Measuring the quality of biomethane

Alternative energy: biogas converted into biomethane

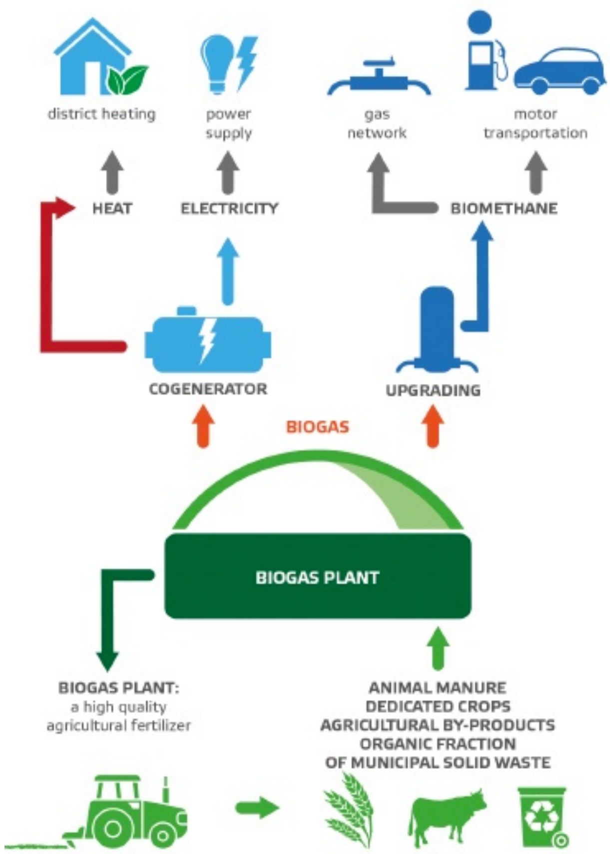
Renewable energy sources are obtained from resources which, due to natural characteristics or human action/cultivation, are renewed over time and are available for an indefinite period of time; they can therefore be considered as non-exhaustible.
Energy becomes **renewable and sustainable** when the reproduction rate of the same source is equal to or greater than its use.
Energy obtained from **biogas** is one of the alternative energies on which great expectations are focused today.
Biogas is a natural gas obtained from a series of biological processes (anaerobic digestion) in which micro-organisms digest in sealed containers:
- organic residues from agricultural waste,
- products from animal husbandry,
- organic substances such as wood, straw, sewage and organic fraction of municipal solid waste (OFMSW).

With the Directive (EU) 218/851, the European Union emphasizes recovery and recycling by indicating the landfill as a bio-resource and identifying in the wet organic waste a source of biomass to be treated in such plants to produce energy and/or nutrient materials.

The biogas obtained from anaerobic digestion (AD) contains:
- 50-80 % methane
- 15-45 % carbon dioxide
- 5 % other gases (such as hydrogen, nitrogen, carbon monoxide)

Biogas has a high calorific value and can be converted into electricity and heat.
The residue of fermentation is the digestate, a liquid material, completely odorless and with a very high agronomic value, with improved characteristics compared to the starting source.

Biogas requires a further purification in order to be used as biofuel for motor vehicles, to be introduced into the national gas distribution network or to be transported and stored for the subsequent production of energy.
The so-called "**biogas upgrading to biomethane**" process consists of removing CO_2 and raising the percentage of methane to approximately 98 vol %. The finished product called biomethane is of higher quality and calorific value than biogas. It has similar chemical properties to natural gas and is often injected directly into the natural gas grid, where it is stored and distributed.



Reference standards

At EU level, standards EN 16726, EN 16723-1 and EN 16723-2 set the gas quality characteristics, parameters and their limits for evaluating the quality of gas and biomethane that are transmitted, injected into and from storage, distributed and utilized, guaranteeing the conditions of safety and continuity of the service, in compliance with current legislation. Related to Biomethane, the EU Reference Standards, and other technical specifications varying from country to country, describe in particular:

- the minimum chemical and energy characteristics of biomethane,
- the methods of analysis and sampling,
- the odorization,
- the data connection and metrological characteristics of the various measuring systems

The injection of biomethane into the grid is allowed on condition that it does not have physical-chemical characteristics that cancel out or cover up the effect of the specific odorous substances. By its nature, biomethane can contain a wide range of trace components which may potentially mask the odor component Tetrahydrothiophene (THT) or Tert butyl mercaptan (TBM) added to the upgraded gas as a safety requirement. The most important substances under investigations are:

- Terpenes (α and β pinene, limonene, carene),
- Butanone,
- Cumene

Parameter	Specification	Unit	Norm
Sulfur (H_2S+COS)	≤ 5	mg/Sm^3	EN 16726
Total Sulfur	≤ 20	mg/Sm^3	EN 16726
Ammonia	≤ 10	mg/Sm^3	EN 16723-1
Amines content	≤ 10	mg/Sm^3	EN 16723-1
Si content	0,3 ÷ 1,0	mg/Sm^3	EN 16723-1
Hydrogen	≤ 0,5	%mol	EN 16723-1
Oxygen	≤ 0,001 or ≤ 1	%mol	EN 16726
Carbon monoxide	≤ 0,1	%mol	EN 16723-1
Carbon dioxide	≤ 2,5 or ≤ 4	%mol	EN 16726
Methane number	≥ 65	%mol	EN 16726
Water Dew Point	- 8°C at 7000 Kpa	%mol	EN 16726

Specifications and concentration range for some parameters in the EU Standards

Renewable energy plays an important and growing role in the energy system of the European Union. First target was to reach 20 % of energy consumption from renewable sources by 2020. The Renewable Energy Directive (EU) 2018/2001 establishes a new binding target of at least 32 % renewable energy for the EU for 2030. In addition, all EU countries must also ensure that at least 10 % of their transport fuels come from renewable sources by 2020. Economic incentives are introduced in several European Countries for the introduction of biomethane into the natural gas network or its use as fuel for transportation.

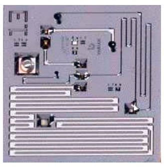
The EN 16723-1:2016 standard specifies the requirements and test methods for biomethane to be introduced into the natural gas networks.
The EN 16723-2:2017 standard specifies the requirements and test methods for natural gas (group L and H according to EN 437), biomethane and their mixtures at the point of use as automotive fuels. The standard applies to these fuels regardless of the storage method (compressed or liquefied).

Determine the quality of Biomethane by Micro-Gas Chromatography

The Micro-gas chromatography technique is ideal for determining the quality of Biomethane and its impurities.

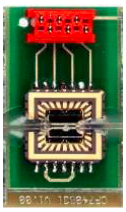
The development of increasingly compact MicroGC systems has been possible thanks to micromachining technology, i.e. the engineering of micro-electro-pneumatic structures very close to the production of chips in the semiconductor industry. Small size means smaller instruments for easier transportation and their installation closer to sampling point.

The modular construction allows the use of different analytical channels in a single instrument which increases potentiality, flexibility and economical benefit.



The injector and the detector are the miniaturized parts of the instrument ; their small dimensions allow the use of chromatographic columns with smaller diameters that make possible faster analytical separations.

The analysis times are in the order of seconds, instead of minutes with conventional chromatography.



The detector used in the MicroGC is a µTCD. Like classic thermal conductivity detectors, it measures the thermal conductivity of gases, in particular the difference in thermal conductivity between a pure gas (carrier) and the sample components. It is a "universal detector " capable of measuring both organic and inorganic compounds and requiring only one gas with very low consumption.

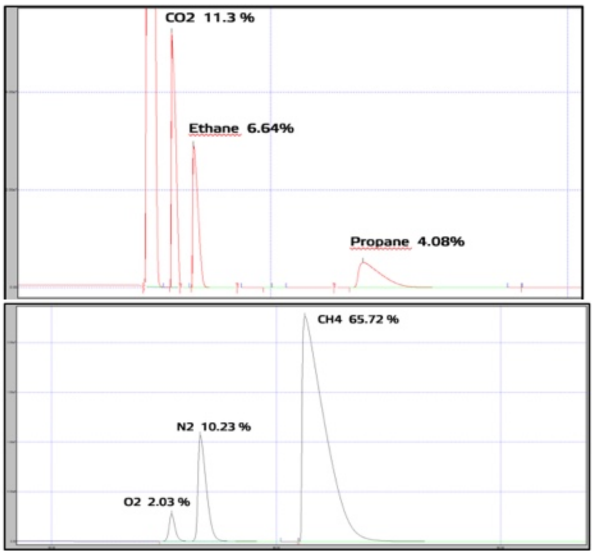
The µTCD is a solid state (SSD) detector consisting of 4 filaments, robust and stable, very sensitive and with a linear dynamic range of 10^6.

Analytical configurations for biomethane analysis

The MicroGC model R490 use a modular plug & play structure and has all the flexibility to be configured to determine the composition of the biomethane and its chemical-physical properties.

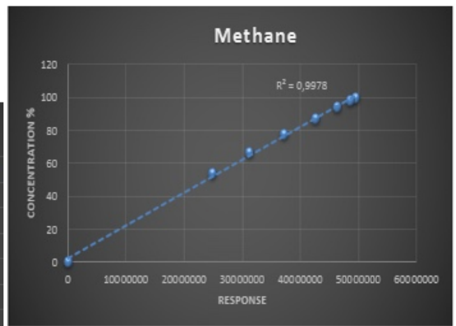
The MicroGC, in its different configurations, can measure the following chemical species and properties:

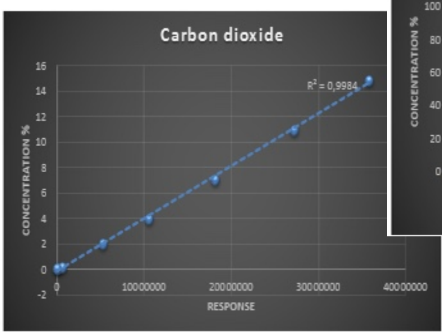
- Superior and Inferior calorific value,
- Wobbe Index, Relative Density, Density, Compressibility
- H_2, O_2, N_2, CH_4, CO, CO_2, H_2S, COS, C_2H_6, C_3H_8
- THT and TBM odorants
- Terpenes and Ketones



Chromatogram of the separation of the main biomethane compounds

Linearity of the µTCD detectors used in SRA Instruments MicroGCs for two of the main components in biomethane





The characteristics of the technology used in the MicroGC analyzers allow:

- precision in the volumes of sample injected into the column,
- stability and linearity of the instrumental response,
- speed of analysis and robustness

Metrological configuration for the analysis of the calorific value of biomethane

The MicroGC R490 has obtained the Metrological Certification for the measurement of the Calorific Value of Biomethane associated with a volume conversion device in accordance with the OIML-R140:2007 recommendation.
In the metrological version, the following biomethane components are measured:
- hydrocarbons from C_1 up to C_3, CO_2, N_2, O_2, H_2S and COS.

The addition of a third dedicated channel allows simultaneous measurement of the odorant (THT or TBM), introduced into the gas, to complete the information obtainable from the instrument in about 3 minutes.
The analyzer has an internal computer for remote control over the Ethernet network and transmission of the results via serial Modbus. The instrument has been validated to request only one annual calibration check.

R490 M - The metrological model of MicroGC

Component name	Chan.	RT (sec)	Area	Unit	Raw Conc.	Normalized
O2	A	42.39	1024204.39	%	1.99	2.03
N2	A	43.93	5461516.11	%	10.00	10.23
CH4	A	49.52	31214695.00	%	64.24	65.72
CO2	B	19.98	27252461.12	%	11.03	11.29
C2H6	B	22.20	17363042.83	%	6.49	6.64
H2S	b	30.12	1266.47	ppmVol	4.52	4.62
COS	b	0.00	0.00	ppmVol	0.00	0.00
C3H8	B	39.32	13387749.36	%	3.99	4.08
THT	c	0.00	0.00	mg/m3	0.00	
			95704935.28		97.75	100.00

Values at 15 °C/15 °C

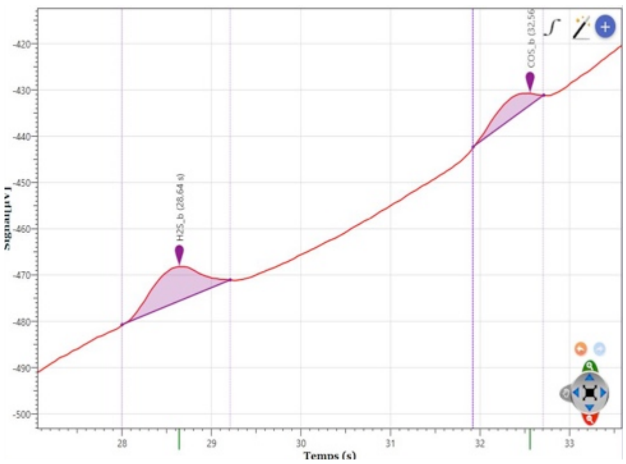
Molair mass :	22.825	g/mol
Ideal density :	0.9654	Kg/m3(n)
Ideal spec. gravity :	0.7881	
Real ICV :	7149.299	kCal/m3
Wobbe index :	8893.507	kCal/m3
Compressibility fact :	0.9973	

Biomethane analysis report obtained with MicroGC SRA from remote computer

Simultaneous analysis of H_2S and COS sulfur species in Biomethane

Hydrogen sulphide (H_2S) is a by-product of anaerobic digestion and can be present in Biogas at a concentration ranging from a few tens of ppm to several thousand ppm.
Due to its corrosive and toxic characteristics, H_2S is removed from the gas during the early stages of the process for upgrading Biogas to Biomethane with desulphurization technologies such as scrubbing or adsorption.
The EN 16726 standard indicates as an admissible limit in Biomethane a concentration of H_2S lower than 5 mg/Sm^3 (3.5 ppm) and as a continuous measurement, also the Carbonyl Sulphide (COS) is indicated as sulfur compound present in traces of similar importance.
These two sulfur species (H_2S and COS) are measured by the MicroGC together with all the main components of Biomethane simultaneously and without repeating the analysis thanks to the exceptional linearity and sensitivity of the μTCD detector used.

Analysis	Peak area H_2S	Peak area COS
H_2S COS rep 1	27401,984	24599,037
H_2S COS rep 2	28491,973	24960,147
H_2S COS rep 3	28345,167	25635,062
H_2S COS rep 4	28045,313	25508,046
H_2S COS rep 5	29282,899	26490,258
H_2S COS rep 6	28885,153	26078,541
H_2S COS rep 7	29351,404	26212,218
H_2S COS rep 8	30575,247	27097,027
H_2S COS rep 9	29845,393	25966,685
H_2S COS rep 10	27460,446	24805,381
Min.	27402,0	24599,0
Avg	28768,5	25735,2
Max	30575,2	27097,0
Rsd (%)	3,552	3,076



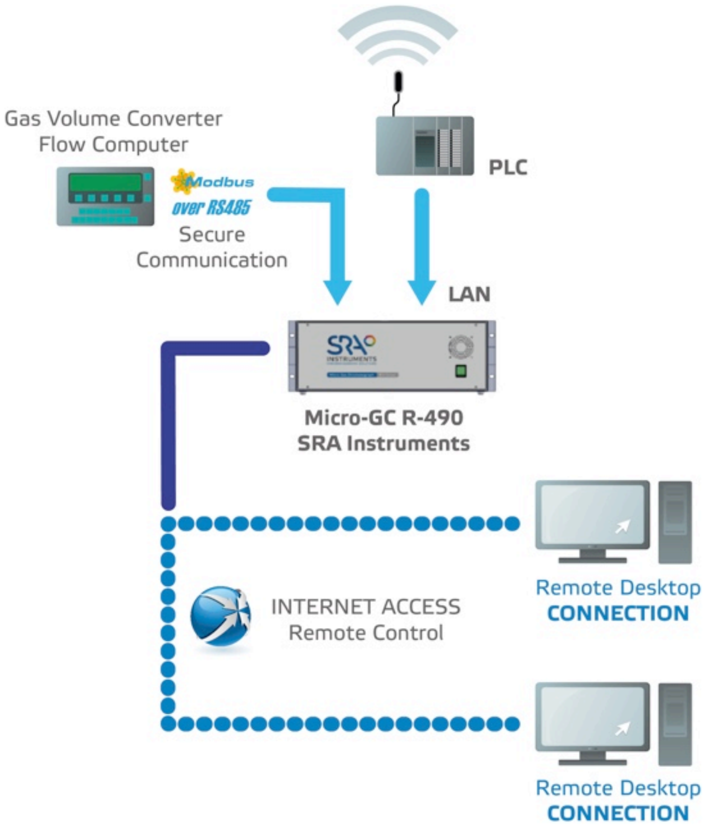
Simultaneous analysis of H_2S and COS sulfur species in Biomethane

MicroGC integration into a Smart Gas Grid

The production of energy from renewable sources, in particular from gas, has contributed to an evolution of the entire distribution chain and transportation networks.

Measurement equipment must play a more complete and complex role today, moving from a simple analytical verification to an active part in the decision-making processes, capable of operating in interaction with the entire system to ensure that the quality of the gas injected complies with the required regulations.

The SRA Instruments MicroGC R490 incorporates a computer with a proprietary software that constantly monitors all measured parameters and instantly communicates any analysis and alarm information. It is also possible to access the system remotely from any PC in the network. Remote access allows the operator to fully control all system functions, eliminating the need to physically inspect the instrument at the installation site.



Integration of the MicroGC R490 into a grid

Conclusions

The decarbonisation path envisaged by the EU's Climate and Energy strategy makes energy obtained from biomethane, one of the alternative energies on which great expectations and large investments are concentrated.

The production phases of biomethane and the intrinsic characteristics of this gas make the characterization of all its components essential before it is introduced into the natural gas networks (for industrial and domestic application) and for the use of biomethane as biofuel for automotive purposes.

Gas chromatography is an excellent analytical technique that has always guaranteed the quality of the measurement, determining both the main components and the impurities in biogas and biomethane in a unique, safe and efficient way.

Micro-gas chromatografy has added new capabilities to the classical technique, reducing size and operating users, while maintaining compact and complete analytical structures, capable of analyzing a wide range of components.

All in a single robust, reliable and rapid system, which simplifies analytical management while reducing costs.

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