Advanced development of process gas chromatography

by **Joachim Kastner**

Current trends in the gas industry include fuel diversification from unconventional and renewable gas sources, global LNG trade and market liberalization. These trends have led to the introduction of new gas components and to greater variation of gas quality in the network. This represents both a challenge and an opportunity for gas quality analysis technology. Current advanced developments in established micro gas chromatography offer extended gas analyses over and above the primary energy measurement required for billing purposes.

1. INTRODUCTION

Natural gas is an attractive primary fossil fuel. It is suitable for a wide range of uses, including heating buildings, highly efficient, flexible power generation in gas power plants, combined heat and power generation using classic heat engines or fuel cells, fuelling motor vehicles, industrial process applications and providing a raw material for the chemical industry. The future potential of natural gas has been extended even further over the last few years, in particular thanks to unconventional gas reserves being discovered such as shale gas which means that former energy importing countries have been able to cover their own needs or even become energy exporters. There is also the fact that the gas industry is generally compatible with regenerative energy sources such as biogas or power-to-gas. The latter is a new energy concept in which regenerative power is used to produce hydrogen through electrolysis and this is then fed into the natural gas grid immediately or after being converted into methane (methanization) [1]. The massive future potential of the gas industry was even described as an alternative "Golden age of gas" scenario by the International Gas Agency in its Energy Outlook for 2011 [2]. In this scenario, the share of natural gas in primary fuels is growing at a disproportional rate and will reach parity with oil by around 2035.

In addition to security of supplies and economy, environmental and climatic compatibilities are other major aspects of a primary fuel. Natural gas also makes the grade in this respect since compared to other fossil fuels it releases relatively little CO_2 per unit of energy during the combustion process. The transition in power generation from coal to gas as is currently taking place at an increased rate in the USA therefore means that, even as a fossil fuel, natural gas makes a contribution to the decarbonization of the energy industry and therefore to protecting our climate. Gas types from regenerative sources are even greener, of course.

The diversification of gas sources (unconventional and regenerative sources) together with increased international gas trading and market liberalization mean that gas quality can fluctuate more widely and more quickly over location and time. The basis of the gas industry is energy trading which must be billed between the trading partners and consumers. Since gas is a physical commodity, efficient measuring equipment is required to ensure an accurate billing process. The trends described above therefore mean new challenges and opportunities, particularly for gas quality analysis.

The primary aim of gas measuring equipment is to provide the information required for energy bills. Network simulations are used at the transport level to manage this even in the light of greater gas quality fluctuations. Current developments are looking at the possibility of continuing network simulation ("reconstruction system") at distribution network level [3]. It remains to be seen whether the greater fluctuation of gas quality on the one hand and improved network simulation on the other results in reduced demand for physical gas quality analysis or just the opposite.

Managing gas billing by means of network simulation even if gas quality fluctuates wildly, however,

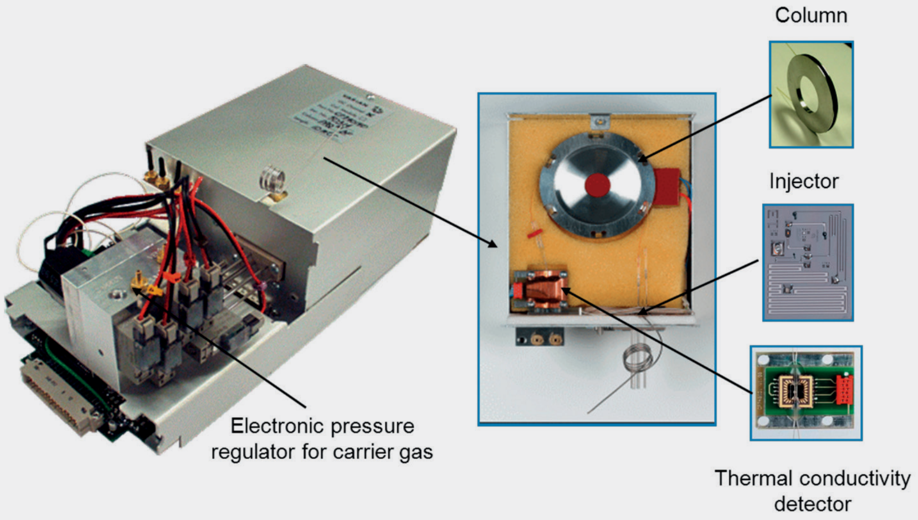

Figure 1. Micro GC module including the injector, separation column, thermal conductivity detector and electronic pressure regulator for the carrier gas.

changes nothing about the actual physical variations which occur. In turn, this constitutes another challenge for gas utilization. As a result, this gives rise to additional demand for gas quality analysis equipment which goes beyond merely measuring the energy content.

Gas quality analysis technology must therefore undergo advanced development to enable it to handle new gas types. Over the last few years, these new gas types initially included biogas which was treated and in some cases conditioned prior to injection into gas grids. The new features in this respect were the components of hydrogen H_2 and oxygen O_2 in a matrix comprising methane CH_4, carbon dioxide CO_2, nitrogen N_2 and, due to the conditioning process, propane C_3H_8 and butane i/n-C_4H_{10}. Current developments are studying the injection of hydrogen from the power-to-gas application into the complex natural gas matrix with higher hydrocarbons. In both cases, this not only constitutes a challenge to the measuring equipment but also to the regulations, PTB approvals and traceability for test and calibration gases.

In addition to primary fiscal energy measurement, gas quality analysis technology must also provide solutions for secondary operational measuring tasks relating to product quality and gas utilization which therefore require extended gas analysis. In concrete terms, these are concentration limits for certain gas components or dewpoints.

The main discipline of gas quality analysis is gas chromatography. This article takes a closer look at current developments in established micro gas chromatography technology.

2. EXTENDED GAS ANALYSIS WITH MICRO GC MODULES

2.1 Micro GC platform

2.1.1 Form factors

The EnCal 3000 process gas chromatograph from Elster provides measuring applications for the gas industry on the basis of the time-tested CP 490 micro GC technology from Agilent. This technology offers a wide range of gas chromatographic separation column types for a wide selection of measuring tasks. The gas chromatographic components including the injector, separation column, detector and electronic carrier gas pressure regulator are integrated in compact GC modules (channels) **(Figure 1)**.

The classical measuring task in the gas industry, measuring the energy content of natural gas, can be conducted using two GC modules. The standard housing of the EnCal 3000 therefore contains two GC modules, a valve block to switch between up to six gas streams using a double-block-and-bleed system, a processor board and communications interfaces **(Figure 2)**.

These new measuring tasks – injection measurement of treated, conditioned biogas, hydrogen after methanization and possibly conditioning, and hydrogen in natural gas – can also be conducted with two modules in a standard housing. However, at least three GC modules are required for extended gas analysis of the new gas types with hydrogen and significant oxygen concentrations in the full natural gas matrix. This is where the EnCal 3000 Quad comes to

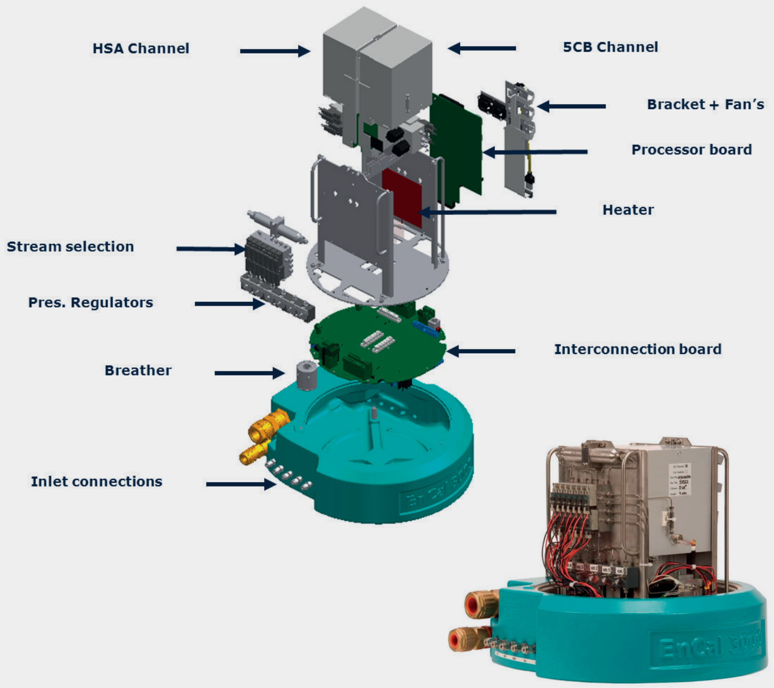

Figure 2. Process gas chromatograph EnCal 3000 standard housing for two micro GC modules, six-stream sample gas switchover system and processor board with autarchic signal processing and communication.

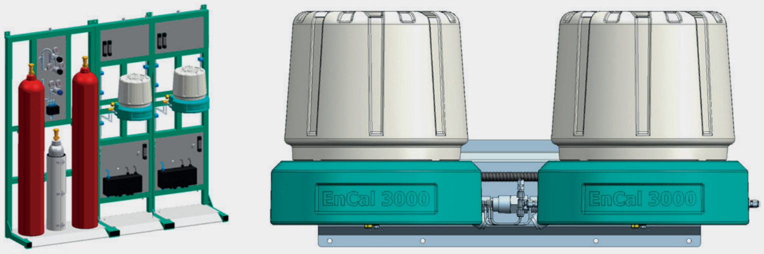

Figure 3. Process gas chromatograph EnCal 3000 Quad – double housing for up to four micro GC modules – mounting frame with EnCal 3000 Quad, carrier gas and calibration gas.

the force. This is a device with two housings which provides space for up to four GC modules, which is where it gets its name suffix "Quad". This device can handle the wide range of micro GC technology in a single process gas chromatograph. One housing is the master to which the sample gases, power supply and the communications interfaces are connected. The second housing is the slave which essentially only contains the GC modules and is controlled and supplied with media by the master **(Figure 3)**.

2.1.2 Carrier gas configurations

One of the main characteristic features of gas chromatography is the carrier gas which transports the sample from the injector through the separation column to the detector. Process gas chromatographs often use a thermal conductivity detector which measures the thermal conductivity of the gas components separated in the separation column compared to the carrier gas. The greater its thermal conductivity differs from that of the carrier gas, the better a gas component can be measured. This means that the carrier gas cannot itself be measured as a component of the sample gas.

Helium is normally used as the carrier gas for a natural gas analysis, but other carrier gases may prove beneficial depending on the measurement application. The introduction of the new gas component hydrogen means that the subject of carrier gas must be viewed from various angles as regards process gas chromatographs in the gas industry.

The thermal conductivity of hydrogen and helium is very high compared to the other gas components and therefore both are extremely suitable in principle for use as the carrier gas for a natural gas analysis. However, they differ from each other relatively little which means that although it is possible to measure hydrogen using helium as the carrier gas, the sensitivity level is reduced if low hydrogen concentrations are involved. However, the sensitivity still generally satisfies the requirements for an official measurement. This means that the new measurement applications of biogas injection and hydrogen in natural gas can still be completed using helium as the sole carrier gas, at least on the basis of the current limit values for hydrogen. This simpler configuration provides costs benefits since there is no need for a second carrier gas frame and the existing infrastructure for process gas chromatographs can be used.

If, however, we consider how the current trends in the gas industry will pan out, the configuration using helium as the sole carrier gas soon hits physical limits. The higher hydrogen concentrations which are currently being discussed as part of the power-to-gas concept increasingly come up against a problem. An anomaly in the thermal conductivity of hydrogen-helium compounds results in a strong non-linearity in the calibration curve which means that the measuring range for hydrogen in a helium carrier gas is limited to just a few mol percent.

One solution would be to use argon as the carrier gas as it has much lower thermal conductivity than helium and hydrogen. On the one hand, this would significantly increase the sensitivity for low hydrogen concentrations and on the other, it would cure the strong non-linearity problem at high concentrations. However, the thermal conductivity of argon is within the range of other major gas components such as carbon dioxide, propane, butane and pentane, which means that it would not be possible to measure these gases properly, so that argon cannot be viewed as a suitable candidate for use as the sole carrier gas.

The perfect gas chromatographic analysis of natural gas which contains higher concentrations of hydrogen therefore requires two carrier gases, typically helium and argon.

This consideration shows therefore that the trends currently under discussion in the gas industry will have major effects on the complexity of gas quality analysis equipment.

As regards the power-to-gas concept, the discussion centres on converting the hydrogen which has been produced by regenerative means into methane (methanization) prior to grid injection. The cost of modifying the gas quality analysis equipment will vary, depending on the level of the maximum hydrogen concentrations in the natural gas. On the other hand, the energy losses which occur during methanization will reduce the overall efficiency of this energy concept. The investments required for the methanization process and the ongoing costs from efficiency losses must be weighed up against the additional investment in future-safe gas quality analysis equipment. However, more powerful arguments in favour of methanization could come from the requirements of gas utilization to ensure compatibility of the gas quality.

Modularized micro GC technology and the concept of the EnCal 3000 are now designed such that each of the maximum of four GC modules can be supplied independently with a separate carrier gas which makes it possible to create measurement solutions for the scenarios currently under discussion. Some new measurement applications can now be implemented on the extended device platform of the EnCal 3000 Quad and these are described in the following.

2.2 Extended hydrocarbon analysis

Established fiscal energy measurement is based on a GC analysis of the gas components up to C6+ or C9. Two GC modules using helium as the carrier gas are sufficient for this. The first module takes care of the separation of nitrogen N_2, methane CH_4, carbon dioxide CO_2 and ethane C_2H_6. The second module separates the higher hydrocarbons from propane C_3H_8 to nonane C_9H_{20} including the isomers, with the hydrocarbons above n-pentane n-C_5H_{12} being typically summarized as a total concentration C6+ when determining the calorific value of the sample gas. In this configuration, the EnCal 3000 in the standard housing has been approved by the PTB for conducting official billing measurements. The use of a third GC module allows the analysis of the hydrocarbons to be continued even further, however. **Figure 4** shows the chromatogram of a calibration gas with components up to dodecane $C_{12}H_{26}$. The concentrations in natural gas of hydrocarbons with such a high boiling point are below the detection limit of the process gas chromatograph of around 1 ppm and they can certainly be ignored for the fiscal measurement of energy. However, these components are significant for other operational gas parameters such as the hydrocarbon dewpoint if they occur in detectable concentrations. This application provides a monitoring facility for this range of components and would detect any unexpected and undesirable concentrations and take due account of them in the hydrocarbon dewpoint calculation.

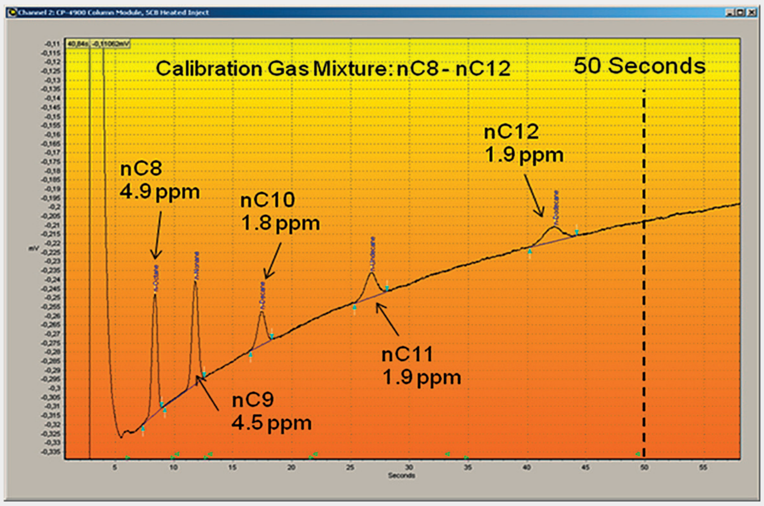

Figure 4. Extended hydrocarbon analysis up to nC12, particularly for determining the hydrocarbon dewpoint.

If the gas chromatograph provides a sufficiently high separation performance, the extended hydrocarbon analysis can also supply the cyclical hydrocarbons benzene, cyclohexane, methylcyclohexane and toluene. These components occur in significant concentrations in natural gas and are very important for the calculation of the hydrocarbon condensation point since they differ from the boiling points scheme of alkanes.

2.3 Hydrocarbon condensation

Hydrocarbon condensation is a potential risk when transporting gas. Condensate can have a detrimental effect on the function and integrity of gas systems, particularly on regulators, valves and measuring systems. Hydrocarbon condensate can also result in problems in gas utilization, for example when combusting it in gas turbines. Condensate may accumulate in the gas transport system and then emerge in a surge, thus causing temporary overheating in gas turbines, for example. But lower, uniform concentrations of condensate may also have a negative effect on a gas turbine by causing ignition delays or subsequent ignitions during the

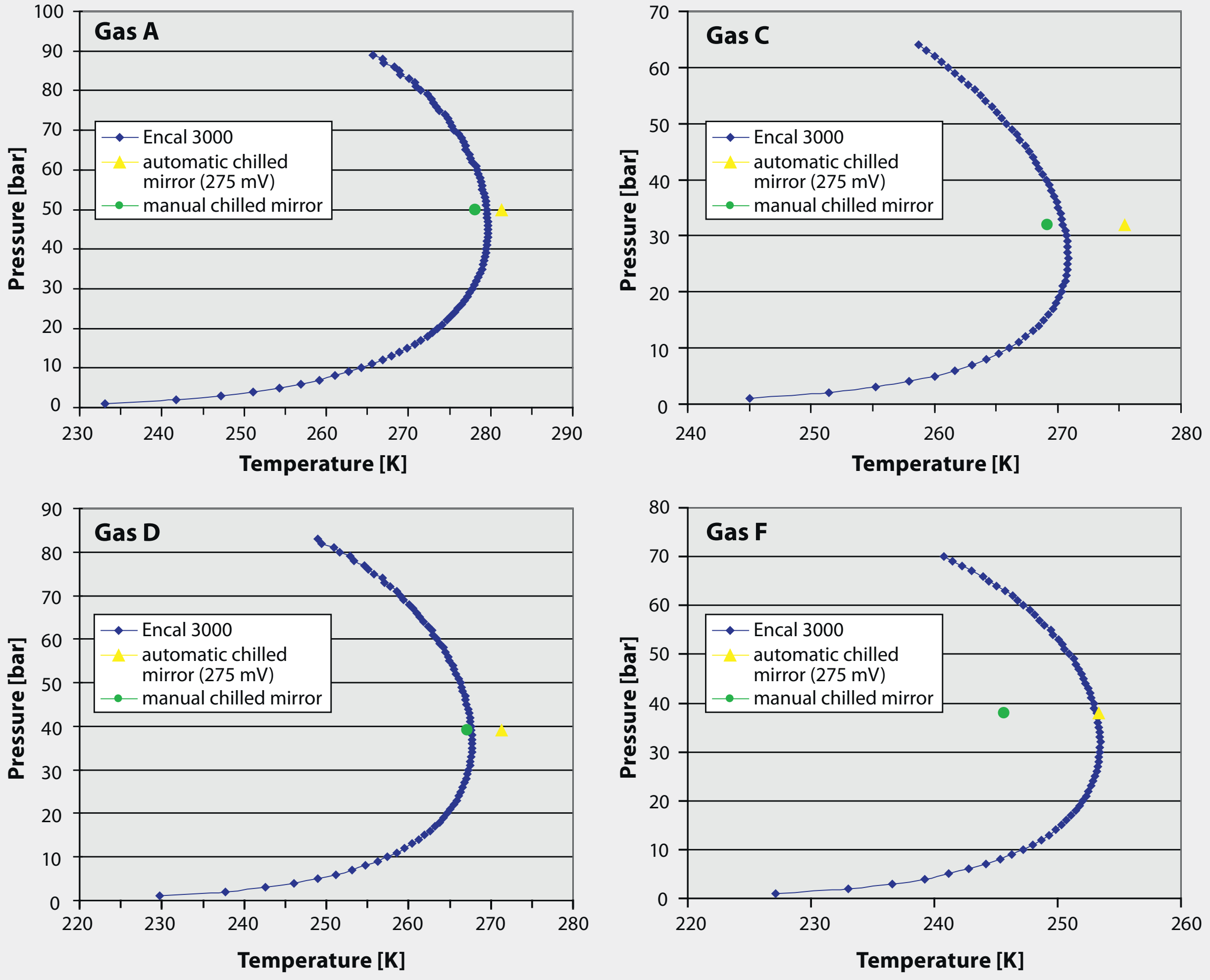

Figure 5. Comparison of hydrocarbon dewpoint measurement methods using real gas samples – direct measurement with a manual (green) and automatic (yellow) dewpoint mirror – the blue line shows the dewpoint curve calculated using the analysis produced by the EnCal 3000 process gas chromatograph (internal measurements and study by the National Physics Laboratory [7]).

combustion process. There are plenty of reasons therefore for all parties in the process chain from production and transport to consumption to know the potential of hydrocarbon condensation in natural gas. The hydrocarbon condensation point is therefore often a gas quality parameter in supply contracts.

As a result of this, hydrocarbon condensation is also specified in a series of technical regulations. The current DVGW regulations demand in Code of Practice G260 that the dewpoint of the hydrocarbons at pipeline pressure be less than the ground temperature [4]. The specification of the EASEE Gas Committee imposes a limit of -2 °C for the pressure range from 1 to 70 bar [5]. Specifications in regulations and contracts also demand in-process tests in the form of a measurement.

The established method for in-process measurement of hydrocarbon condensation is the dewpoint mirror in which a mirror is cooled to a point at which precipitation of the condensate can be detected.

The dewpoint can also be found by indirect methods, however, by being calculated from the gas analysis using state equations. One advantage of this method compared to actually measuring the dewpoint is the possibility of calculating the phase curve for the gas over a wide range rather than simply measuring the condensation point at the applied pressure. This method, however, requires a very detailed and highly precise analysis of the gas up to the hydrocarbons with a high boiling point. ISO 23874 describes the requirements for a gas chromatographic analysis and the algorithm for the evaluation of the chromatogram for calculating the phase curve in state equations [6]. The standard describes the following key steps:

- Standard analysis of the main components of natural gas: nitrogen N_2, carbon dioxide CO_2 and hydrocarbons from methane CH_4 to pentane n-C_5H_{12}
- Analysis of the higher hydrocarbons from pentane n-C_5H_{12} to dodecane n-$C_{12}H_{26}$ including the separation of the unidentified isomers.
- Individual analysis of the cyclical hydrocarbons such as benzene, cyclohexane, methylcyclohexane and toluene
- Modelling of the boiling points of the unidentified hydrocarbons from the retention time

Various direct and indirect methods for measuring the hydrocarbon dewpoint were investigated in a study by the National Physics Laboratory (UK) [7]. This study showed a wide variation of the various measurement methods in a range of around 10 °C. On the one hand, the study demonstrated that determination of the "true" dewpoint is technically demanding and depends to a large extent on the analytical method employed. On the other hand, the study also showed, however, that indirect determination of the hydrocarbon dewpoint using GC analysis can be a real alternative to the established direct methods using a dewpoint mirror.

On the EnCal 3000 GC platform, a hydrocarbon dewpoint determination method has been implemented which has been derived from ISO 23874.

In a simpler version, natural gas is analyzed up to nonane nC9 using two GC modules which can be housed in an EnCal 3000 standard housing. A modelling system is used to calculate the hydrocarbon condensation point for the higher hydrocarbons above nonane. The device holds a PTB type approval for official measurement variables and finds the hydrocarbon dewpoint as an operational value in addition to the official natural gas analysis.

In an extended version, the hydrocarbon condensation point is found using an analysis up to dodecane n-$C_{12}H_{26}$ in three GC modules as described above.

To validate the value of the hydrocarbon dewpoint, the available test gases from the study conducted by the National Physics Laboratory were analyzed and evaluated using the C9 version of the EnCal 3000. **Figure 5** shows the results in the form of a comparison between manual and automatic mirror dewpoint meters. The blue line is the phase curve as found from the GC analysis conducted by the EnCal 3000. The green dots indicate the measurement results of the manual mirror dewpoint meter and the yellows ones are taken from the automatic version. The study shows that determination of the hydrocarbon dewpoint may result in wide variations but that the results produced by the EnCal 3000 process gas chromatograph are well within the variation range of the established process measurement methods.

A process chromatograph is generally not used as a dedicated measuring device to find the hydrocarbon dewpoint. However, it does allow this important gas parameter to be monitored as an operational value parallel to the fiscal measurement with comparatively low additional investment being required.

2.4 Biogas and hydrogen injection

As described above, the gas industry is currently experiencing a diversification of gas sources. Gases from regenerative energy sources are injected into gas grids after undergoing treatment and conditioning to a greater or lesser extent. This therefore presents a challenge to gas quality analysis equipment to determine hydrogen and oxygen in the simpler biogas matrix or in the more complex natural gas matrix.

For the fiscal measurement of biogas injection, a device (EnCal 3000 Biogas) has been developed on the basis of the GC technology described in this article and has also been approved by the PTB. This device uses two GC modules to determine the main gas components of hydrogen H_2, oxygen O_2, nitrogen N_2, methane CH_4, carbon dioxide CO_2, ethane C_2H_6, propane C_3H_8, and i- and n-butane i/n-C_4H_{10}. The objective of the ongoing development of this device is to extend the measuring range so that it can also handle raw biogas.

The same gas quality analysis equipment can be used in principle for an injection measurement in the context of the power-to-gas concept as for the biogas injection measurement as long as most of the hydrogen is converted into methane and conditioned using the standard procedures adopted for liquefied gas/air.

A device which uses two GC modules in a standard housing has been developed for the fiscal analysis of hydrogen in the natural gas matrix (EnCal 3000 e-Gas) using the GC technology described in this article. The measured components are hydrogen H_2, nitrogen N_2, methane CH_4, carbon dioxide CO_2, ethane C_2H_6, propane C_3H_8, as well as i- and n-butane i/n-C_4H_{10}, neo, iso and n-pentane neo/i/n-C_5H_{12} and the total of significant higher hydrocarbons, designated as C6+. This device can be used with configurations with one (helium) or two (helium and argon) carrier gases featuring the measurement benefits and measuring ranges described above. The type approval process is currently being completed by the PTB.

As more and more biogas and hydrogen is injected into natural gas grids, it will become necessary to be able to measure both higher concentrations of hydrogen H_2 and significant quantities of oxygen O_2 in the complex natural gas matrix. When using the GC technology described in this article, three GC modules (types HSA, 5CB and molecular sieve) are required, which can be installed in the extended EnCal 3000 Quad housing. There are several carrier gas concepts available for this, featuring one (helium) or two (helium and argon) carrier gases.

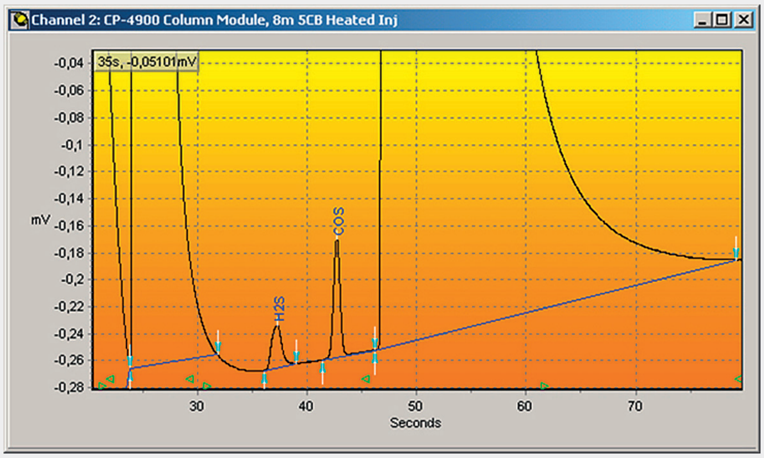

Figure 6. Measurement of sulphur components hydrogen sulphide H_2S and carbonyl sulphide COS, in this case 6 ppm each.

2.5 Other operational variables

Das EnCal 3000 Quad housing provides sufficient space for up to four GC modules with three GC modules being required for the extended natural gas analysis measurement including hydrogen and oxygen. The fourth GC module position can be filled with another GC module type as required to allow additional measurement applications. As described above, a further analysis of the hydrocarbons up to dodecane n-$C_{12}H_{26}$ could be carried out, for example. Using the appropriate column types, however, it would also be possible to measure typical sulphur components such as hydrogen sulphide H_2S, carbonyl sulphide COS and methyl mercaptane (methanthiol) CH_4S **(Figure 6)**. Another application is the measurement of odorants such as tetrahydrothiophene THT or tert-butylthiol TBM. The detection limits for these components are in the single-figure ppm range. This means that normal concentrations in the transport line cannot be quantified with any great precision and thus dedicated measurement equipment or laboratory investigations will still be necessary. The almost continuous process monitoring of operational limit values which are otherwise only recorded at random may constitute a genuine additional benefit for measuring primary energy sources for gas billing purposes in the liberalized gas industry, however.

The prerequisite for an extended gas analysis is generally a configuration with three or four GC modules. An application for a national PTB type approval for the EnCal 3000 Quad GC platform is being planned for the near future. This would make it possible to conduct an official measurement of the extended natural gas matrix including oxygen and hydrogen in a wide range of concentrations as well as a combination with a vast array of operational measurement applications.

3. SUMMARY

Current trends in the gas industry are dominated by the diversification of gas sources. In addition to gases from unconventional deposits (shale gas), new gas components such as hydrogen and oxygen are being injected into transport grids as a result of regenerative gas generation. Due to international gas trading and deregulation of the markets, this is resulting in ever increasing and faster variations in gas quality in the gas grid.

This represents both a challenge and an opportunity for gas quality analysis technology. Current established micro GC technologies already offer a wide range of measurement applications which go beyond primary energy measurement for gas billing purposes. New device concepts and the development of methods focussed on the gas market will mean that these new measurement applications will increasingly be available for process measurements in the natural gas industry.

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