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FTTCA – Gasanalyse mit thermisch modulierten Wärmeleitfähigkeits-Sensoren mit Fourier-Analyse des Messsignals

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Temperature Modulated Thermal Conductivity Gas Analysis Sensor Properties and Applications

Introduction to Temperature Modulated Thermal Conductivity Analysis

Temperature Modulated Thermal Conductivity Analysis is a fairly new method in gas analysis. Classical thermal conductivity analysis is limited to binary gas mixtures, whereas this new approach opens the way for the analysis of three, four and more gas components.
It makes use of both a physical effect and of the availability of new types of Thermal Conductivity Analysis (TCA-) sensors.

The sensor is a miniaturized TC-sensor with an extremely low thermal mass. It allows a sinusoidal temperature variation of ±40….±70°C within the fraction of a second. The physical effect lies in the differences of the temperature dependence of the thermal conductivity of various gases. Reliable theoretical or experimental data for this temperature dependence are not available. The application of fast Fourier-Transform algorithm to the sensor signal and subsequent establishing of a calibration matrix make the analysis of three- and four-component gas mixtures feasible.

Brief Description of the method

Gas analysis by measuring the thermal conductivity (TC) of a sample gas is the oldest and -- considering its importance for Gas Chromatography -- probably the most widely used gas analysis method. The common operating principle for all methods and instruments is the measurement of the rate of heat loss of an electrically heated resistor, which is exposed to the sample gas.
Since its invention in the early 1910's, it has become known as a reliable tool for gas analysis [1] with one important draw-back : it is applicable to binary gas mixtures only.

Classical thermal conductivity analysis operates with the sensor at a fixed temperature. This was always a necessity, as TC varies with temperature and a stable measurement requires a stable temperature of the measuring cell.

The complexity of the measurement is sharpened by the fact, that the contribution of any gas component to the TC of a gas mixture is a non-linear function of all the gas components in this mixture [2]. Direct theoretical approaches to the calculation of the TC of a gas mixture have therefore been only successful in very selected cases.

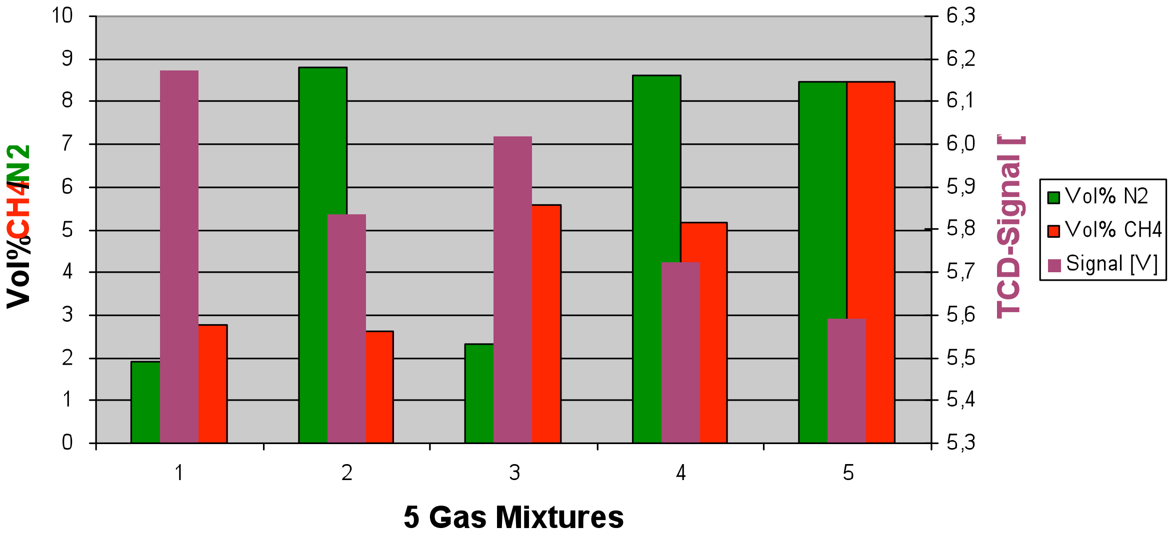
Several years ago, a method was published to measure a gas with n components at n-1 different temperatures and to then solve a non-linear equation system [3]. Yet, there is no known instrument available using this method.

The approach reported here is therefore purely experimental : The Fourier coefficients of the signal of a temperature modulated TC- sensor are used to determine the gas concentrations within complex gas mixtures like landfill gas or natural gas.

The following example shows fairly large variations of CH_4- and N_2-impurities in H_2
In a classical TCD-Analyser, they all result in a fairly similar TCD-Signal and a precise determination of the impurities is not possible (or requires a second, e.g. an Infrared-Analyser):

Fig. 1 : Signals in conventional TCD-Analysis

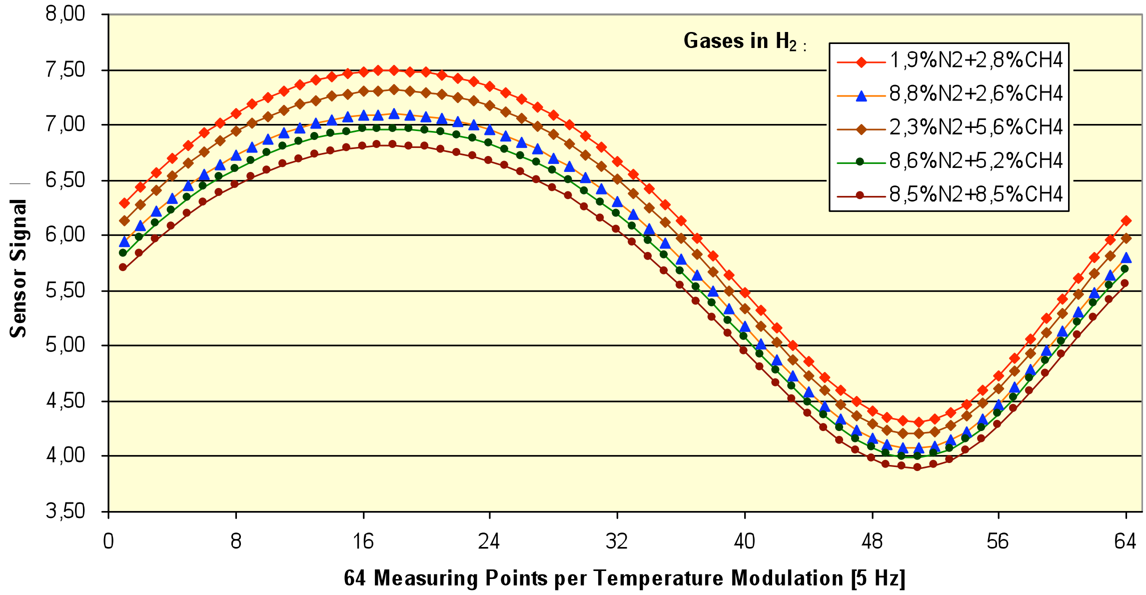
Example : 5 mixtures of CH_4 and N_2 (0…10 Vol% each) - balance H_2



But not only the TC itself, also its temperature gradient are characteristic values for any gas or gas mixture [4]. The next diagram shows the same 5 gases as above, but now the sensor is a thermally modulated TCD :

Fig. 2 : Signals of modulated TC-Sensor :

Example : 5 mixtures of CH_4 and N_2 (0…10 Vol% each) - balance H_2



The temperature modulation follows a sinus-curve; at 64 points along this curve, the sensor measures the TC. The temperature modulation can be varied between 2 Hz and 20 Hz. We found a modulation rate of 5 Hz quite sufficient and providing satisfactory results.
To characterise the signal curves, we use the first five Fourier-Coefficients of the sensor signal curve. From this approach, we named the method 'Temperature Modulated Thermal Conductivity Measurement with Fourier-Analysis of the Sensor Signals' – in short : FTTCA.
For the set of gases in the example mentioned, the resulting set of coefficients would be :

	N2	CH4	H2	… the first five Fourier-Coefficients				
	Vol%	Vol%		B0	B1	A1	B2	A2
Gas 1	1,9	2,8	bal.	6,171	-0,081	0,770	0,126	0,040
Gas 2	8,8	2,6	bal.	5,837	-0,075	0,733	0,118	0,037
Gas 3	2,3	5,6	bal.	6,019	-0,078	0,753	0,122	0,038
Gas 4	8,6	5,2	bal.	5,724	-0,072	0,721	0,116	0,036
Gas 5	8,5	8,5	bal.	5,593	-0,070	0,707	0,113	0,035

It should be noted however, that the mean value (B0) of the sinus-curves depend upon the mean temperature of the sensor membrane; this is exactly as in conventional TCD's, where the sensor signal for a given gas is a function of the sensor temperature – e.g. the temperature of a heated wire; the other coefficients depend then upon the amplitude of the temperature modulation.

APPARATUS

THE SENSING ELEMENT AND THE SENSOR MODULE

The sensing element is a miniaturised TC-sensor which is commercially available [5] and is used in a variety of TC-analysers on the market and also in use for Pirani-type vacuum meters.

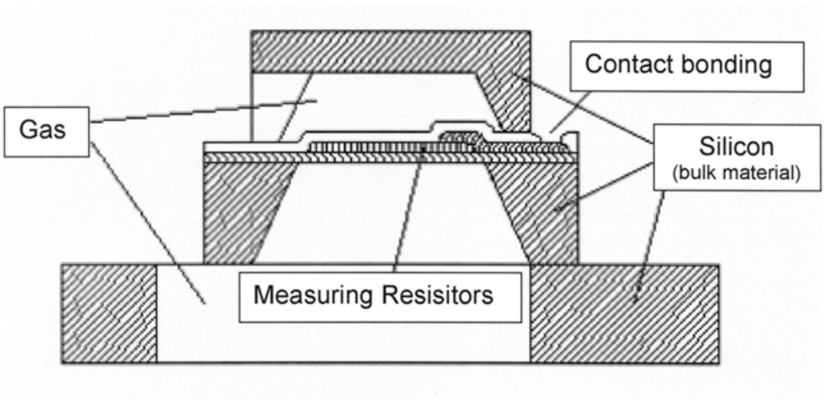


Fig. 3 : Cross Section of the Sensing Element
(copyright GRW-Sensors, DE 61169 Friedberg/H)

The sensing element consists of a Silicon-chip with a thin membrane of electrically and thermally extremely well isolating material. The membrane carries two thin-film resistor-meanders. Those resistors serve both for heating the membrane and for measuring the temperature. The resistors, the contact bonding and the and the conductors are protected against corrosive gas components by a passivating protective layer.

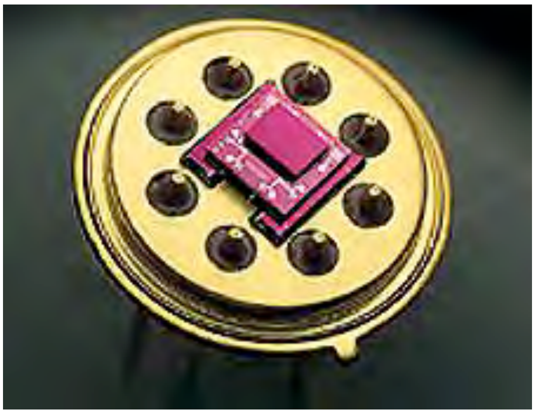


FIG. 4 Sensing Element Mounted onto a TO-8 package

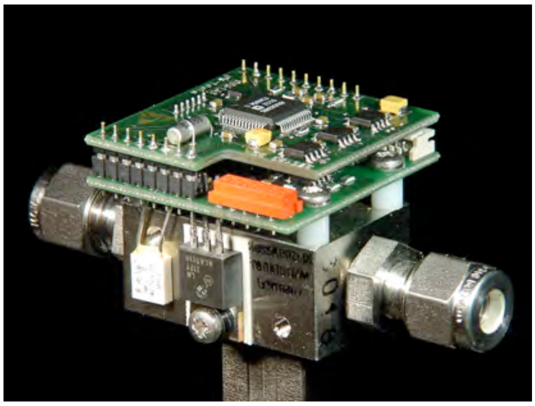


FIG. 5 Sensor Module with heater control and signal electronics

The sensing element, as shown in FIG. 3, is packaged onto standard TO-8 housing for further integration (Fig. 4). As has been shown by Grunewald [6], this sensor allows a temperature variation up to ±70°C within the fraction of a second. His company 'Messkonzept GmbH' in Frankfurt (Main) produces the sensor module, shown in FIG. 3 with an integrated sensor control and a heated and temperature controlled gas flow cell.

Parameters for the sensor head are :

- Gas flow cell temperature (typical are 40…60°C);
- Mean temperature of the sensor membrane (ca. 60°C .... 160°C);
- Amplitude of the sensor membrane temperature modulation (up to ±70°C);
- Shape of the modulation (e.g. triangular, trapezoidal, sinusoidal,...);
- Frequency of the temperature modulation (2 Hz ….. 20 Hz)

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THE INSTRUMENT FTTC 1100

The instrument FTTC 1100 consists of the sensing head and a control unit, built into an IP65-housing (or an EEx-d-housing, if required by the application) with all the necessary accessories for control of temperature, flow and pressure.

The control unit also allows a calibration with certified calibration gases as well as a re-adjustment with one reference gas in regular intervals; it stores all calibration parameters, performs the fast Fourier-Transformations and calculates the measurement results.
The control unit also organizes a constant inner temperature of the instrument and – depending upon the application – either pressure compensation via software or a pressure control.

Fig. 6 :
The instrument FTTC 1100
ATEX version (EEx de IIC T4)

Interferences and compensations :

The instrument is not influenced by the flow rate of the sample gas in the range 2 litres/hour … 50 litres per hour.

Thermal conductivity is usually not very sensitive to ambient temperature fluctuations. But here we measure a signal following the temperature modulation of the sensor. The heating and cooling of the sensor however is influenced by the ambient temperature fluctuations. It is therefore necessary to provide a reasonable thermostatting of the interior of the instrument.

The Fourier-coefficients of the sensor response curve is very slightly influenced by the sample gas pressure.
Depending upon the accuracy required, either a compensation of the influence of the ambient temperature or a pressure control may be advisable.

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Applications – and limitations

The measurement of Hydrogen in complex gas mixtures

The application, this project had been started, was the measurement of Hydrogen in a complex gas mixture of (e.g.) CO2, CH4 and N2

The FTTC 1100 measures within a few seconds the following gas values :
- H2-concentration and
- Gas Density

Sensors to measure the purity of Hydrogen in a density range of 0,100 kg/m3 to 0,200 kg/m3 corresponding to a H2-purity of 98,4%....99,5% are now running successfully for years with virtually no maintenance and a minimum of recalibration requirements.

The measurement of accompanying gases in Hydrogen

This application clearly shows the limitations of the method :
The influence of H2 to both the mean value and the temperature gradient of the thermal conductivity is quite heavy [7].
So, the measurement of the accompanying gases with satisfying accuracy is only possible in 3-component mixtures (e.g. H2-CO2-CH4 or H2-CO2-N2). Even there, a tight temperature control and a pressure control of the sample gas is necessary to achieve good and stable results.

Natural Gas – use in large industrial boilers

With rising gas prices, this application has become the most important one.
The FTTC 1100 measures within a few seconds the following characteristic fuel gas values :
- LCV Lower Calorific Value
- SG Specific Gravity (Density relative to air)
- The Wobbe-Index, calculated from LCV and SG
- CO_2 concentration
- Hydrocarbon concentration C1 and C2

The underlying problem is very mundane and an every-day one :
A process boiler is fired by natural gas. This natural gas has relatively small variations in it's gas compositions. The relation of the three main components
Methane + (higher) Hydrocarbons : Carbon-Dioxide : Nitrogen varies only slightly.

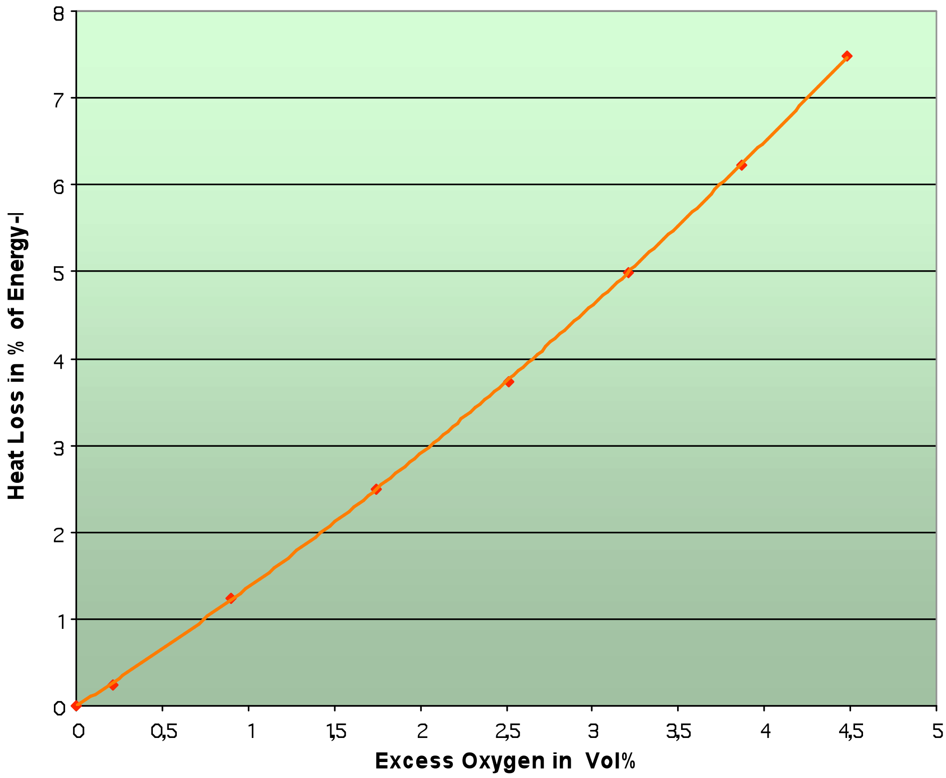
In most cases, gas suppliers warrant only the lower or the upper calorific value of the natural gas delivered – and in many cases they guarantee only an average value over a certain period of time.
But for an efficient burner control, the Wobbe-Index (= the density-corrected lower calorific value) and the density corrected air demand are necessary – and both values in ‚real time'.

In large industrial boilers, the usual measurements for control purpose are : temperature, the concentration of O_2 in the flue gas and recently also the content of CO or CO-equivalent.
All these measurements however are done after the combustion is already (more or less) completed. This allows only to re-act to the measurements.
Much better is a fast forward control strategy for burner control.

For best efficiency, the mixture air : fuel should be adjusted in time with the arrival of an altered gas at the burner nozzle.
To make this possible, a fast measurement of Wobbe-Index and Air Demand is necessary.

In technical Literature, we find Siegert's formula, which allows calculating the flue gas heat losses for a variety of fuels, flue gas temperatures and excess-O_2-concentrations.
The following diagram shows the additional heat loss by excess air as a function of the excess O_2 in the flue gas at an assumed boiler exit temperature of the flue gas at burner exit of ~700°C :

Fig. 7: Additional Heat Loss of a Natural-Gas-fired Burner by Excess Air



As a rule of thumb we may say, that one Vol% excess O_2 correlates with an additional energy loss of ~1%. It is quite reasonable, to correlate this loss with the annual bill for the fuel consumed.

Using te fast FTTC-Analyser, it becomes possible to approach more closely the stoichiometric point (λ =1,0), follow quickly even small changes in gas quality and still operate the burner in the safe region : The exact air demand for a complete and safe burning is known in advance and not only by an O_2-measurement downstream from the burner.
The O_2-measurement after the burner nevertheless remains a necessity as a redundant safety measure.

It should be noted here, that the application to Bio-Gas fuelled burners is limited to gases with a negligible content in Hydrogen. As outlined above, the influence of H_2 to the thermal conductivity parameters of the accompanying gases is detrimental to the accuracy of their respective measurement.

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Conclusion and Outlook

Temperature modulated Thermal Conductivity Analysis is a practical way to extend the use of thermal conductivity sensors into applications, which haven't been accessible to TC-Analysis until now.
FTTC will be especially helpful, where conventionally a second analyser has been used to compensate for cross interferences.
Best explored applications till now are the measurement of Landfill Gas, of Natural Gas and similar gases.
Good results have also been achieved in more complex gas matrices for H_2-purity measurement and in the determination of gas density.
The limits of the method are yet to be explored.

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