Trends in custody transfer gas quality analysis

by **Achim Zajc**

Introductory concepts for the measurement of natural gas quality using the principle of the determination of the natural gas quality are discussed. The advantages and disadvantages of each method are described. Also an outlook is given at the end of the paper and is discussed too.

1. INTRODUCTION

After the replacement of the calorimeter for the determination of the calorific value of natural gas by process gas chromatography, the scope of chemical components to be measured has been clearly defined for years. Here, the following components are measured by the process gas chromatographs for determining the calorific value:

Nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), n-butane (n-C_4H_{10}), iso-butane (i-C_4H_{10}), n-pentane (n-C_5H_{12}), iso-pentane (i-C_5H_{12}), neo-pentane (neo-C_5H_{12}), n-hexane (C_6H_{14}).

In November 2007, the new "Technical Directive TRG 14: Injection of biogas into the natural gas network" [1] was adopted by the Metrological Institute (PTB). This substantially modified the requirements of gas quality analysis. Hydrogen (H_2) and oxygen (O_2) were added to the above named chemical components. Since biogas does not contain higher boiling hydrocarbons like pentane or hexane, it is not necessary to measure these components in this case. It was, however, necessary to adapt the existing systems to the new requirements.

The increasing mixture of biogas with natural gas in the pipeline network overall in Germany generates new requirements for the determination of the calorific value by means of gas chromatography. Now hydrogen (H_2) and oxygen (O_2) as well as all other components like: nitrogen (N_2), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), n-butane (n-C_4H_{10}), iso-butane (i-C_4H_{10}), n-pentane (n-C_5H_{12}), iso-pentane (i-C_5H_{12}), neo-pentane (neo-C_5H_{12}), n-hexane (C_6H_{14}) must all be measured to determine the calorific value, since the REKO-systems (mathematical model to calculate the calorific value at any exit point of the grid) require the C_5 and C_6 components. Therefore, a process gas chromatograph must now be capable of separating and detecting minimum 13 individual chemical components. This is where a new trend comes in. This trend provides the "Power-to-Gas" technology [2, 3] and raises the question of how to define the measurement range for hydrogen, in order to comply with the new requirements.

2. GAS CHROMATOGRAPHY METHODS FOR THE GAS QUALITY ANALYSIS OF NATURAL GAS

2.1 The current status of the determination of the calorific value of biogas by process gas chromatography

As already explained, the 11 chemical components to be measured for the determination of the calorific value were clear up to the end of 2007 and were defined for years. With the injection of biogas, this has fundamentally changed. **Table 1** shows a typical composition of raw biogas and biomethane.

This implies that for biogas injections, there is no need to measure and quantify higher boiling hydrocarbons like pentane and hexane. According to these findings, the process gas chromatographs of all known manufacturers have been PTB-certified in the meanwhile in the market and meet the requirements for the metrological gas quality analysis of biogas injection.

The requirements include the separate measurement of the following chemical components:

- Hydrogen (H_2)
- Oxygen (O_2)
- Nitrogen (N_2)
- Carbon dioxide (CO_2)

- Methane (CH_4)
- Ethane (C_2H_6)
- Propane (C_3H_8)
- n-butane (n-C_4H_{10})
- iso-butane (i-C_4H_{10})

For the separation of hydrogen and oxygen, it is necessary to employ a molecular sieve column. This application has been explained in detail already, and therefore please refer to the literature [5]. From **Table 2** it is clear that hydrogen is the best carrier gas for determining all natural gas and biogas components. With an exception: hydrogen itself. It is obviously impossible to use hydrogen as a carrier gas when it is required to measure and quantify it, too. This dilemma offers two potential approaches:

- Two carrier gases
- Argon as a carrier gas for hydrogen
- Helium as a carrier gas for all other components
- Argon as a carrier gas for all other components
- Helium as a carrier gas for all other components (including hydrogen)

The use of two carrier gases provides the optimum solution from a technological viewpoint. This ensures that the maximum conductivity difference for the carrier gas is provided for the analysis of each substance and therefore the best determinability of each substance is ensured. On the other hand of course this requires a higher logistical effort to provide two different carrier gases, the space requirement is substantially higher and not least the bottle rack is more complicated (4 carrier gas bottles instead of 2 carrier gas bottles with a suitable switch-over system).

The use of argon as a single carrier gas solves the problem of capturing and analysing hydrogen optimally, however, the table shows that in all other scenarios the thermal conductivity difference between the carrier gas and the substance to be measured is much lower. To illustrate this effect, it is very helpful to compare the amounts of the conductivity differences between argon and the substances to be measured like hydrogen, methane and butane. The following result shows this comparison:

- Thermal conductivity difference between argon and hydrogen: 162.5 W/m*K
- Thermal conductivity difference between argon and methane: 13.6 W/m*K
- Thermal conductivity difference between argon and butane: 1.6 W/m*K

It is immediately obvious that the accuracy of the gas quality analysis is highly limited if argon is used as a sole carrier gas.

Substance	Chemical formula	Raw biogas	Biomethane	DVGW G260/262
Methane	CH_4	40 to 75 Vol.-%	> 97 %	> 96 % natural gas H > 90 % natural gas L
Carbon dioxide	CO_2	25 to 45 Vol.-%	< 3 %	≤ 6 Vol.-%
Water	H_2O	4–6 Vol.-% (mesophile) 10–15 Vol.-%	< 0.03 g/m³	≤ 50 mg/m³
Hydrogen sulphide	H_2S	(thermophile) 20–20,000 ppm (2 Vol.-%)	< 5 mg/m³	≤ 5 mg/Nm³
Nitrogen (i.d.R. ammonia)	NH_3	< 100 mg/m³	< 100 mg/m³	No maximum levels ≤ 3 Vol.-% (N. dry)
Oxygen	O_2	< 2 Vol.-%	< 0.5 Vol.-%	≤ 0.5 Vol.-% (N. wet)
Hydrogen	H_2	< 1 Vol.-%		≤ 5 Vol.-%
Calorific value	$H_{S,M}$	6–7.5 kWh/m³	max. 11 kWh/m³	8.4–13.1 kWh/m³

Table 1. Typical composition of raw biogas and biomethane [4].

Substance	Chemical formula	Thermal conductivity [W/m*K]
Hydrogen	H_2	180,3
Helium	He	151,3
Methane	CH_4	34,1
Oxygen	O_2	26,6
Nitrogen	N_2	25,8
Ethane	C_2H_6	21,2
Propane	C_3H_8	18,0
Argon	Ar	17,8
Carbon-dioxide	CO_2	16,8
Butane	C_4H_{10}	16,2

Table 2. Thermal conductivities of different chemical components.

Helium is considered as a good compromise. On the one hand, the established accuracy is not sacrificed for all components to be measured like for hydrogen and on the other hand the logistical efforts are minimized. For this solution, no modification of the bottle rack is required. On the other hand, there is the disadvantage of the anomaly of hydrogen in helium [6]. Hydrogen is, however, analytically measurable with helium up to 5%, in order to meet the requirements of metrological gas quality analysis, however, this measurement range was reduced to 1.5 % in the scope of the pattern approvals of the PGC 9302 of the RMG company [7]. Since, according to **Table 1**, raw biogas contains less than 1 % hydrogen, this limitation does not imply any restrictions.

2.2 The future solution for gas quality analyis of natural gas transport networks with consideration of the injection of biogas

The injection of biogas will have a long-term influence on the gas quality in whole Germany. The problem of biogas injection can be regarded as solved. The "biogas-solution", however, cannot be applied 1:1 to gas quality analysis of gas transport networks. The "biogas solution" cannot be used because for biogas injections, there are no higher boiling hydrocarbons like pentane and hexane and therefore these do not need to be measured. These higher boiling hydrocarbons occur in the transport networks and must therefore be also measured. Also, the REKO systems do not function without the information of what concentrations of pentane and hexane are present.

Therefore, a process gas chromatograph must measure the following chemical components for this application:

- Hydrogen (H_2)
- Oxygen (O_2)
- Nitrogen (N_2)
- Carbon-dioxide (CO_2)
- Methane (CH_4)
- Ethane (C_2H_6)
- Propane (C_3H_8)
- n-butane (n-C_4H_{10})
- iso-butane (i-C_4H_{10})
- neo-pentane (neo-C_5H_{12})
- n-pentane (n-C_5H_{12})
- iso-pentane (i-C_5H_{12})
- n-hexane (n-C_6H_{14})

The only question here is how the measurement range should be set up for hydrogen. From the previous discussion it is clear that a measurement range for hydrogen > 2 % with helium as a carrier gas cannot be realized technically with the requirements of metrological gas quality analysis. By considering the injection of hydrogen from the "power-to-gas" process into the natural gas network, it is also possible that the measurement range of hydrogen must rise up to 20 %. In this case, a process gas chromatograph must be equipped with two carrier gases. Currently, two scenarios are discussed:

- Injection of hydrogen into the natural gas network
- Conversion of hydrogen to methane (methanization) and subsequent injection into the natural gas network

Currently it is completely unclear which technology will be adopted. This is however very decisive to how the gas quality analysis is to be configured. In case if hydrogen > 2 % is to be measured, all process gas chromatographs that are already installed shall be replaced and the infrastructure (bottle rack and different carrier gas bottles stocked) becomes also more complex.

If the methanization technology is adopted, that is hydrogen is fed into the natural gas system after chemical conversion into methane, the investment costs are kept within limits and process gas chromatographs can be configured already today to meet the new requirements.

Figure 1 shows the measuring unit of the new process gas chromatographs manufactured by RMG. It is important to mention that 3 gas chromatographic modules may be installed in the measurement unit, but this is not a requirement. For the classic gas quality analysis of natural gas for the 11 standard components (without hydrogen and oxygen), only two modules are required and installed. If the application later requires modification, for example an additional measurement of hydrogen and oxygen, the required module can be installed at a later time. Now remains only the question of selecting the carrier gas. RMG intends to acquire a PTB type approval from August 2012 for an extended natural gas analysis system (13 components) including 0–2 % hydrogen analysis and with using a carrier gas (helium). The measurement range of 0–2 % for hydrogen is currently defined by the approval of natural gas tanks in automobiles. The approved level of these tanks is currently limited to 2 % and this limits the hydrogen content in the natural gas network, too. This 2 % limit is not jeopardized solely by the injection of biogas, in case the methanization technology is adopted.

The consequent development of the successful PGC 9000 VC allows to act flexibly in each application case and to stay up-to-date with a proactive planning of the setup of the gas quality analysis equipment all the time without having to replace the whole system. This aspect is enormously important because currently nobody can judge how politics will decide and which scenario from those described will be adopted.

2.3 Trends in gas quality analysis

A trend in biogas injection equipment is clearly evident. The biogas calorific value must be frequently harmonized to the calorific value in the natural gas transport network. This takes place in so-called conditioning equipment. This either raises or reduces the calorific value. In case the value is raised, propane and/or butane is added to the biogas. Therefore, a modern process gas chromatograph must be capable of measuring propane up to 9 % and iso- and n-butane up to 4 % within the scope of an official gas quality analysis. The PGC 9302 from RMG is the first process gas chromatograph that follows this trend [7].

During recent months, the focus was increasingly shifted to the fact that helium as a carrier gas is becoming more scarce and expensive. This obviously raises the operating costs of a gas chromatograph [8, 9]. If you think about how many process gas chromatographs are installed all over Germany, this is a factor that will be strongly considered by manufacturers of such analysis equipment in the near future. One solution could be hydrogen. Hydrogen from a chromatographic point of view is surely the best choice, if, however, hydrogen is to be measured in natural gas or biogas, the use of a second carrier gas cannot be avoided. This also raises the question whether hydrogen could be used as a carrier gas from high-pressure bottles or electrolytic generators, produced on-site. It is definitely worth to wait for how the market develops in the next few months.

3. SUMMARY AND OUTLOOK

As a summary, it can be stated that from a present point of view metrological gas quality analysis of biogas can be regarded as a solved problem. Official gas quality analysis for transport networks is clearly just before a breakthrough and it is worth waiting to see how the "power-to-gas" technology is adopted. It is clear, however, that the classic 11-component gas chromatograph became obsolete in the field of transport networks and was replaced by a 13-component gas chromatograph. The

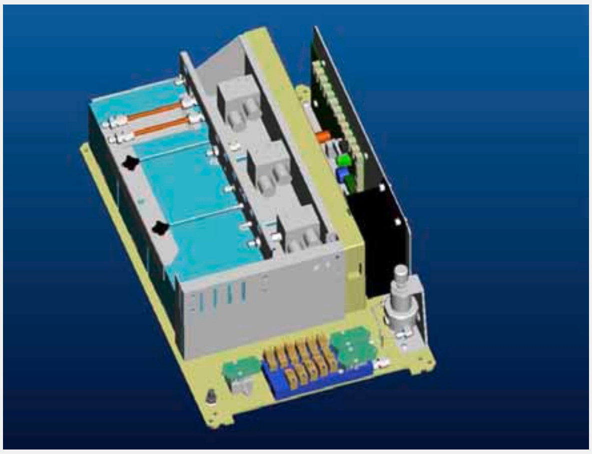

Figure 1. Schematic of the new process gas chromatograph (PGC 930X) manufactured by RMG.

Figure 2. The first PTB-approved PGC controller manufactured by RMG (GC 9300) based on the WINDOWS CETM operating system from Microsoft [7].

question here is whether hydrogen is to be measured with a range of 0–2 % or 0–20 %. The decision, as mentioned before, will have a definitive influence over the gas quality analysis system.

4. REFERENCES

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AUTHOR

Achim Zajc
Product Marketing Manager
Gas Metering
Honeywell Process Solutions
RMG Messtechnik GmbH
Butzbach | Germany
Phone: +49 6033 897 138
E-mail: achim.zajc@honeywell.com