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1222-2022  
**800**  
ANNI



UNIVERSITÀ  
DEGLI STUDI  
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Consiglio Nazionale  
delle Ricerche

# ***Diagnostica ottica per la misura di composizione su biogas e biometano***

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***Biometano sinonimo di sostenibilità. La ripartenza del settore dopo  
il nuovo DM 15 settembre 2022***

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10 marzo 2023

# 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.
- ▶ Main fuel gas families, typical HHV in MJ/Nm<sup>3</sup>:
- ▶ 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 H<sub>2</sub>S) and water vapour must be removed to avoid damage to the infrastructure.

# Composition of natural gas

- ▶ Raw natural gas typically consists primarily of methane (CH<sub>4</sub>), the shortest and lightest hydrocarbon molecule. It also contains varying amounts of:
  - ▶ Heavier gaseous hydrocarbons: ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>), normal butane (n-C<sub>4</sub>H<sub>10</sub>), isobutane (i-C<sub>4</sub>H<sub>10</sub>), 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 (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and mercaptans such as methanethiol (CH<sub>3</sub>SH) and ethanethiol (C<sub>2</sub>H<sub>5</sub>SH).
  - ▶ Other gases: nitrogen (N<sub>2</sub>) 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 <sub>4</sub> %	C <sub>2</sub> H <sub>6</sub> %	Other HC %	CO <sub>2</sub> %	N <sub>2</sub> %	Other gas %	HHV [MJ/m <sup>3</sup> ]
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

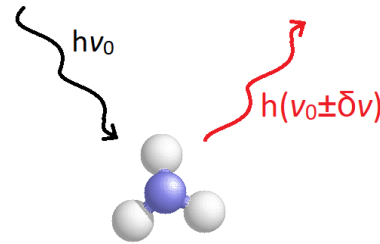
- ▶ Some of the used techniques are sensitive to contamination or require frequent recalibration; unable to sense nitrogen; good for trace-level contaminant detection in biogas.
- ▶ Measurement of ammonia and hydrogen sulfide levels for process control.

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

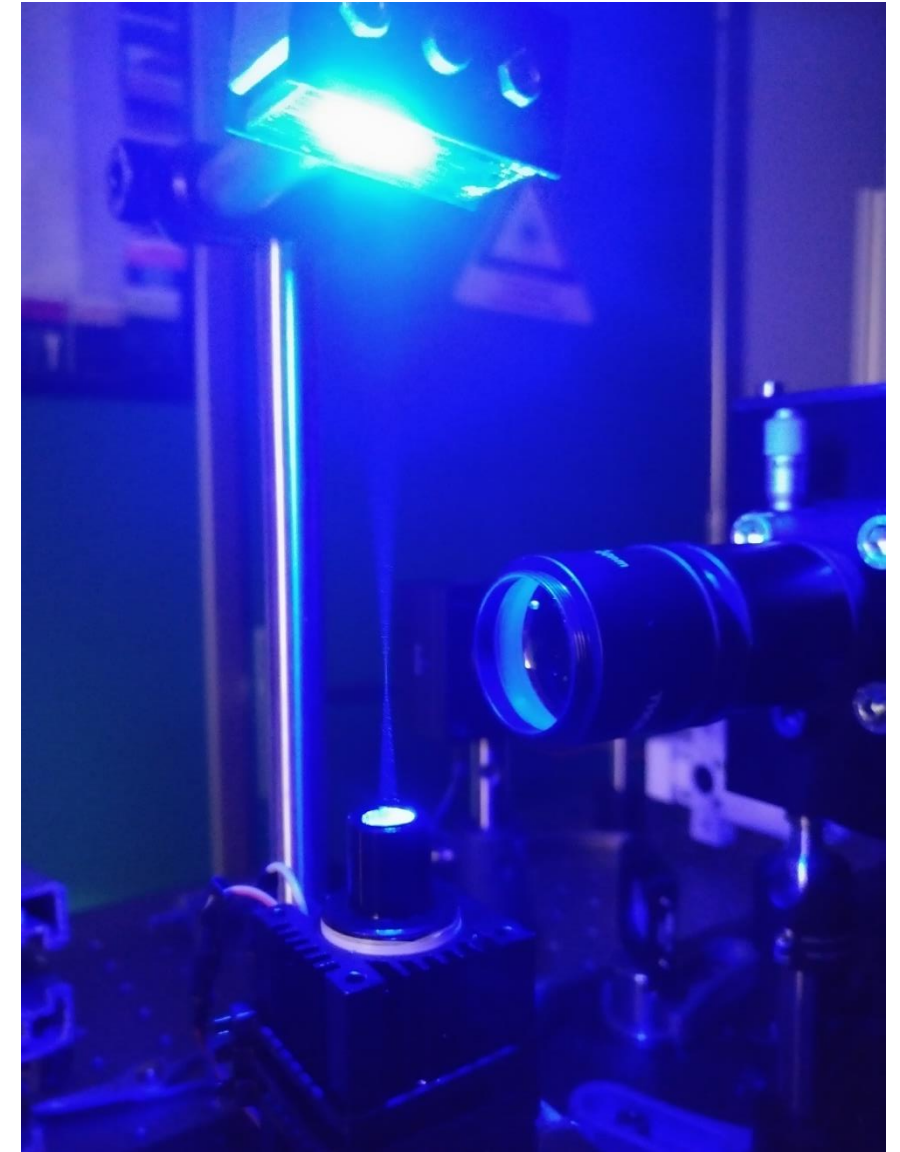
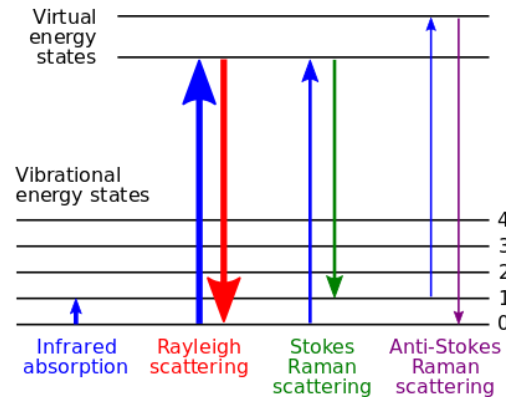
# Raman spectroscopy

- ▶ 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



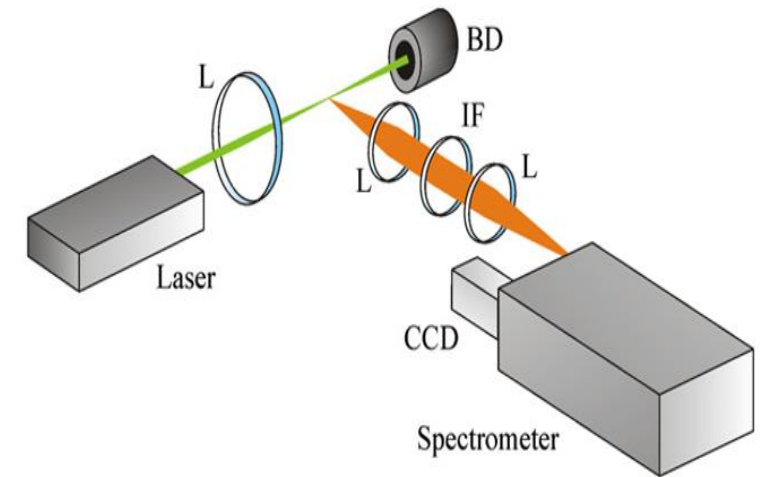
- ▶ Anelastic photon scattering:
  - Interaction leaves the molecule in a different rotovibrational state. Differently from Rayleigh scattering, the emitted photon has a different wavelength (energy) from incident radiation.
  - Energy difference between incident and Raman scattered radiation is a property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

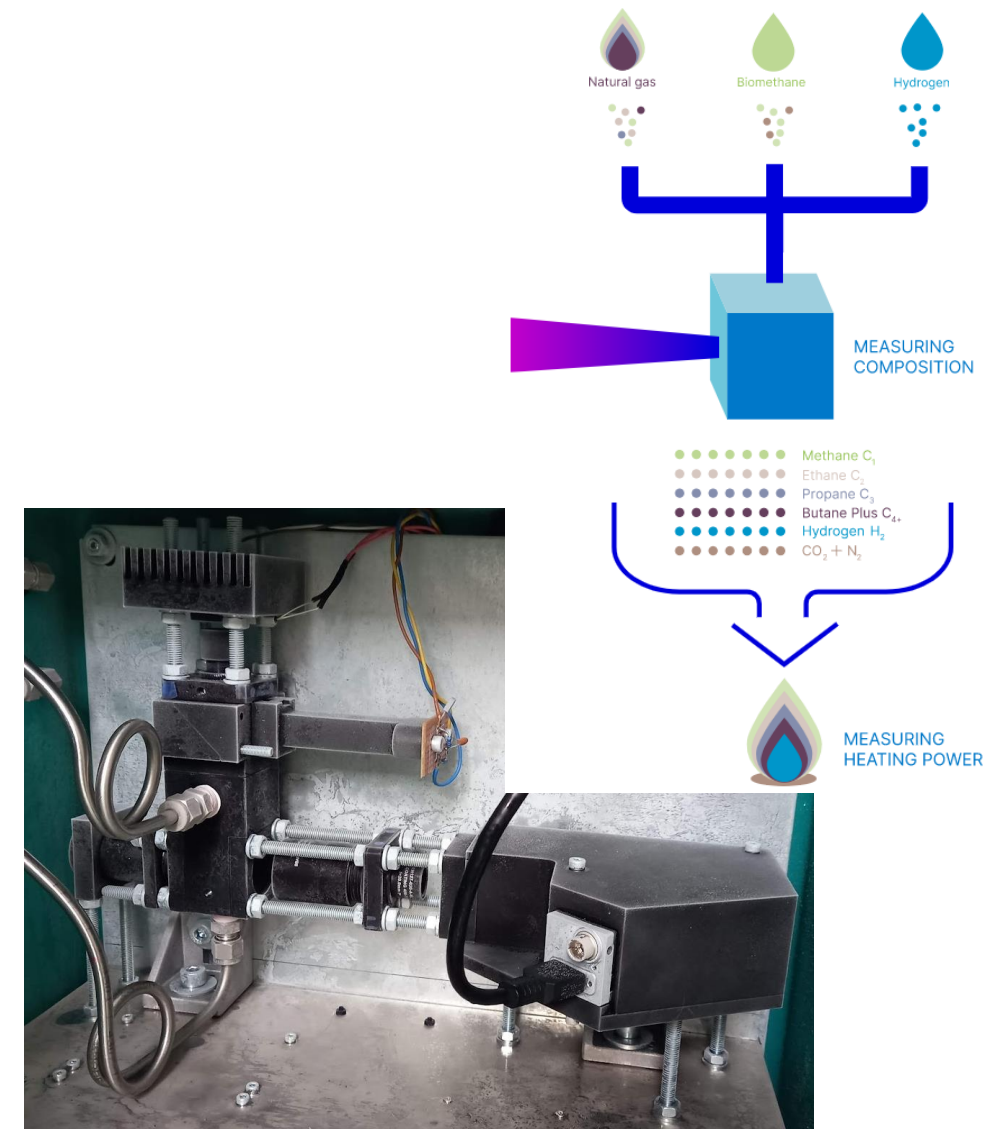
- ▶ CW radiation from a pump laser is focused on a gas sample in order to maximize power density in a given region.
  - ▶ Diffused radiation is collected in the direction orthogonal to both the pump propagation and its electric field. An achromatic optical system couples diffused radiation to a spectrometer 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.
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- ▶ 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.





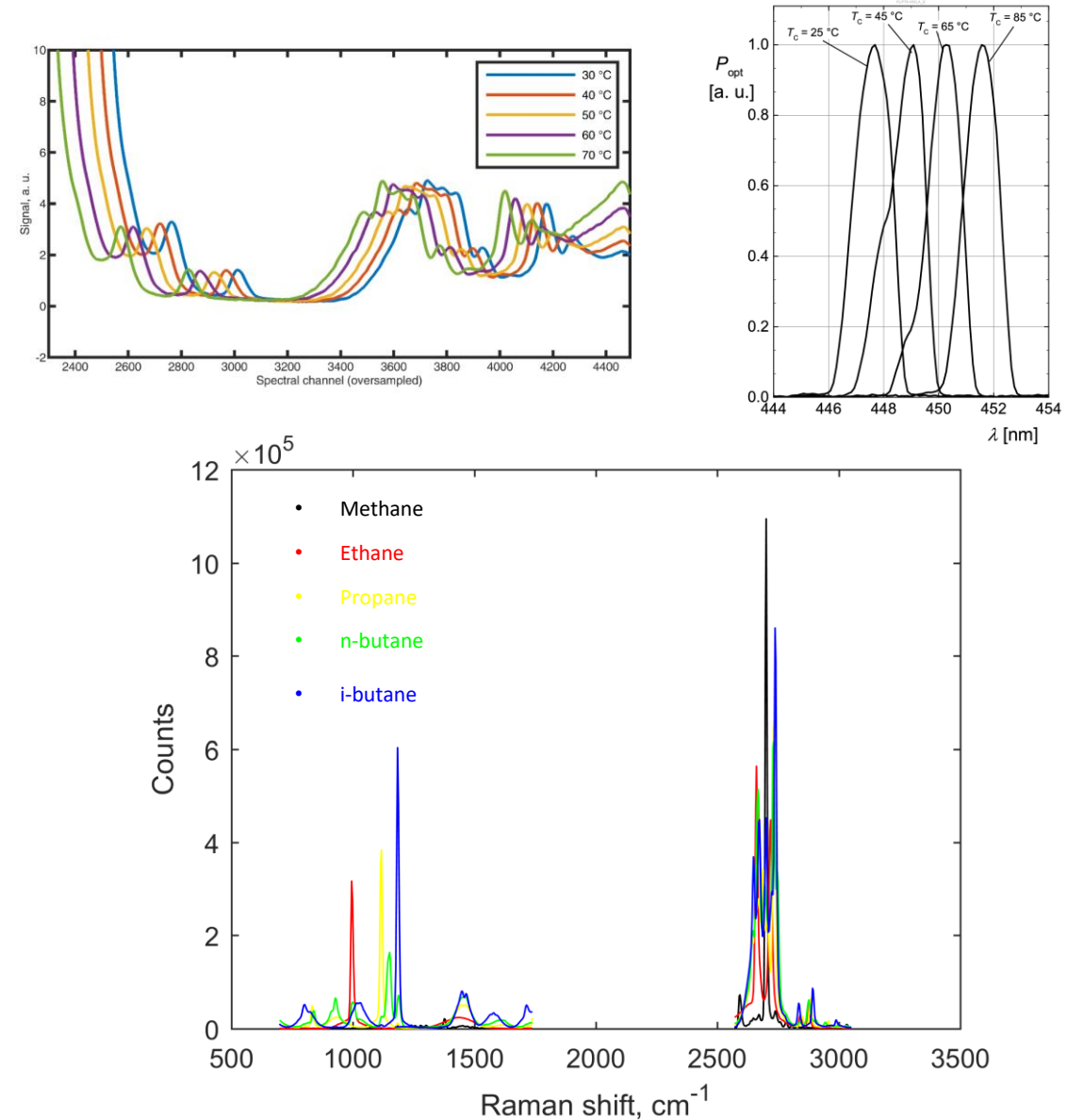
# ATTRACT Prototype analyzer

- ▶ 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.



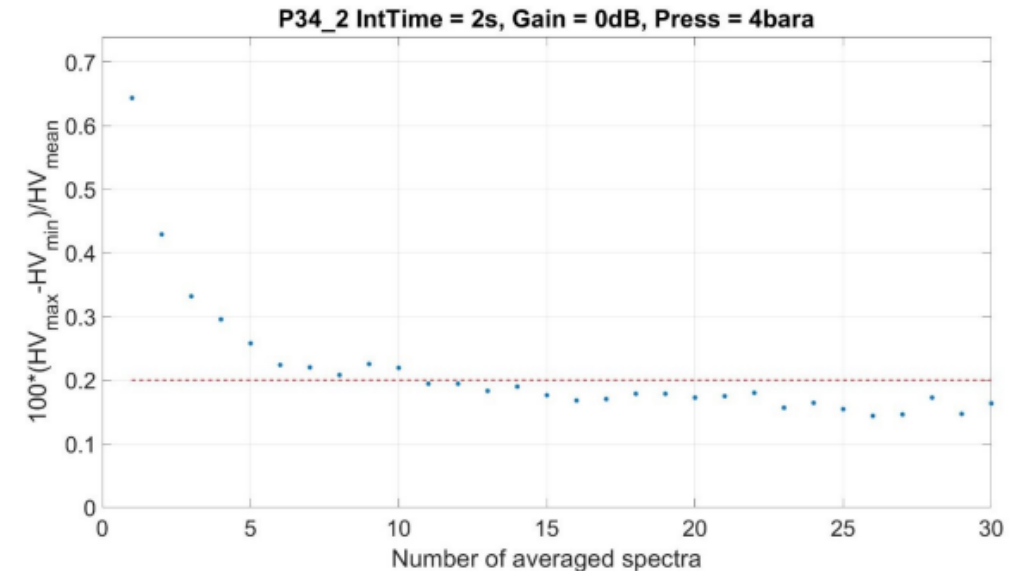
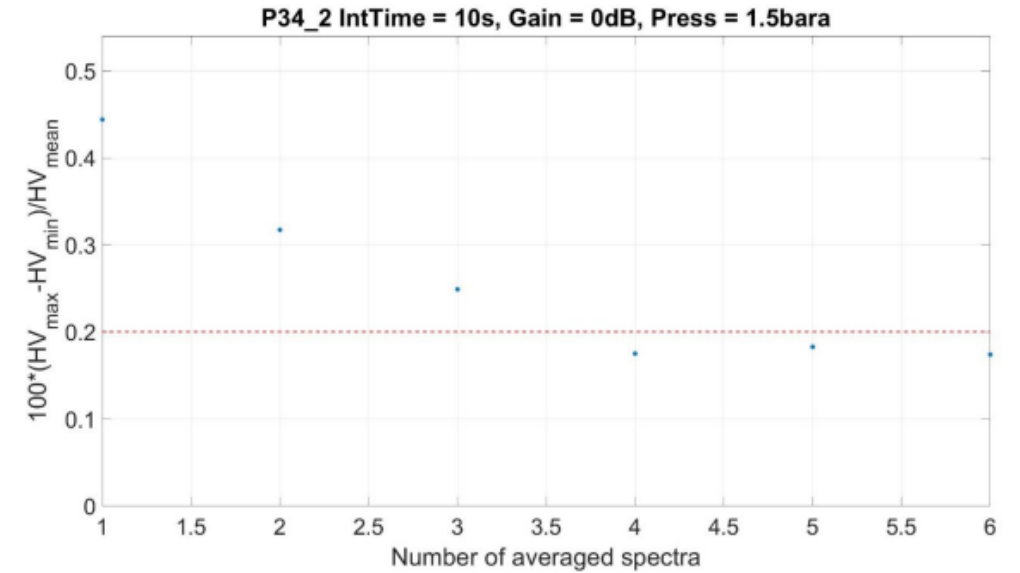
# Signal processing

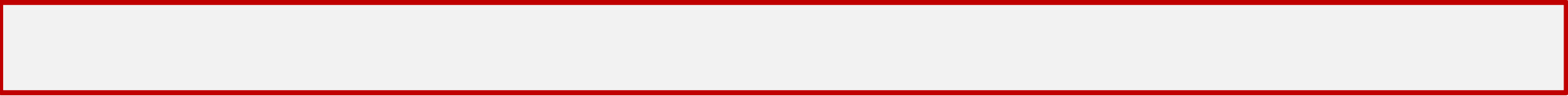
- ▶ A signal processing software provides compensation against drifts in source emission wavelength, linewidth and power
- ▶ A specifically tailored fitting routine provides evaluation of the components in the sample mixture, detecting the volume mixing ratio of methane, ethane, propane, n- and i-butane, 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)



# Performance evaluation

- ▶ With a proper calibration, the device can work over a  $-20^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  temperature range while meeting the 0.5% HHV accuracy specification as required in the OIML 140 standard for accuracy class “A” instruments.
- ▶ The device has been tested on a variety of certified sample mixtures representing biogas, natural gas from different sources, regassified LNG as well as hydrogen-enriched natural gas.
- ▶ The flexibility of the acquisition software allows to choose the measurement integration time depending on the operating pressure to achieve the best filling of the detector dynamic range.
- ▶ Integration times from 2s to 10s appeared to be the best trade off for meeting the OIML 140 class “A” specifications about repeatability of the measurement at operating pressures ranging from 1.5 to 4 bar (abs).





▶ Thanks for your attention!

# TITOLO SLIDE