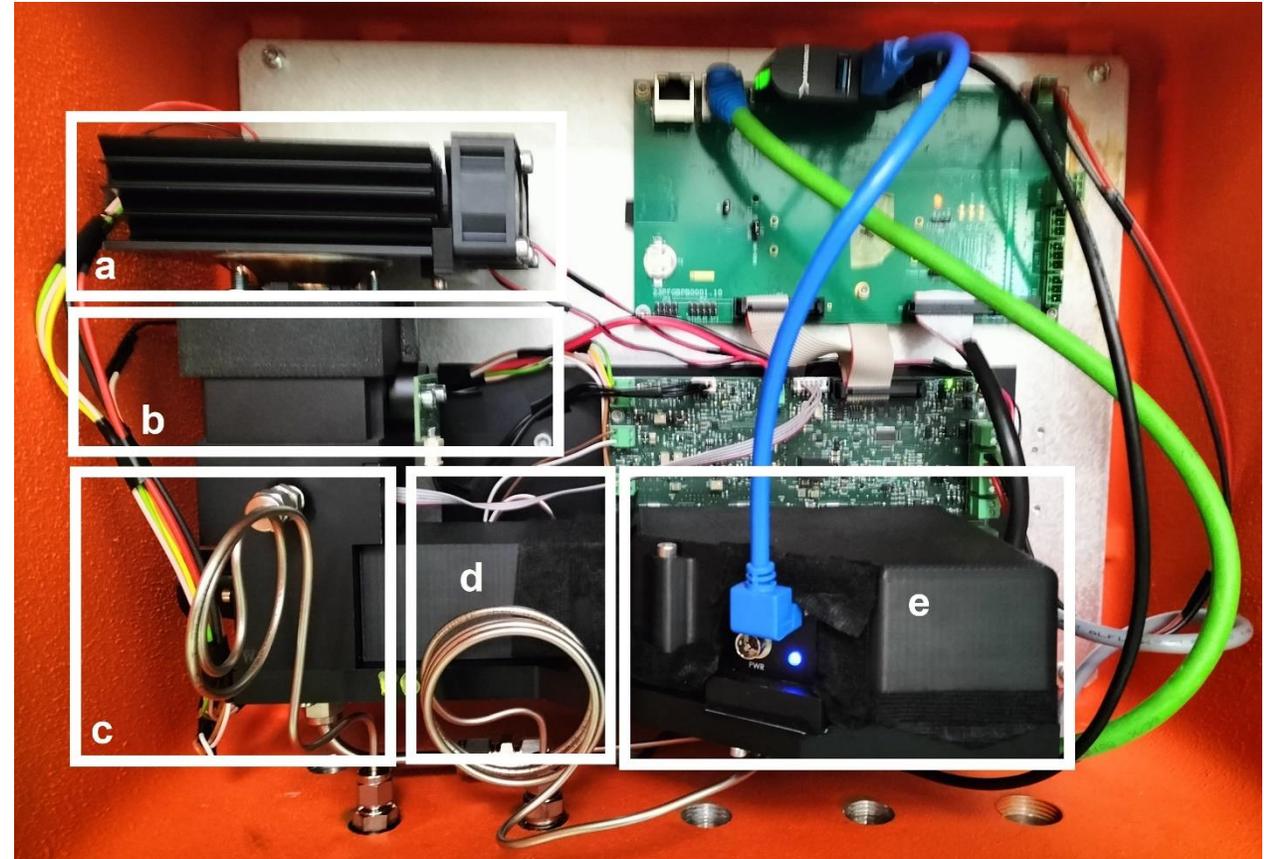


ATTRACT industrialized prototype

Features:

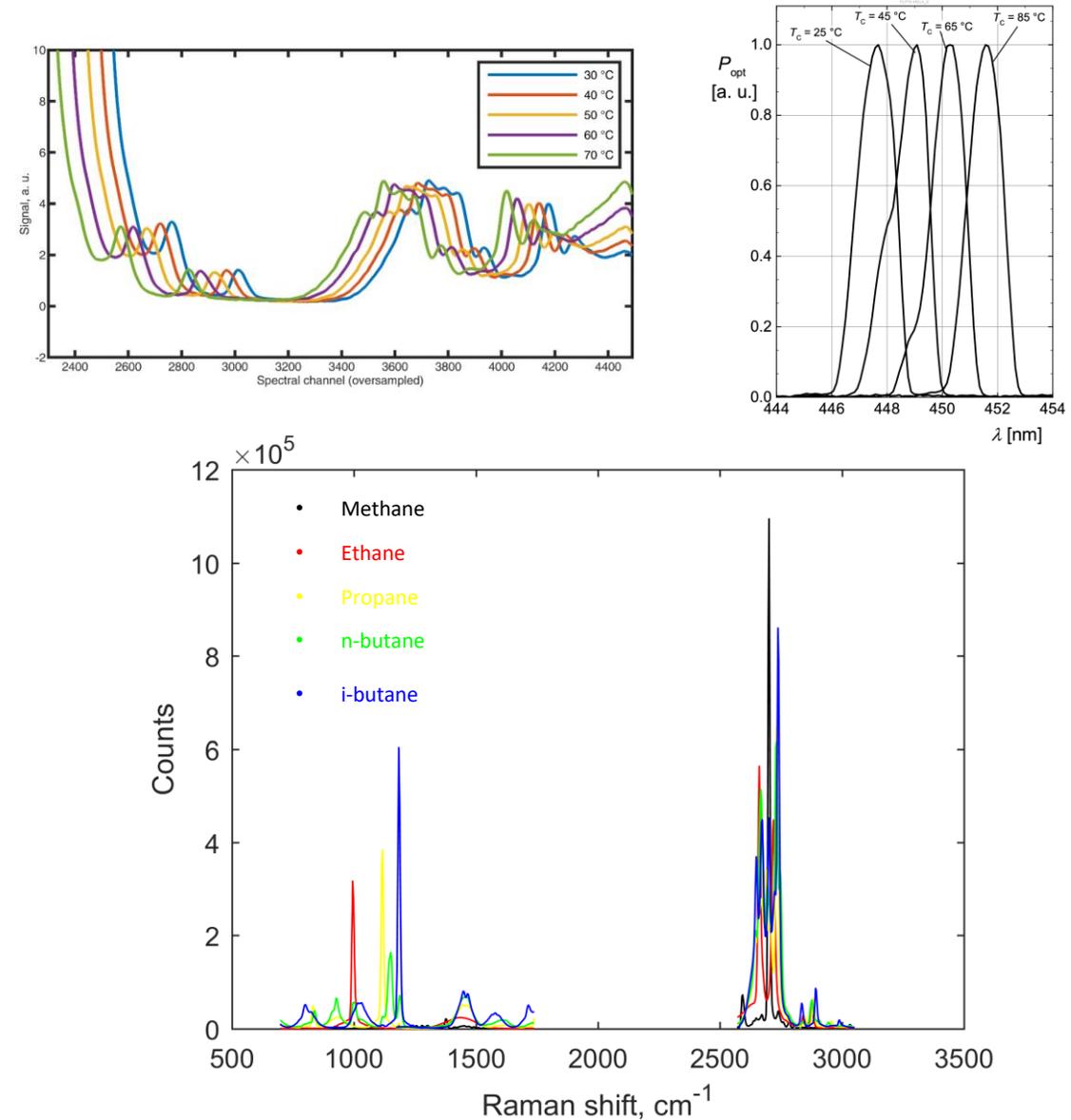
- **ThermoElectric cooled** laser source.
- **Custom** electronic boards.
- Measurement acquisition time **30 seconds**.
- Total power consumption below **15W**.
- The instrument requires only **one calibration set** carried out at room temperature.
- **ATEX** box encapsulation for on-site use.
- Maximum pressure in the measurement cell: **17 absolute bar**.
- **No consumables** and sample handling are required.

a) Laser source; b) Laser optics; c) Gas interaction cell; d) Collection optics; e) Spectrometer

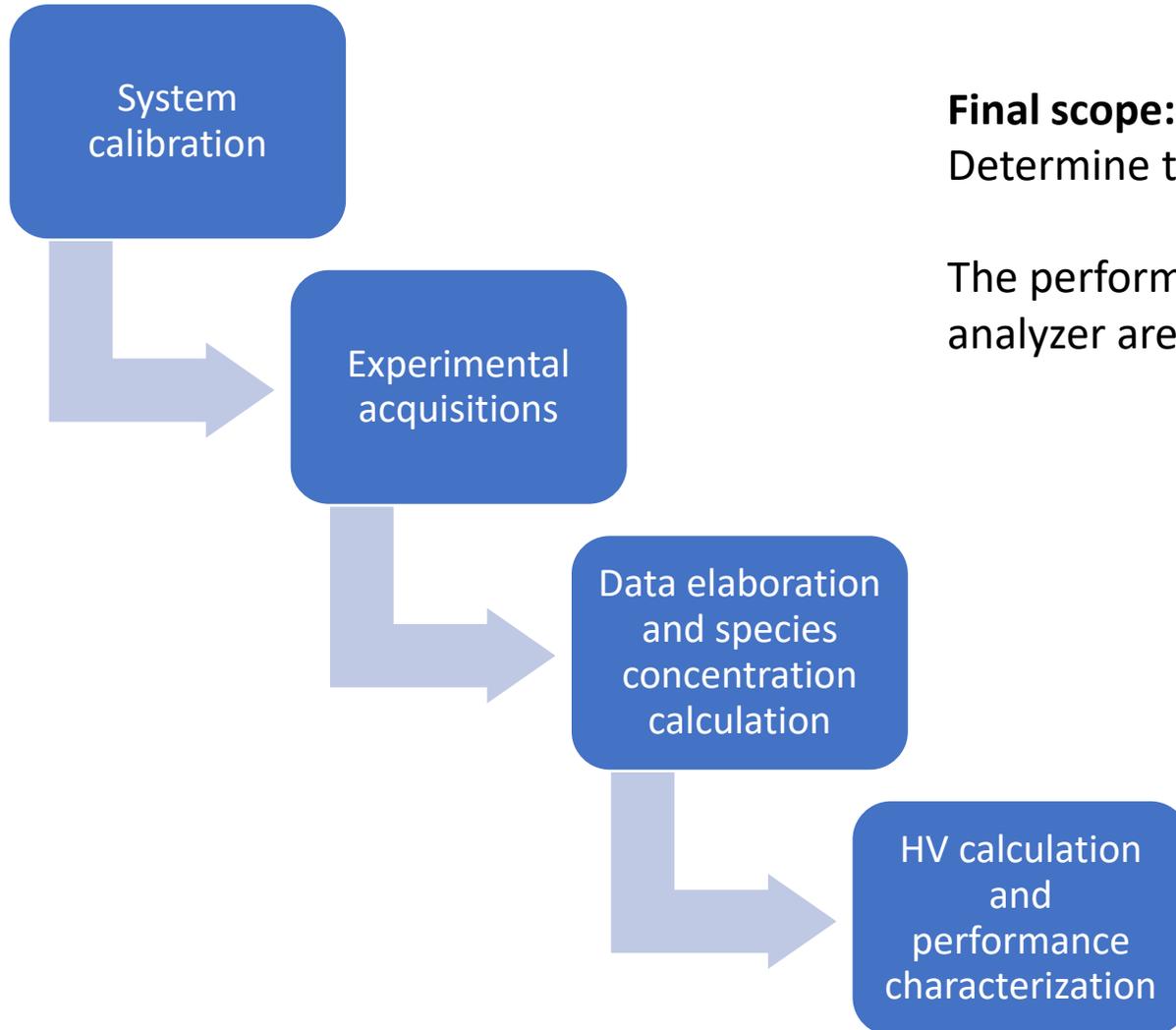


Signal processing

- ▶ A signal processing software provides compensation against drifts in source emission wavelength, linewidth and power
- ▶ A specifically tailored fitting routine provides evaluation of the components in the sample mixture, detecting the volume mixing ratio of methane, ethane, propane, n- and i-butane, carbon dioxide, nitrogen, hydrogen as well as oxygen and water vapour if relevant.
- ▶ The instrument software provides calculation of the heating value according to ISO 6976 standard (as done with the output of gas-chromatographs)



Experimental structure



Final scope:

Determine the system performance in terms of HV calculation.

The performance, in terms of HV accuracy and repeatability, for gas quality analyzer are defined by the OIML R 140 recommendation.

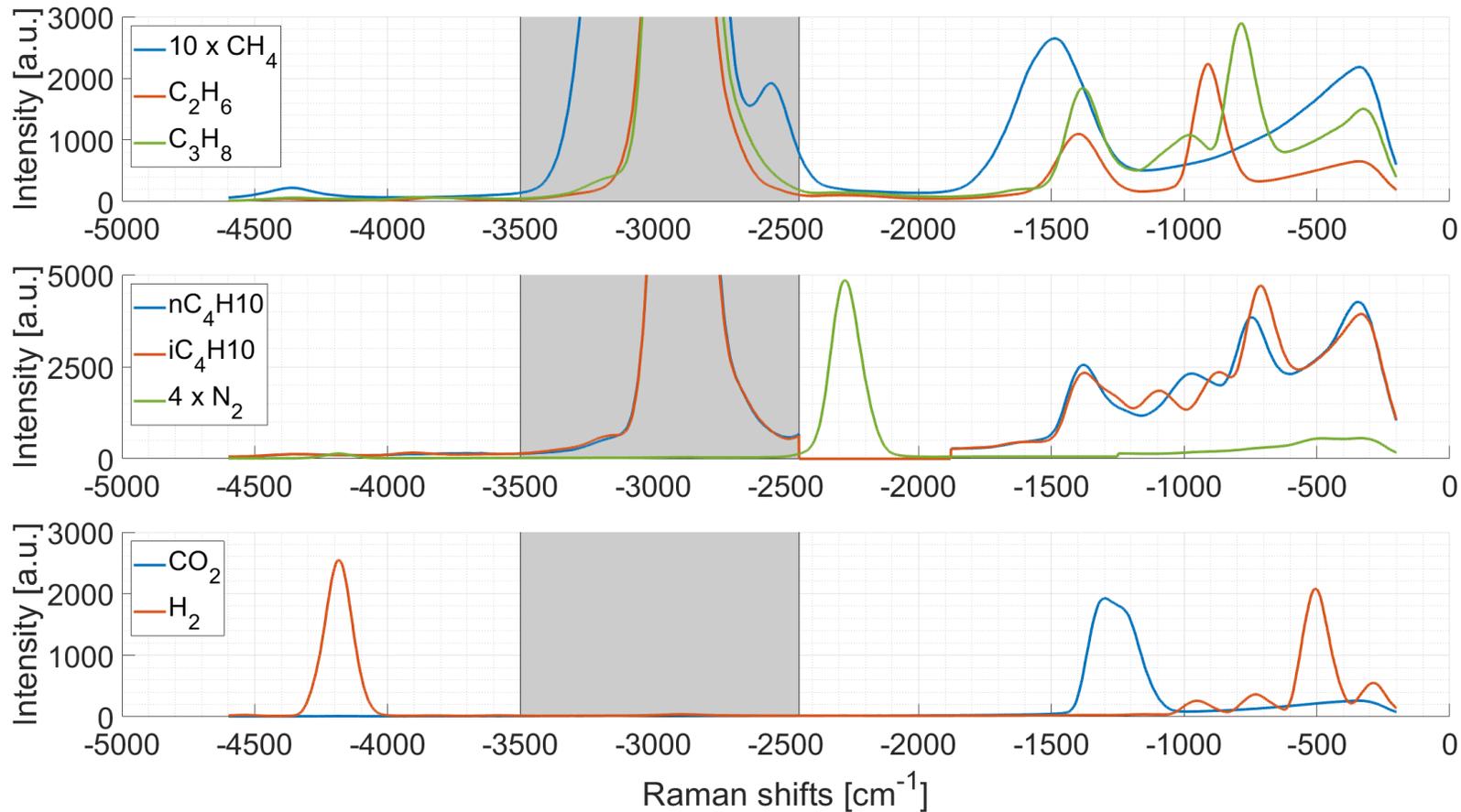
Accuracy: $| HV_{\text{calculated}} - HV_{\text{real}} | < 0.5\%$, class A

Repeatability: $(HV_{\text{max}} - HV_{\text{min}}) / HV_{\text{mean}} < 0.2\%$, class A

Experimental conditions:

- System thermalized at -20°C, 20°C and 50°C.
- 3 representative natural gas mixtures and one H₂ enriched natural gas mixture pressurized at 6 bar (abs).
- 10 subsequent measures (30 s).

Calibrations acquisition

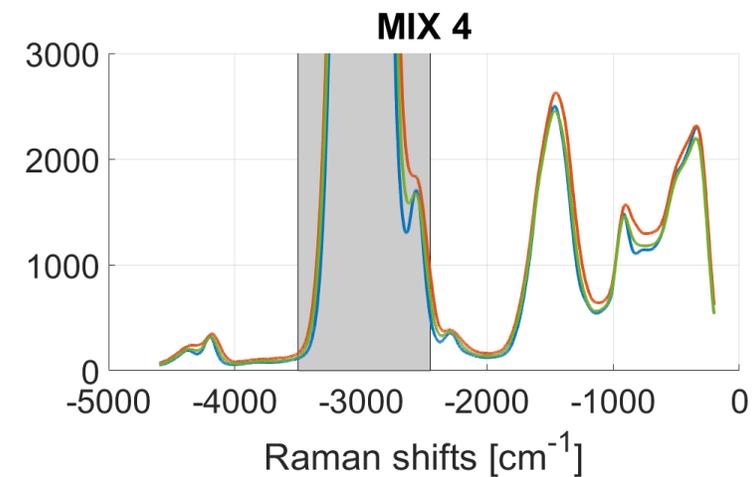
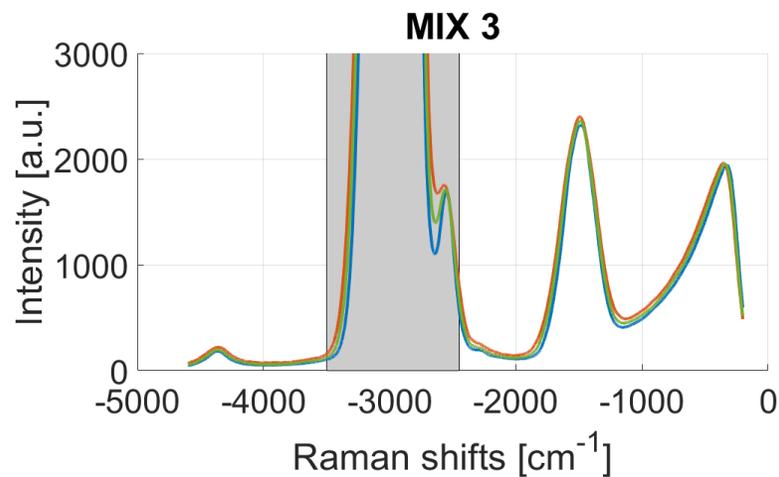
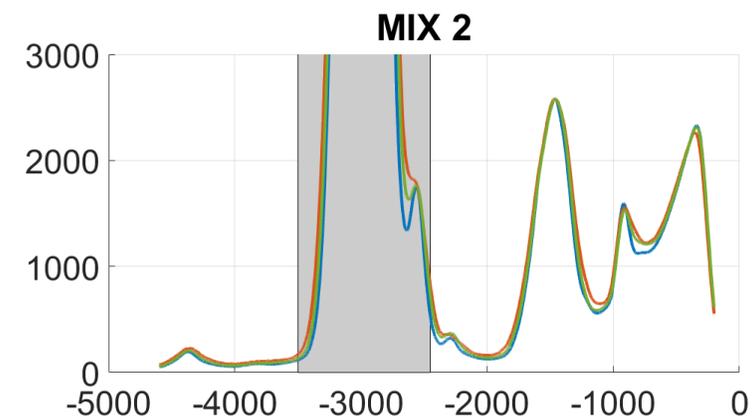
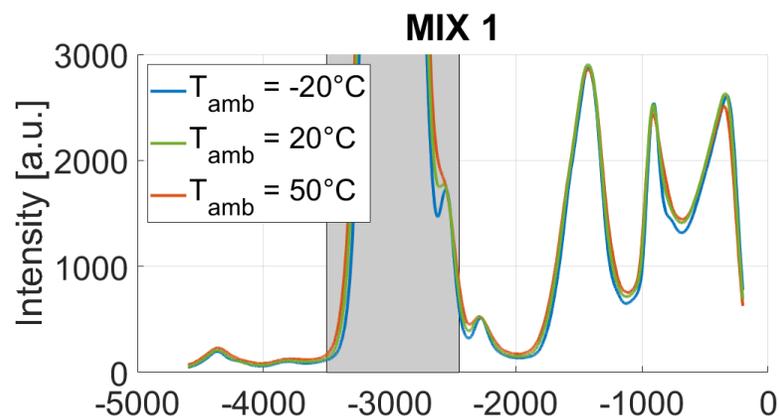


System calibrated with the Raman emission spectra of:
 CH_4 , C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $i\text{-C}_4\text{H}_{10}$, N_2 , CO_2 and H_2

- Spectra generated by averaging 60 seconds of molecular Raman emission (12 frames x 5 seconds)
- Spectra normalized to: gas cell pressure, photodiode readings, camera acquisition time and molecular concentration (in case of binary mixtures)

Experimental spectra acquisition

	MIX1	MIX2	MIX3	MIX4
CH ₄	85.09	92.21	99.40	91.88
C ₂ H ₆	9.00	4.54	0.04	4.13
C ₃ H ₈	1.52	0.72	0.09	0.81
nC ₄ H ₁₀	0.21	0.10	0.00	0.14
iC ₄ H ₁₀	0.15	0.12	0.00	0.12
N ₂	2.47	1.04	0.40	0.40
CO ₂	1.43	1.20	0.05	0.05
H ₂	0.00	0.00	0.00	1.00
HV [MJ/m ³]	40.20	38.92	37.64	38.75



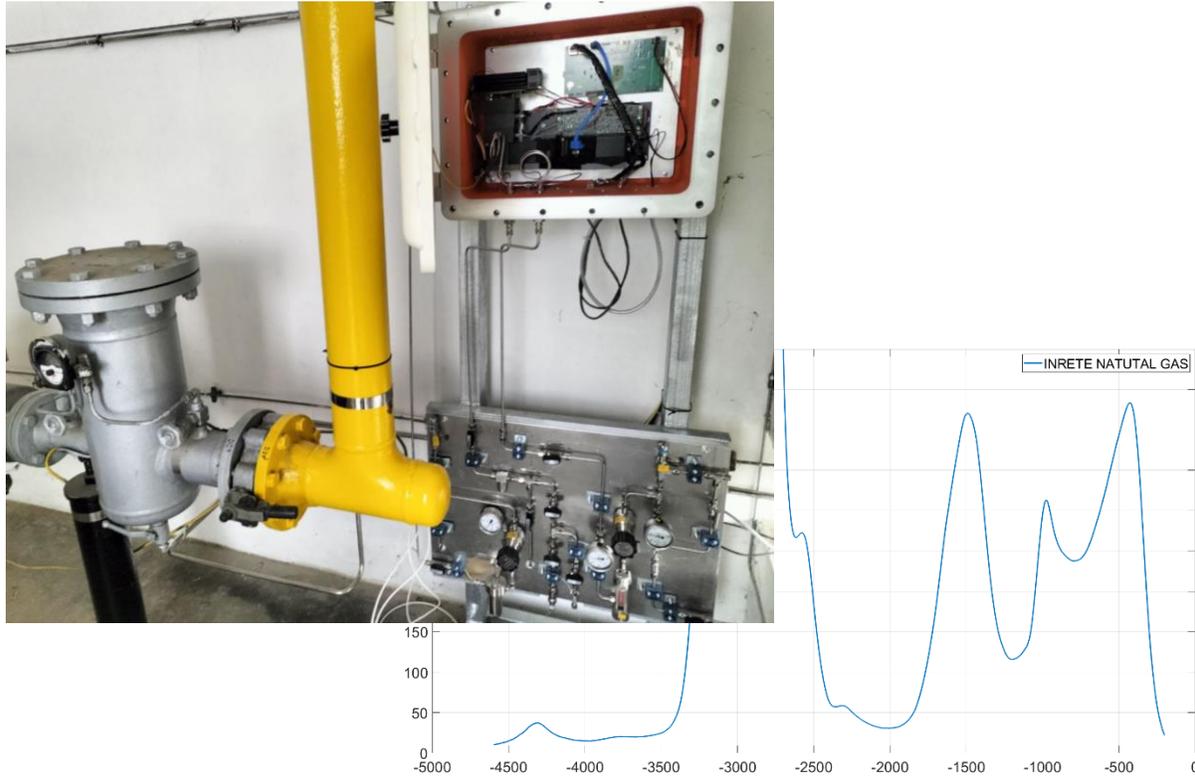
Data elaboration and results

	T_{chamber} [°C]	HV_{measured} [kJ/m ³]	Accuracy [%]	Repeatability [%]		T_{chamber} [°C]	HV_{measured} [kJ/m ³]	Accuracy [%]	Repeatability [%]
MIX 1	-20	40269.549	0.166	0.028	MIX 2	-20	38999.876	0.208	0.043
	20	40192.375	-0.026	0.031		20	38933.686	0.038	0.025
	50	40132.629	-0.175	0.112		50	38954.678	0.092	0.067
MIX 3	-20	37652.808	0.045	0.046	MIX 4	-20	38727.315	-0.049	0.044
	20	37633.640	-0.006	0.037		20	38696.491	-0.128	0.051
	50	37720.244	0.224	0.036		50	38710.987	-0.091	0.033

Note: validated accuracy and repeatability in OIML R 140 **class A** for measures carried out at **1.5** and **17** absolute bar.

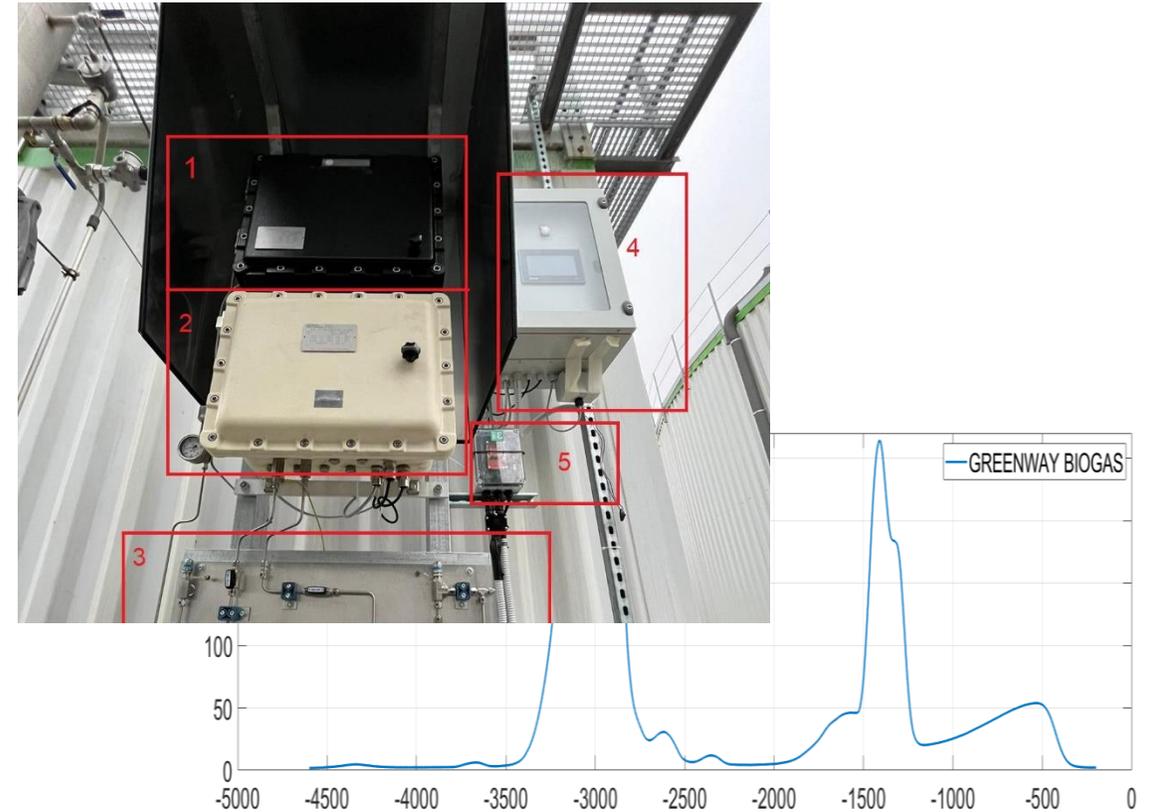
ATTRACT pilot installations

Natural gas pressure reduction cabin – REMI Forlimpopoli (FC)



1 measure every 10 minutes
Results in accord with GC periodical measurements

BioGas production plant – Greenway Bertiola (UD)



1 measure every 2 minutes
Results in accord with plant's measurements
(electrochemical)

Conclusions

- A new **non-invasive** approach for the HV estimation has been validated in a wide temperature range. The HV estimation accuracy and repeatability comply the **OIML R 140 accuracy class A**. The instrument is also able to provide a **main components evaluation**.
- For the first time a **broadband diode laser** has been used for high-precision Raman spectroscopy on gaseous mixtures.
- Only **one calibration set** is required to operate **from -20°C to 50°C**.
- The instrument provides **self-standing operations**, without using consumables or any other sample manipulation (only occasional cleaning required).
- It is able to operate at the transport and distribution **networks pressure** (up to 17 abs bar) without environmental sample dispersion, no supplementary equipment is required.
- The system's performance on Hydrogen enriched Natural Gas blends with more than 1% hydrogen content are currently under investigation.



▶ Thanks for your attention!

TITOLO SLIDE