ON-LINE MEASUREMENT OF BIOMETHANE, SYNTHETIC METHANE AND NATURAL GAS ENERGY, QUALITY AND ODORIZATION BY ONE DEDICATED MICROGC

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INTRODUCTION

Biomethane is an important source of green and renewable energy. To allow injection of biomethane into the natural gas grid or the use as a vehicle fuel, it should meet the quality standards for natural gas.

The timely and accurate measurement of the biomethane energy is of fundamental importance for users and distributors. The MicroGC technology supply features ideal for fast and accurate on-line analysis of biomethane and calorific value measurements. Minor organic contaminants like hydrogen sulfide, carbonyl sulfide, terpenes, ketones can be determined, as well biomethane odorization. As connection tool, an important role is played by the software architecture of the MicroGC system, it must be flexible and open to any specific installation requirement, like sampling switching, data communication and, at the same time, fully user accessible for data analysis management.

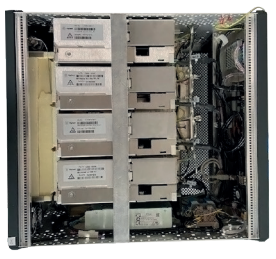
The R990 M MicroGC from SRA Instruments Company is just starting its metrology certification process by the LNE (National Laboratory of Tests) according to the international recommendation OIML R140:2007 (OIML = International Organization of Legal Metrology), this will ensure the reliability and the reproducibility of the results, but also the reliability and the safety of the conditions of use. The metrology certification will concern the energy measurement of biomethane as well as natural gas with hydrogen.

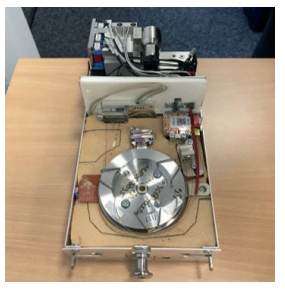
INSTRUMENTATION

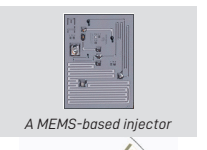
The analyzer uses the 990 channels from Agilent. This instrument can use from 1 to 4 MicroGC channel simultaneously.

The 990 technology makes some differences compared to previous 490 platform by :

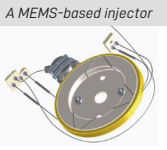
- Improved channel design for easier exchange (less than 10 minutes)
- Better robustness. The use of fewer advanced connections limits diffusion and thus to extend the instrument's operating time.



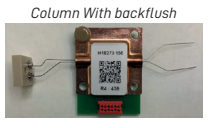




A MEMS-based injector



Column With backflush



A µTCD

Features :

- Heated sample inlet and injectors
- Integrated sensor for sample pressure alarm and monitoring within Soprane SW)
- One dedicated inlet for the optional non-metrology channel
- Inert membrane filter to ensure that no droplets nor particles enter in the injector
- Temperature range for each channel : up to 180 °C and only isothermal
- Possibility of having 1 or 2 carrier gases depending on the application

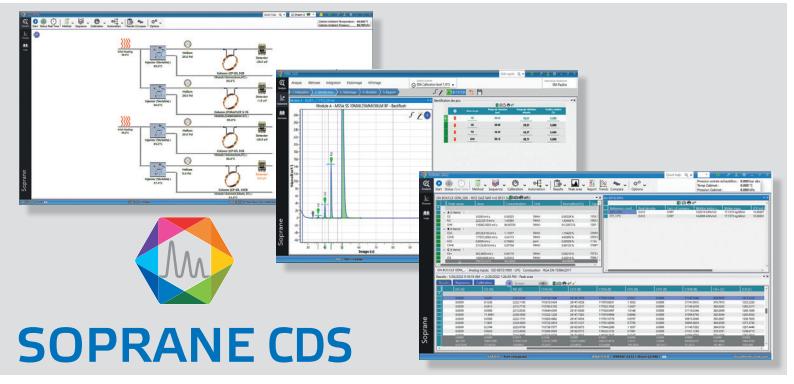
SOFTWARE

Inside the R990 is an on-board computer system driven by Windows 10 IOT.

Other specifications include : • Front panel touchscreen
• Modbus : serial and/or TCP-IP
• I/O Digital & Analogic

The software used is a dedicated chromatography Data System for MicroGC providing function for automation and process application. Soprane CDS integrates calculations including those of the ISO 6976:2016 standard.

It is able to manage user and alarms. Its diagnostics is facilitated by the emission of log files and can handle many others (Automatic restart, stream selector, remote access...)



METROLOGY CERTIFICATION

According to OIML R140 – Measuring systems for gaseous fuel

Calculation : • SCV – volumetric basis
• ICV – volumetric basis
• Wobbe index
• Density or relative density
• Gas composition

Sample	Biomethane and Natural Gas including H_2
International Standard for Calorific Values Calculation	ISO 6976:2016
Accuracy class	Classe A (0.5%)
ISO standard reference conditions	0°C/0°C ; 25°C/0°C ; 15°C/15°C
Calorific value measurement range	9 to 14 kWh/m³
Environmental temperature	-10°C to +40°C

BIOMETHANE AND SYNTHETIC METHANE ANALYSIS

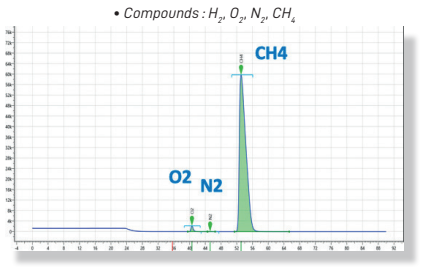
The analysis of all compounds contained in biomethane, or synthetic methane, requires a two-channel configuration : a CP-Molsieve 5Å for "light" gases and a PoraPlot U for hydrocarbons up to C_3 and sulphur compounds.

Only one carrier gas is used : *helium*

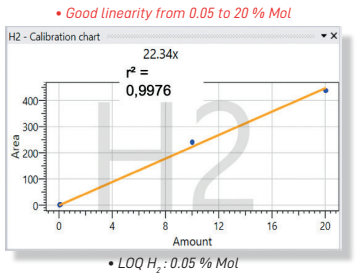
Cycle time : 180 seconds

Channel CP-MolSieve 5Å

• *Compounds : H_2, O_2, N_2, CH_4*

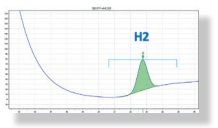


• *Good linearity from 0.05 to 20 % Mol*

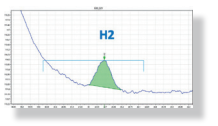


• *LOQ H_2 : 0.05 % Mol*

• *2.0 % Mol*



• *0.07 % Mol*

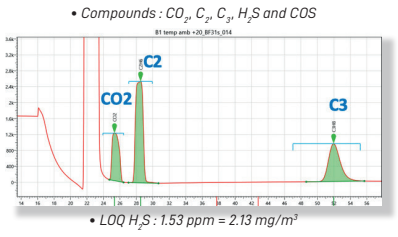


• *Reproducibility calculated over 10 analyses*

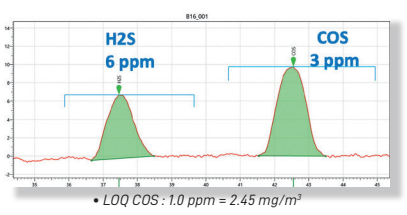
COMPOUND	AREA (mV.s)	RSD (%)
H_2 (6 % Mol)	114.70	0.15
H2S (2 ppm)	1.96	3.5
COS (3 ppm)	9.23	2.9
CO_2 (0.05 % Mol)	1195.9	0.02
C_2 (0.10 % Mol)	2664.2	0.02
C_3 (0.05 % Mol)	1585.3	0.56

Channel PoraPlot U

• *Compounds : CO_2, C_2, C_3, H_2S and COS*



• *LOQ H_2S : 1.53 ppm = 2.13 mg/m³*



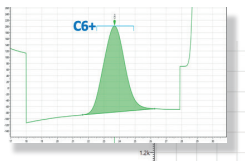
• *LOQ COS : 1.0 ppm = 2.45 mg/m³*

NATURAL GAS ANALYSIS

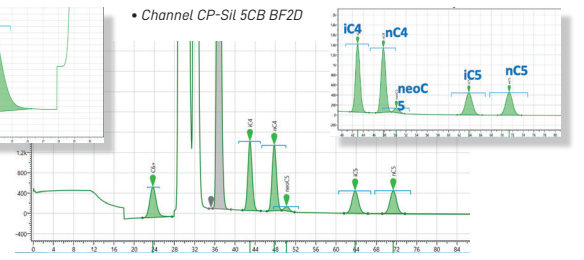
The analysis of natural gas (with or without hydrogen) uses a three-channel configuration : a CP-Molsieve 5Å, a PoraPlot U and a CP-Sil 5CB BF2D.

This channel can analyze compounds from C_3 to C_{6+}. All compounds after C_6 are eluted in a single peak before the matrix peak

Only one carrier gas is used : *helium*



• *Channel CP-Sil 5CB BF2D*



COMPOUND	Tr (s)	RSD (%)	AREA (mV.s)	RSD (%)
iC_4 (0.18 % Mol)	42.9	0.01	1362.7	0.57
nC_4 (0.18 % Mol)	47.8	0.01	1337.0	0.46
iC_5 (0.07 % Mol)	63.6	0.01	666.5	0.36
nC_5 (0.08 % Mol)	71.4	0.01	692.0	0.37
$neoC_5$ (0.017 % Mol)	50.2	0.01	100.7	0.41
C_{6+} (0.1 % Mol)	23.7	0.02	903.6	0.31

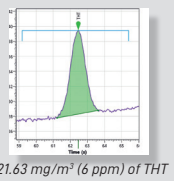
THE OPTIONAL CHANNEL

The two common odorant compounds in combustible gas are THT (tetrahydrothiophene) and TBM (terbutyl mercaptan), which are ideal for making a leak detectable. It is therefore necessary to prevent their concentration from being "below" or "above" the regular level, which requires thorough and monitoring

The modularity of the instrument allows the choice of the module according to the odorant molecules added to gas. Thus, the CP Sil 19CB channel allows the quantification of THT while the CP Sil 13CB channel allows the quantification of TBM.

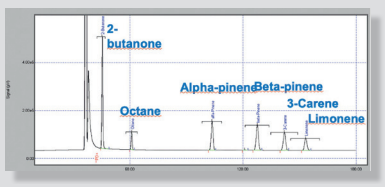
On the other hand, some injection sites may require the monitoring of other compounds belonging to the terpene family. For this, the CP Sil 13CB channel is the best choice to control their content in the gas.

Channel CP-Sil 19CB for THT



• *21.63 mg/m³ (6 ppm) of THT*

Channel CP-Sil 13CB



CONCLUSION

The previous version of metrology-certified instrumentation according to the same recommendations and standards, has already proved its worth. More than 150 analyzers from SRA have been installed for the on-line monitoring of injected biomethane. The new generation R990, with all its extended application range, will meet tomorrow's requirements for the analysis of biomethane, synthetic methane and natural gas including hydrogen compound. The dedicated Soprane CDS software is a powerful asset for the R990 on-line in the industrial and new energy field.

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