Fraunhofer IPM

Quantifying gas mixtures
Hydrogen and gaseous fuels

FTIR spectroscopy plus thermal conductivity detector

The gas analyzer installed at a hydrogen injection site: Hydrogen from a power-to-gas system is added to the natural gas line of a local gas supplier. The gas mixture is quantified using FTIR spectroscopy and a thermal conductivity detector.

Fluctuating quality of natural gas and increasing feed-in of renewably produced gases, such as green hydrogen, are challenging conventional gas measurement technology. Fraunhofer IPM has developed a spectroscopic gas analyzer to quantify regeneratively produced gases. The measurement system has already proven itself in continuous operation over eight months at a power-to-gas injection point – and may be adapted to quantify complex gas mixtures in various other applications.

Regenerative gases: a challenge for gas measurement technology

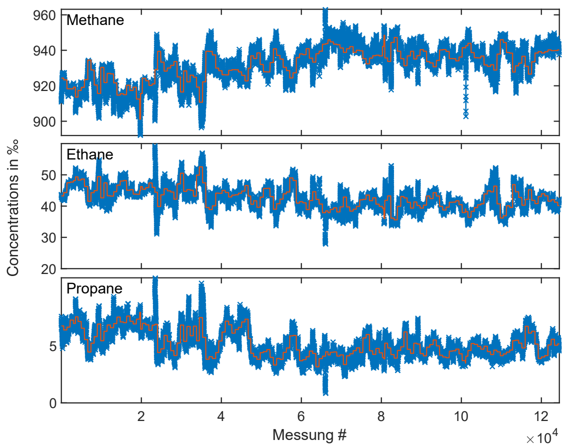
Natural gas is, as its name suggests, a natural product. It contains over 90 percent methane, along with ethane, propane, butane, and other hydrocarbons. Nitrogen and carbon dioxide are usually also natural gas components. In Germany, gas from various countries is fed into the grid, supplemented by biogas and increasingly also green hydrogen, which is generated according to the power-to-gas principle from renewable energy sources. The calorific value, as the decisive factor in billing, varies significantly with the gas composition. Therefore, measurements at distribution points in the gas network or at industrial consumer sites are essential and yield information about the actual amount of energy provided.

Infrared spectroscopy instead of chromatography

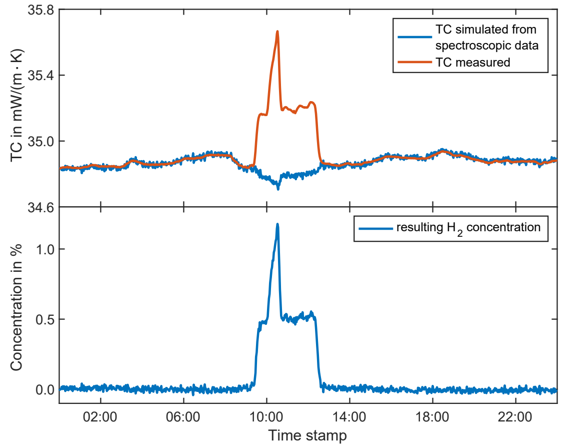
By default, gas chromatography (GC) is used to determine the calorific value. However, GC is comparatively expensive, quite slow and complex in general (e.g. carrier and calibration gases are required). Fraunhofer IPM relies on Fourier transform infrared spectrometers (FTIR) for quantifying complex gas mixtures. The measuring light from the spectrometer is passed alternately through an optical cell with sample gas or through a reference cell, and then analyzed spectrally. The infrared spectrum (i. e. discrete absorbed intensities from a broadband light spectrum) result from the interaction of light with the vibrational and rotational modes of the molecules. The latter are characteristic of each molecule and serve as a kind of fingerprint for identification. In addition, the level of absorbance is proportional to the

Infrared spectroscopy

IR -spectroscopy is an established technique for identifying and quantifying chemical substances. When illuminated by a broad-band light source, the spectral absorption of a sample reveals characteristic patterns based on the discrete vibrational and rotational energy levels of multi-atom molecules. This pattern provides a fingerprint for each chemical substance in a complex mixture. The technique can be used on solids, liquids, and – as shown here – on gases.



Time-courses of gas concentrations measured with the FTIR + TCD gas analyzer: More than 120,000 measurements were performed over 8 months. The measured concentrations in blue are compared to the daily averages provided by the gas supplier and measured by gas chromatography.



Example of a hydrogen injection event: The simulated thermal conductivity (TC) calculated from the spectroscopically quantified gases is permanently compared to the measured TC. A significant difference between those values results during hydrogen injection and can be used to calculate the present hydrogen content. Here, only one percent hydrogen was added.

concentration of the gas in the mixture, so that the concentration of each gas component may be determined chemometrically based on a spectrum of the gas mixture.

The difficulty, however, is in the details, especially if custody transfer accuracies are to be achieved. The extreme range of concentrations in natural gas – from methane in the 90 %-range to pentane and hexane in the sub-per-mill range. This results in a complex calibration routine and places high demands on the stability of the measurement system.

In its current version, the spectroscopic system detects the nine hydrocarbons up to C6 (isomers differ spectrally and therefore need to be detected individually) as well as carbon dioxide. Nitrogen is not infrared active and is detected indirectly.

Spectrometer plus thermal conductivity detector

Quantifying hydrogen in a gas mixture is the most important task when expanding the spectroscopic measurement system to the analysis of gases from renewable energy sources. The challenge here is that hydrogen gas – similar to nitrogen – has no dipole moment, which is why it cannot be measured using absorption spectroscopy. Therefore, a thermal conductivity detector (TCD) was integrated into the sample cell. The thermal conductivity (TC) of hydrogen is a factor of seven greater than that of all other fuel gases, so that the sensor's reaction is extremely sensitive to admixtures.

The measurement system detects gas concentrations down to the single-digit-per-mill range, well within custody transfer levels, and will be approved for these applications in the future.

In addition, this measurement system may easily be adapted to different applications in process technology to analyze complex gas mixtures with high accuracy.

Technical specifications

Method	Infrared absorption spectroscopy by means of an FTIR spectrometer
Dimensions	56 cm × 62 cm × 32 cm (H × W × D)
Weight	Approx. 70 kg (including explosion-proof housing)
Accuracy	Down to the ppm range (depending on measuring time and gas)
Measuring time	Typically 90 s, minimally approx. 10 s

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