Use of Modern Process Gas Chromatographs in the Oil and Gas Industry

Proven and widely used technology with numerous applications and new innovative approaches as well

Harald Mahler, Siemens AG, Process Automation and Drives
Karlsruhe, Germany
Email: Harald.mahler@siemens.com • Web: www.siemens.com/chromatography • www.siemens.com/gas-chromatography
Tel: +49 721 595 3335

Process gas chromatography has proven its worth in the oil and gas industry as an important tool for process analytics. This technology has high availability and is extremely flexible for a variety of applications despite the varying requirements of the market. New innovations through standardisation and consistent modular design of the analysers ensure that they will remain indispensable for industrial users in the future as well.

For decades, the oil and gas industry has relied on process gas chromatographs (process GCs) for optimisation of energy consumption and product throughput in the industry's plants, assurance of product quality as well as for determination of the energy content of fuel gases for legal metrology. Additional applications include plant safety and emissions monitoring. For these applications, the chemical composition or important product properties (such as calorific value, density, RVP) of samples taken from the process are typically analysed. The analysers are used on gas platforms, in pipeline stations, in gas processing facilities and, in particular, within refineries and the hydrocarbon processing industry (HPI) – predominantly in distillation columns and reactors. Process GCs are characterised above all by their high degree of flexibility in regard to their analytical device configuration. For example, by cleverly selecting injectors, separation columns, and detectors, the technical system solution can be adapted to the measurement task, allowing a variety of gaseous and liquid process samples to be analysed. The process GC provides reliable and efficient solutions for measurement tasks ranging from analysis of individual key components all the way to multi-component measurement of a wide range of concentrations (from 100% to a few ppm or ppb). This high degree of flexibility of gas chromatographs in terms of performance and applicability has underpinned their important position within the field of process analytics up to the present day, in spite of the ever increasing presence on the market of spectroscopic methods that are often easier to use but have significantly limited applicability (e.g. number of measured components, cross-sensitivities, robustness). Figure 1presents the major technological innovations of the past decades that have contributed to the success of process GC technology.

Modular analysis supports innovative maintenance concepts

Currently, there is a general trend toward standardisation of individual analysers as well as complete system solutions. This enables further reduction of investment and operating costs. This can be achieved through miniaturisation of analysers for example, through gas chromatographs in microsystems technology, or through simplification of the analytical separation sections of a conventional GC, for example, through so-called parallel chromatography in which multiple measurement sections are integrated in parallel in one analyser. This aspect, as well as new maintenance concepts, are supported in particular by GCs in which the complete analysis (analytic module) is incorporated in the GC oven in a modular design. Besides making on-site repair possible, this also enables fast replacement of the complete analytic module with all relevant components (dosing valves, separation columns, backflush valves, detectors). This opens up new opportunities, in particular for critical processes in which very high availability of the process analytics used is vital. A company's own maintenance staff can easily repair the complete analytic module in-house and test it for proper functioning using an affordable test monitor. The test includes an electrical check of the detectors and a check for tightness of the analytical components. As an alternative, the existing analytic module can be replaced by one that has previously undergone analytic testing by the manufacturer. The module can be removed and installed in a few minutes allowing the process GC to return to process mode after only a very short delay. Figure 2 shows a dual analytic module with up to 3 separate analytical separation sections including dosing valves, separation columns and detectors.

Separation tasks are very important in the hydrocarbon processing industry and the process equipment required for this account for a significant fraction of overall investment. A typical application of process GCs with a modern modular oven type (MAXUM Modular Oven) can be found in plant units that break down hydrocarbons into individual groups in distillation columns (e.g. demethaniser, deethaniser, depropaniser, C3 splitter, C4 splitter). This type of equipment can be found in different forms in gas liquefaction facilities (natural gas liquids/ NGL or liquefied petroleum gas/ LPG), in fluid catalytic crackers (FCC) and, in particular, in ethylene plants. Table 1 shows a typical sample composition, including requirements for repeatability of measurement data.

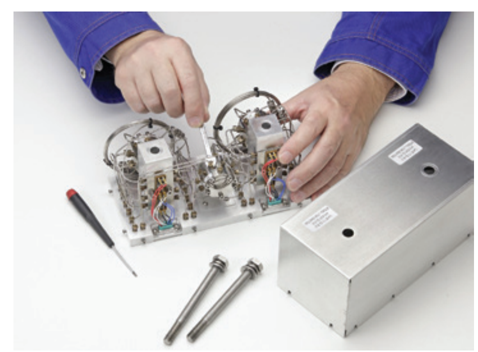

Figure 2: Standardised analytic module can be replaced as a unit

The measurement task is simplified by separating it into 2 analytical sections with a backflush switch. The built-in diaphragm valve has two integrated functions – dosing and backflushing – and simplifies the device configuration significantly. The complete chemical analysis is carried out in a single module (see Figure 3).

Sample Specification				Process GC Solution	
Components	Normal	Measuring Range	Unit	Repeatability	Analytical Train
Propylene	70	0-100	Vol%	0.5%	R2
Propane		0-10	Vol%	0.5%	R2
Propadiene		0-10	Vol%	0.5%	R2
Methylacetylene (Propine)		0-10	Vol%	0.5%	R2
Hydrogen		0-5	Vol%	0.5%	R1

Table 1: Typical sample specification in plants for separation of hydrocarbons (example "C3 Split Bottom) – including the GC solution

Demand for trace analytics continues to grow!

As quality standards for products increase, and environmental requirements for production become more strict, the demand is increasing for suitable measuring methods for determining trace components in process gases. The process GC offers various options for analysing substances from the ppm to low ppb range. This is accomplished mainly through the use of trace detectors such as flame photometric detectors (FPD), flame ionisation detectors (FID) and even pulsed discharge detectors (PDD). Another option is to use pre-column concentration followed by thermal desorption ("purge and trap"). Table 2 shows typical detectors that are used for trace analytics in process GCs. FIDs and FPDs are most commonly used for trace analysis in the oil and gas industry.

A typical example application that uses a GC FID/FPD combination for trace measurement can be found in the O&G upstream sector in natural gas processing plants. Methanol and monoethylene glycol (MEG)

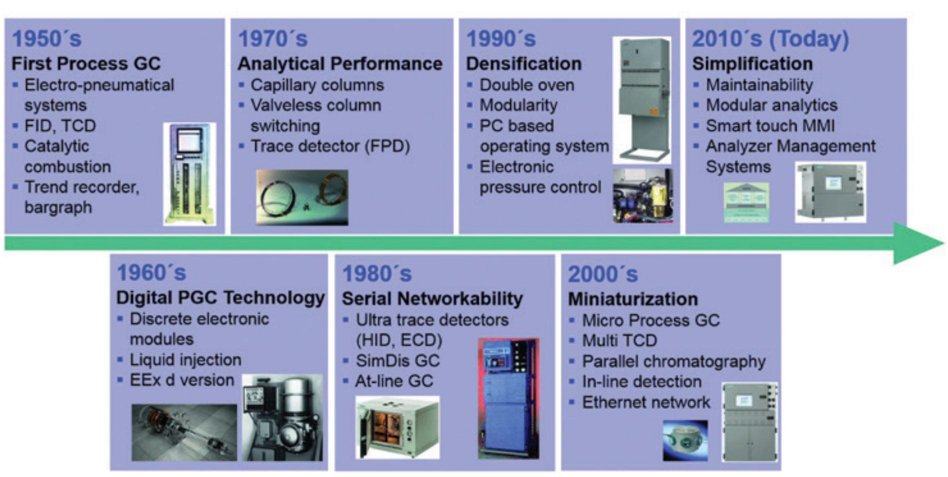

Figure 1: Technological development of the process GC

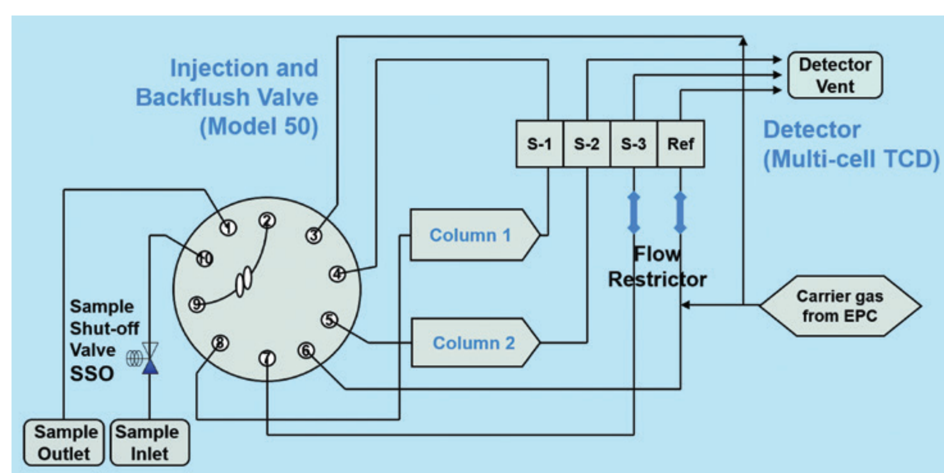

Figure 3: Analytical configuration (2 measurement sections, each with a 10-way diaphragm valve for metering and backflushing, 2 micro-packed separation columns, multi-cell TCD and electronic pressure control)

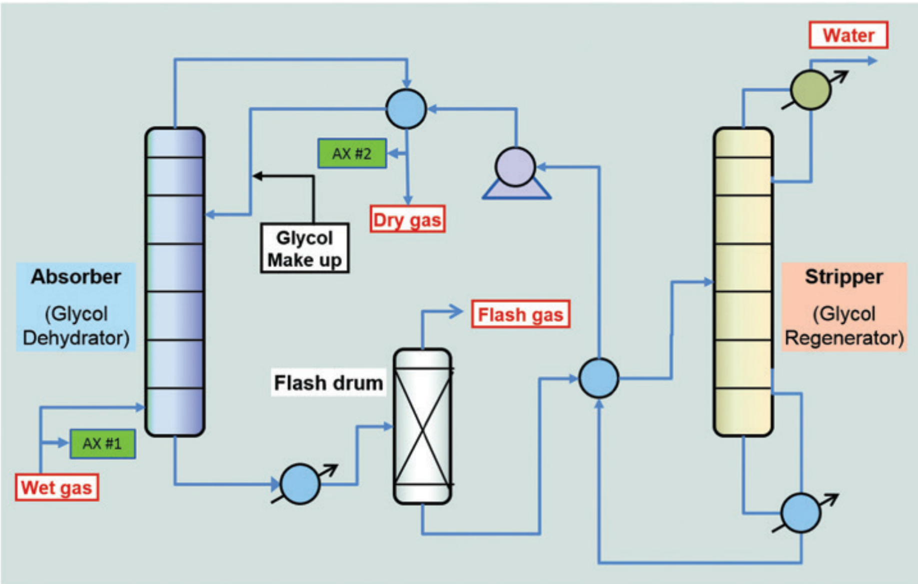

Figure 4: Process flow diagram of a natural gas processing plant (scrubber) with sampling points for process GCs

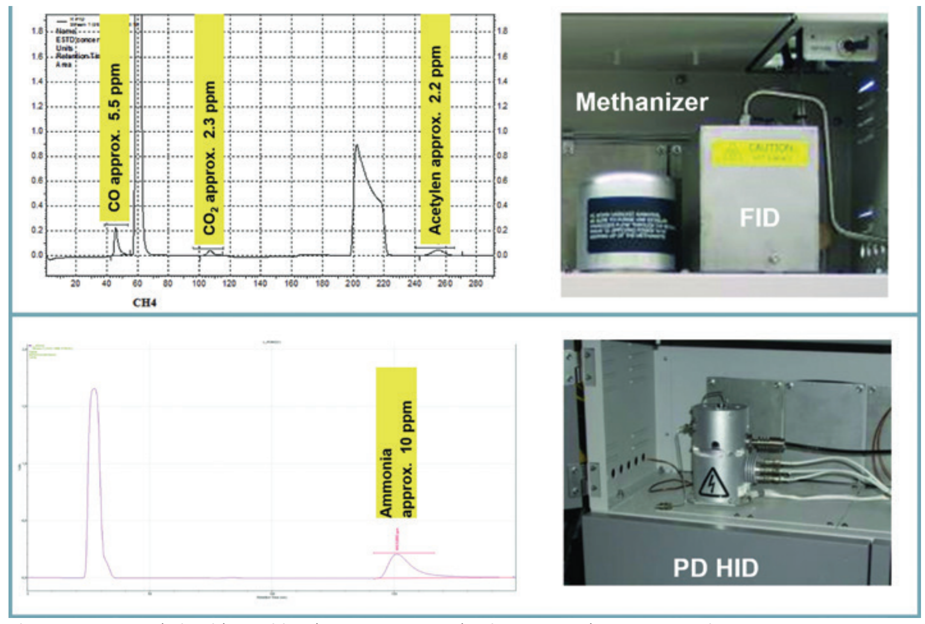

Figure 5: Trace analysis with sensitive detectors - GC methaniser / FID and GC PDHID variants

are added to the raw natural gas in the vicinity of the gas production to prevent hydrate formation and, thus, to protect pipelines from blockage and corrosion. An additional glycol (triethylene glycol, TEG) is added in the central natural gas processing plant via a dosing process. TEG acts as a desiccant. This lowers the water dew point to the level required by the specifications. A process GC monitors the drying process in the glycol dehydrator and, in so doing, analyses the concentrations (down to the ppb range) of methanol, MEG, TEG (with FID) and H_2S (with FPD) and the calorific value in the dried, processed gas. Figure 4 shows a typical process flow diagram with sampling points for the GC and the required measurement components.

A common application for use of GC methaniser/FID variants is found in ethylene production plants, where CO/CO_2 traces and acetylene are measured in various cracked and saturated gases. For example, very strict purity specifications apply to polymer-grade ethylene, in particular. Concentration ranges in process applications are frequently specified as low as <1 ppm. By combining various measurement tasks in a single process GC, the cost-effectiveness and return on investment (ROI) is substantially increased without significant loss of performance. Analysis of ammonia in gas mixtures and pure gases in these plants represents another important trace measurement. The analysis of ammonia requires a GC variant with PDD detector in HID mode (helium ionisation mode). Figure 5 shows a chromatogram with analysis of CO, CO_2 and acetylene and a separate GC analysis for trace ammonia.

Trace analytics also increasingly calls for special sample preparation methods including special materials with high chemical inertness for the sample-carrying components (sulfinert, electroplated, special sampling) in order to ensure delivery of a representative sample.

Summary and outlook

Process GCs with modular design increase the flexibility of this instrument technology and ensure its leading position within the process industry. New options can be offered for instrument maintenance and operating costs can be minimised. At the same, the analytical performance can be kept at a high level thanks to proven technology.

Through the use of detectors of varying sensitivity, the process GC is able to integrate analytical solutions for a variety of applications involving increasingly important trace analytics in process plants of the oil and gas industry. The expandability of the measurement task in a single GC (parallel chromatography) and the resulting optional multi-component analysis means that an optimal cost-effectiveness of the analysis system is also guaranteed.

Future cross-collaboration among instrument developers, users and research bodies is also vital for ensuring that performance, cost-effectiveness and ease of maintenance are taken into consideration in further development of the technology.

References:

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Standardisation and Modularity Make Process Analytics More Economical, ACHEMA15 PraxisForum, Frankfurt, Germany

[2] Mahler H. (2013) Advances in Process Gas Chromatography, APACT13 Conference, Chester, UK

[3] Farmer B, Trimble S (2009) Options in Gas Chromatographic Techniques For Measurement Of H2S In Fuel Gas, ISA 54th Analysis Division Symposium, Houston, TX, USA

[4] Maurer T., Müller H. (2006) Prozess-Gaschromatographie, In: Prozessanalytik: Strategien und Fallbeispiele aus der industriellen Praxis (Kessler, R.W., Hrsg), Wiley –VCH Verlag, 12: S. 390-427

[5] Mahler H. (2008) Process analysis with MEMS technology. Refineries benefit from micro-process gas chromatographs, P&A Select Oil&Gas, p. 22-24

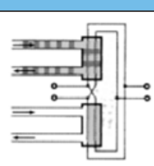
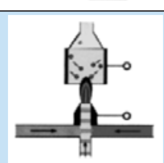
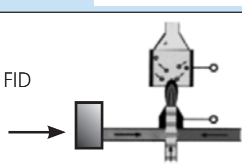
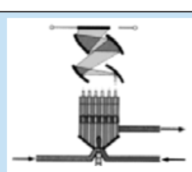
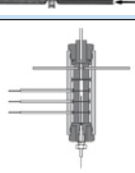
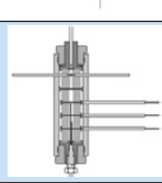
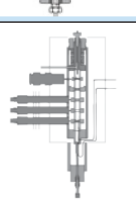
Detector type	Measured values depending on	Selectivity	Minimum measuring range (typical)	Application examples in oil & gas industry
Thermal Conductivity Detector (TCD) 	Concentration	Universal	0-500 ppm	All hydrocarbons, inert gases, H_2S
Flame Ionization Detector (FID) 	Mass flow	Organic substances (C-C and C-H selective)	0-1 ppm	All hydrocarbons, aromatics at trace levels
Methanizer / FID combination 	Mass flow	Conversion of CO and/or CO_2 to methane by using a methaniser (catalytic)	0-1 ppm	CO_2, CO at trace levels
Flame Photometric Detector (FPD) 	Mass flow	Sulphur (S) or Phospor (P) containing substances	0-200 ppb	Hydrogen sulphide (H_2S), COS, mercaptans, total sulphur at trace levels
Pulsed Discharge Detector (PD-HID) Helium ionization mode 	Mass flow	Universal (except He and Ne)	0 -100 ppb (component dependent)	Purity of noble gases and other permanent gases, ammonia at trace levels
Pulsed Discharge Detector (PD-ECD) Electron capture mode 	Mass flow	Strongly electron affinitive substances	0-100 ppb (component dependent)	Traces of halogenated hydrocarbons
Pulsed Discharge Detektor (PD-PID) Photo ionization mode 	Mass flow	Using doping gas (Ar, Kr, Xe) Selective for aliphates, aromatics and amines	0-100 ppb (component dependent)	Aromatics and amines at trace levels

Table 2: Typical GC detectors for trace analysis