New Developments in On-line Calorific Value Analysis

Harald Mahler, Product Manager Siemens AG, Karlsruhe, Germany Tel: +49 721 595-3335 Fax: +49 721 595-6375 Email: harald.mahler@siemens.com

Process gas chromatograph using microchip technology, with multiple and in-line analytical functions

An important parameter in the analysis of natural gas is the chromatographic determination of the calorific value, which is essential in many applications for monitoring the delivered quantity of energy. The demands placed on chromatographs with respect to analytical accuracy and reliability are extremely high in such applications. An intelligent and compact process gas chromatograph based on micro-machined systems is now available. In particular, the unique multiple and in-line analytical functions open up new possibilities and provide shorter analysis times.

Natural gas is one of the most important global sources of energy. Process gas chromatographs (process GCs) are widely used in the natural gas industry. During the pipeline transport of natural gas, it is important to determine quality parameters such as calorific values and hydrocarbon dew points using process GCs, as well as hydrogen sulfide and other sulfurous components, the odorants (1). Determination of the calorific value plays a particularly important role in the energy measurements of the natural gas for billing purposes (fiscal metering) at gas transfer stations in the widely branched pipeline network. The energy flow is calculated there from the product of the volume flow under standard conditions and the calorific value. The volume flow is determined using flow measuring systems, e.g. based on ultrasonics. An equation of state according to SGERG (2) delivers the volume flow corrected to standard conditions with consideration of the standard density and the concentration of CO_2. Current state-of-the-art technology normally applies a single process gas chromatograph for determination of the calorific value, the standard density and the concentration of CO_2. Due to the growing global demands for natural gas as a source of energy, liberalization of the markets, as well as the international networking of pipeline systems, a further increase in the necessity for calorific value analysers in custody transfer plants is expected. The demands placed on the chromatographs with respect to analytical accuracy and reliability are extremely high for such applications. Remote monitoring is also a significant factor when considering the infrastructure associated with the transportation of natural gas. Therefore remote monitoring, remote maintenance, remote diagnostics and system ruggedness are of increasing importance.

As a result of their technological design, micro process gas chromatographs provide the ideal prerequisites for satisfying such demands.

Technical design and analytical concept

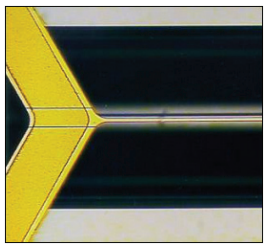

Fig. 1: Macro shot of the heater wire of a thermal conductivity detector designed using microchip technology

The process GC (3-5) described here is based on micro-machined systems on the scale of microchip technology. Fig. 1 shows a thermal conductivity detector, indicating the typical component dimensions. Miniaturisation of the most important components using this pioneering technology permits an extremely compact design for the complete device which is also associated with high resistance to environmental influences. High protection against moisture, dust and corrosion (IP65, NEMA4X), against extreme ambient temperatures (-20 to +55 °C), as well as explosion protection using a pressurised enclosure without purging, are indispensable for typical field installations which are frequently directly at the sampling points.

The analyser comprises three modules (analytics, pneumatics and electronics) which are integrated in a transmitter housing. These modules have standardised designs, connection systems and interfaces. This allows rapid replacement. Furthermore, the stocking of spare parts can be reduced to a minimum.

The analytical module (Fig. 2) has been specially designed for the analysis of natural gas. All hardware components such as the valveless live injection, the high-resolution narrow bore capillary columns, the valveless column switching (6) as well as the multiple and in-line detectors (μ-thermal conductivity detectors, μ-TCDs) are matched to one another, e.g. through almost identical internal diameters (usually 0.15 mm). This ideal interaction without dead volumes (and the resulting impairment in separating performance through diffusion effects) makes a significant contribution to the analytical performance of the complete system.

Fig. 3 indicates the analytical configuration as well as the separation and detection of the measured components. μ-TCDs are present in-line at various points in the analytical system; it is then possible to monitor the injection peak (TCD 2a), the progress in the separation following each column (TCD 4a, TCD 4b, TCD 1a) and all gas outputs (TCD 1b, TCD 2b). The polarity and length of the columns are designed such that the measurement can be carried out in the fastest and simplest manner. Through the possibilities provided by multiple detection, the system delivers additional information on the injection quality (TCD 2a) and the exact setting of the backflushing or the time for the cut (TCD 1b, TCD 2b). These can be used for system verification.

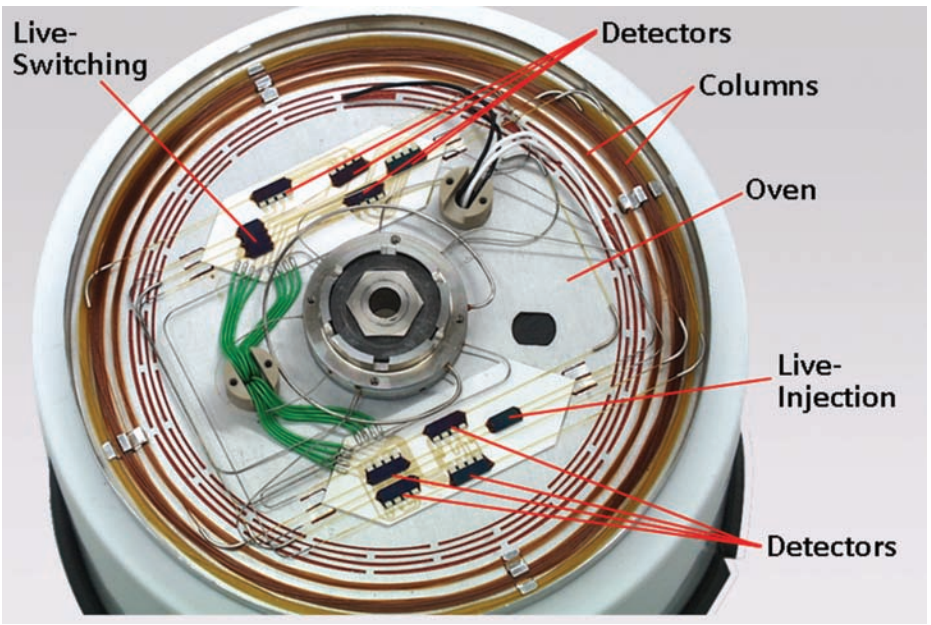

Fig. 2: Analysis module in chip technology of a modern calorific value GC

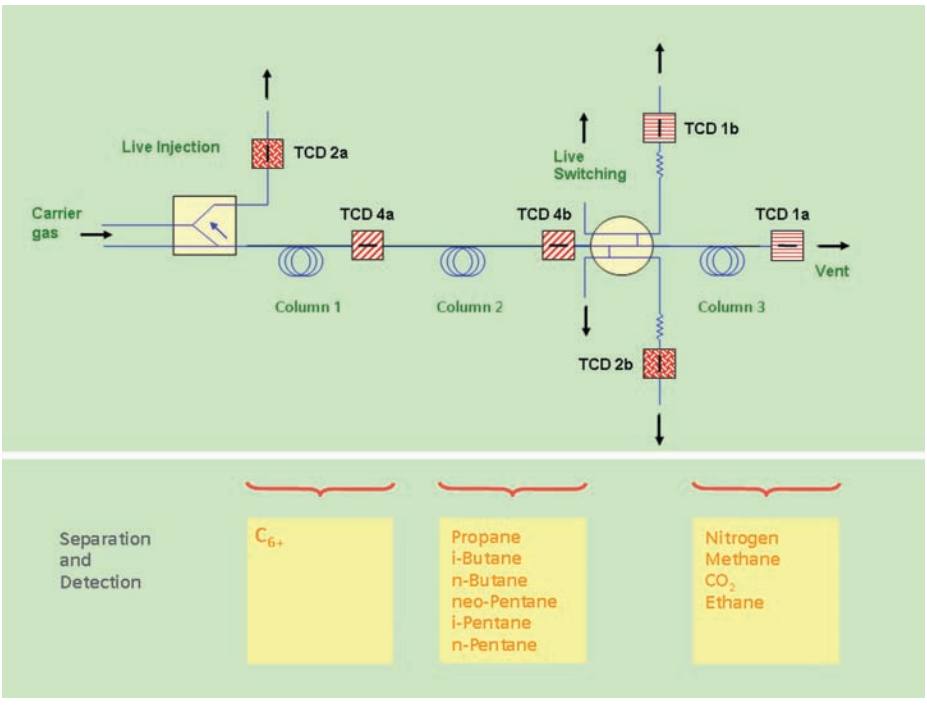

Fig. 3: Analytical configuration and separation of components

In addition to the components described in Fig. 3, the system can individually evaluate hydrocarbons of higher boiling point (C6+) as additional groups C6, C7, C8 and C9. A calorific value analysis is also available where oxygen and CO are separated in addition. The analysis time of < 180 s for all options is not extended by this.

The micro process GC is equipped with simple, clear and intuitive Windows-based software. Data saving (> 30 days) and generation of mean values (for all components and calorimetric values) are already implemented internally.

Furthermore, the analyser provides the facility for automatic setting of the method or for auto-optimization during process operation, e.g. during a regular calibration cycle. Important in this context is that the optimum pressure setting of the electronic pressure controllers (EPCs) can be computed and need not be set by a complex empirical method. For example, the software-based auto-optimization of the method checks the response times of the components, their evaluation parameters, and the switching point for backflushing, and automatically readjusts these as necessary. This procedure makes a significant contribution to the high long-term stability of the complete system.

The integral interfaces of the analyser permit communication to host equipment such as process control systems and flow computers (over RS485/MODBUS) and to the control computer (over Ethernet TCP/IP).

Evaluation of performance

Fig. 4: Typical complete solution with sample preparation for field installation at sampling point

On-line calorific value analysers are usually installed on unmanned gas measuring stations which are frequently in remote locations (Fig. 4). High demands are therefore placed on the precision of the measurements and their long-term stability, especially when used for fiscal metering purposes. Important criteria for evaluation of the performance – in addition to accuracy – are the separation of individual components, the component repeatability, the calorimetric values, the detection limits for components of low concentration (especially higher-boiling hydrocarbons), and the component linearity.

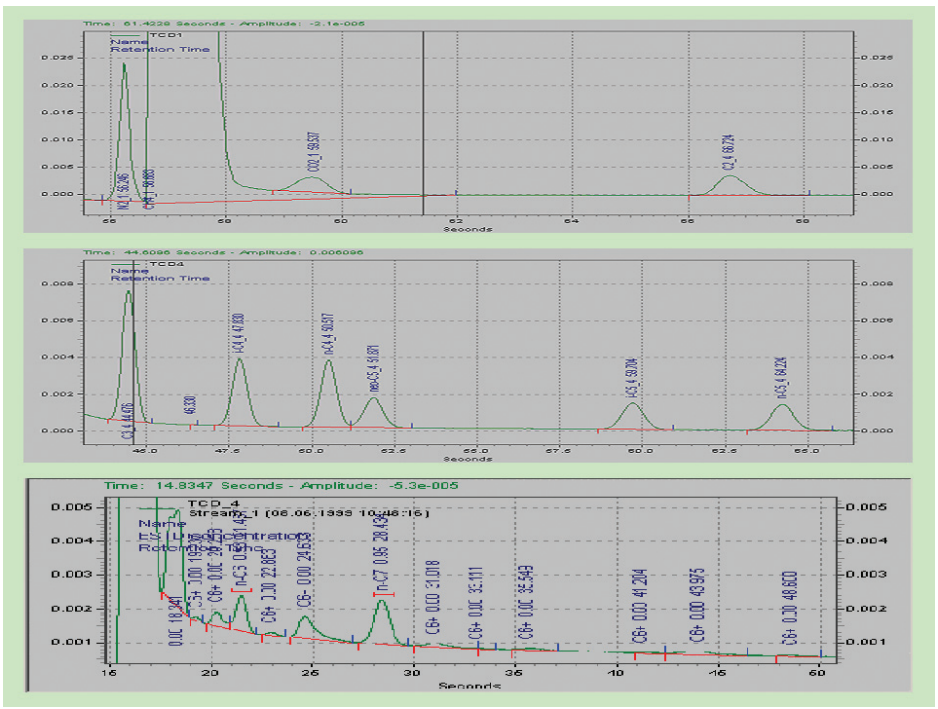

Fig. 5: Chromatographic separation of individual components at different detectors
A: N2 – CH4 – CO2 – C2; B: C3 – i-C4 – n-C4 – neo-C5 – i-C5 – n-C5; C: C6+ as individual groups C6 – C7 – C8 – C9

Fig. 5 shows the detection of the components by various in-line detectors following separation by narrow-bore capillary columns with different separating properties. The resolution between nitrogen and methane peaks is then sufficient to even permit analysis of concentrations of 25% nitrogen with methane in special natural gases. The resolution between n-butane and neo-pentane allows a detection limit for neo-pentane of <10 ppm. Table 1 lists the standard deviations as proof of the repeatability of all measured components as well as the calculated values. The process GC provides a repeatability which significantly satisfies the minimum requirements placed on highly precise calorific value analysers.

Table 1 Repeatability of components and calorimetric values with use of one calibration gas (type H1)

Measured components and calorimetric values		Concentrations (mean value)		Standard deviation (absolute) Mol%	Standard deviation (relative) %
Higher heating value	Ho	39.8284	MJ/m3	0.002753	0.006913
Lower heating value	Hu	35.9134	MJ/m3	0.002507	0.006981
Density		0.7433	kg/m3	0.000072	0.009645
Rel. density		0.5749		0.000056	0.009661
Wobbe index		52.5300		0.004761	0.009064
Nitrogen	N2	1.3464	Mol%	0.006531	0.485036
Carbon dioxide	CO2	0.3480	Mol%	0.001111	0.319118
Methane	C1	97.3048	Mol%	0.008428	0.008662
Ethane	C2	0.3982	Mol%	0.001433	0.359759
Propane	C3	0.1996	Mol%	0.000715	0.358462
iso-butane	i-C4	0.0995	Mol%	0.000553	0.556262
n-butane	n-C4	0.1031	Mol%	0.000615	0.596241
neo-pentane	neo-C5	0.0509	Mol%	0.000437	0.857970
iso-pentane	i-C5	0.0494	Mol%	0.000536	1.084269
n-pentane	n-C5	0.0500	Mol%	0.000479	0.956977
Total C6+	C6+	0.0502	Mol%	0.000422	0.841165

When used for fiscal metering, calorific value analysers must be calibrated regularly, usually weekly. The calibration is carried out using a procedure comparable to gas chromatography where an external calibration gas is mainly used which is directly connected to the analyser and usually supplied to this automatically. As a result of the high linearity of all measured components, the micro process GC presented here only requires a single-point calibration using just one calibration gas, even during initial startup of the analyser. Complex multi-level calibrations on site with up to seven calibration gases are not essential.

Summary and Prospects

Compact process GCs are particularly suitable for on-line calorific value measurements in natural gas. Miniaturisation of the devices opens up new possibilities for low-cost field installation. The uniform analytical concept based on micro-machined systems, in particular with narrow-bore capillary columns and multiple and in-line detectors, results in an analyser which offers a high separating performance for all components within a short analysis time. The performance criteria for calorific value analysers are fulfilled by the technical opportunities described here. The auto-optimization is a new software tool which can significantly contribute to further improvement in long-term stability.

It is expected that the possibilities provided by the functions of multiple detectors, such as the injection peak, will permit the development of new software-based verification strategies which will continue to improve the confidence in calorific value analysers.

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Level Control for Fina in Ant-werp

In the petrochemical industry, a reliable back-up system is absolutely necessary in order to survey the level of the medium inside the tanks. Certain tanks are used for filling ships or trucks and therefore, an accurate level indication, working at all time, is mandatory.

At Fina Antwerp Olefins (Belgium), level control is done by **Weka AG** (Switzerland) with the VLI Petro-Line, and this in several areas. In an overhead condenser, liquid gazes, like ethylene are constantly monitored by a Petro-line VLI with process connection specially designed for the customer. In another area, Weka AG installed level indicators on a flare drum where liquid gases like ethylene (C2-), ethane (C2+), propylene (C3-), propane (C3+), menthylacethylene (MA) and propadiene (PD) are processed. Also installed at the Antwerp site were the Weka Visual Level Indicators which have been designed according the customer's specifications. The most critical area of the Fina Antwerp Olefins plant is the Sulzer area where different mediums like cyclohexaan, benzene, toluene, PFO, heavy gasoline, hydro treated gasoline and more, are temporarily stored and then directly filled inside the tanks of the ships. This area is controlled by 5 Weka Petro-line Visual Level Indicators all isolated with Armaflex insulation shields.

For Fina Antwerp Olefins, Weka AG's Petro-Line Visual Level Indicators are extremely reliable. Where others failed, Weka AG was able to deliver a very safe system with their special designed floats in titanium. The visibility of the indication rails is assured in all weather conditions due to the protection tube on the indication rail, and the Armaflex insulation.