The success story of gas chromatography as an analysis method began in the middle of the last century, when it became a commercial process. In 1957, Siemens, one of the leading suppliers in the field of analysis technology, launched its first gas chromatograph, the L50.

Separation methods
In principle, nothing has changed since then in terms of the analysis method for the separation of gas mixtures into individual chemical compounds: An inert or non-reactive gas such as helium or nitrogen acts as the mobile phase. The test substance is injected into this carrier gas and forced through a heated capillary type tube, known as the 'column'. The column often has a winding structure and a length of between 30 - 200m.

Depending on the polarity and vapour pressure of the individual substances, the components of the sample spend different times in the stationary phase, which nowadays usually consists of polysiloxanes. A detector registers the retention time of the different molecules, while evaluation and recording of the detector signals provides information about the type and quantity of the individual substances.

Gas chromatography
Depending on the type of sample, the state of matter of the stationary phase, the type of detector used and the separation efficiency, quite different chromatographic methods and techniques are used. For the reliable determination of the composition and quality of natural gas almost 50 years since its first chromatograph, Siemens developed Sitrans CV - a gas chromatograph that aims to deliver results with minimal requirements on space and infrastructure, due to its microsystem technology.

The miniaturisation, with the aid of micro electrical mechanical systems (MEMS) technology, not only means a compact design, but also low consumption of energy and gas, and short measurement times. The injection into the separating columns is by means of valveless micro-injection systems. This avoids the high dead volumes that continued »
Combustion efficiency

occur with conventional valves. The valveless live injection method is not affected by fluctuations in the sample or ambient pressure and ensures reproducible measuring results.

The analyser consists of a basic unit and an analysis module, which is designed for the examination of natural gas and all components for the chromatographic analysis. All hardware components, such as the valveless live injection, high-resolution narrow-bore capillary columns and inline detectors, are designed to work with each other.

The system operates with a maximum of four capillary columns and detectors. The polarity and length of the capillary columns are dimensioned in such a way that the high separation power of the components can be performed as quickly and easily as possible. The thermal conductivity detectors (TCDs) are integrated at different places in the analytical separation way (in-line detection), which are based on silicon-wafer technology. These ‘micro-TCDs’ continuously measure the different thermal conductivities of the carrier gas and of the components to be determined. The electronic pressure regulators supply the columns with carrier gas and carry out the switching functions (injection, back flushing and cut).

Compared to conventional gas chromatographs, the principle of in-line detection has the advantage that the quality of the separation can be checked virtually after every column. This information is useful when checking the measurement system: Changes in the system functionality can be promptly detected and compensated. Column 1 separates those hydrocarbons with the higher boiling points like C6 and higher. Column 2 is responsible for separating propane, butane and pentane, as well as the components nitrogen, methane and ethane. Oxygen and CO₂ are determined by means of the last separation column. The analysis time of 150 seconds is not exceeded for any measurements. In the standard configuration, the Sitrans CV requires 100 seconds for analysing energy gases and calculating the quality parameters, which according to the company, makes it two to three times faster than other gas chromatographs.

The calibration of the device takes place by means of an automatic calibration gas charger. Due to the particularly high linearity of the micro TCDs, only a single calibration gas is required for each measurement component. This one-point calibration is aimed at reducing the amount of work and costs in comparison with the usual multipoint calibrations, using higher numbers of calibration gases.

**Qualities of natural gas**

Natural gas is a mixture of different hydrocarbons: In addition to the main component of methane, it also consists of longer-chained hydrocarbons such as ethane, propane or butane. In addition, there are various accompanying substances such as nitrogen, oxygen and CO₂. Even the strictly regulated preparation of natural gas by means of various separation and purification processes does not mean that, when delivered, natural gas will have the same composition at all times and in all places. Apart from the composition, two essential quality parameters describe the quality of natural gas. The gross calorific value and the Wobbe index are the determining factors for precise combustion processes, especially in the industrial environment. The gross calorific value is determined on the basis of the exact gas composition and specifies the thermal energy content of the natural gas, which is permitted to fluctuate between 8.4 and 13.1 kWh/m³ according to German standards.

The second decisive parameter, the Wobbe index, is calculated from the ratio of the calorific value to the relative density of the gas. It allows statements to be made about the load on the heating surfaces of burners and is not only relevant from a safety point of view, but also affects the choice of burner nozzles: Given otherwise identical boundary conditions, flame height and heating intensity increase significantly in proportion with the Wobbe index, although the calorific value determined is the same.

In line with ISO standards 6974 and 6976, the Sitrans CV gas chromatograph determines the concentrations of nitrogen, oxygen, CO₂ and C1 to C5. The hydrocarbons C6 to C9 are measured as group isomers. Due, in particular, to the measurement of individual components, the quality parameters such as gross calorific value can be calculated accurately. In addition, the repeatability of measurements of the different components with gas chromatographs is crucial, the minimum requirements for standard deviation are given in the ISO standard.

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