# New Gas Sensors

W.G. Haije **(ECN)**
F.P. Bakker **(ECN)**
S. Gersen **(DNV GL)**
R. Wolffenbuttel **(TU Delft)**
G. de Graaf **(TU Delft)**
B. Dam **(TU Delft)**
R. Westerwaal **(TU Delft)**

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# New Gas Sensors

Final report

Wim Haije, Frits Bakker : ECN

Sander Gersen: DNV GL

Reinoud Wolffenbuttel, Ger de Graaf, Bernard Dam, Ruud Westerwaal : TU Delft

Sixth Research day, 24 April 2014, Nunspeet

# Overview presentation

1. Project objectives
2. What has been done?
3. Valorization
4. Conclusions

Title Project: New Gas Sensors
Project number: A3
Theme 1: From Mono to Multigas, 1.3 Measurement techniques for gas quality determination
Theme 2: Robust future energy systems, 2.2: Subprogram Flexible energy conversion systems

Project leader: ECN
Research leader: Dr W.G. Haije
Partners: ECN, TUDelft TNW, TUDelft EWI, Gasunie (supported by DNV GL)

EDGaR
Energy Delta Gas Research

# New gas sensors project

*Is it possible to demonstrate a gas meter and gas appliance with special sensors for safe and efficiënt use of new gases (hydrogen, biogas) in order to facilitate the transition to a sustainable energy infra structure in the most cost efficiënt way?*

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# Objectives

- Overview of suitable sensors for new gas metering
- Development of an innovative hydrogen sensor, geared towards the aimed multi sensor concept, based on inherent safe principles
- Performance characteristics of potential sensor systems (range, accuracy, stability)
- Proof of principle of the combination of the preferred new gas sensor lay-out and the intelligent boiler/burner concepts
- Design of the sensor chip lay-out

# Tasks

ECN

- Design and build sensor test rig
- Select sensors to be tested
- Perform the sensor tests

# Tasks

DNV GL

- Define the new gas ranges
- Design and build test facilities
- Perform tests

# Tasks

## TU Delft, group R. Wolffenbuttel

- Design and produce MEMS based new gas sensors
- Lab tests
- Field tests

## TU Delft, group B.Dam

- Prepare optical hydrogen sensor for new gas application
- Lab tests
- Field tests

# ECN

Design and build the test facilities

# Performance characteristics test facility

5 0799-11gr02 prestatie kenmerken testopstelling EDGaR (2).pdf - Adobe Reader

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## 3. Resultaten metingen

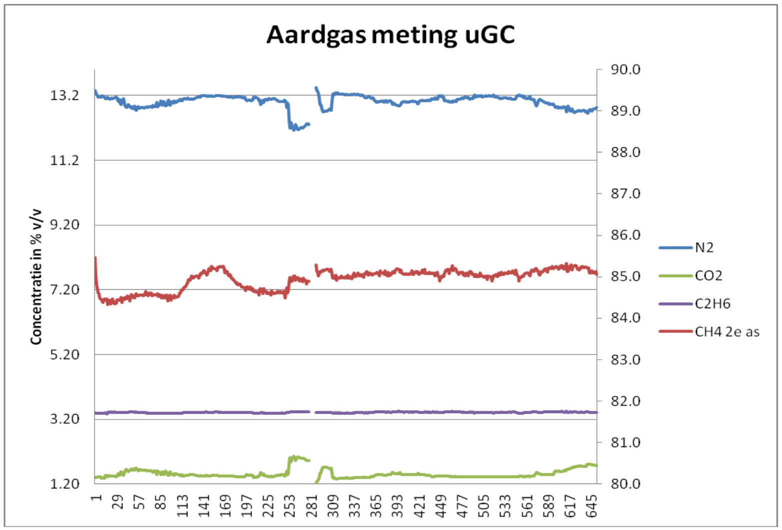
Zie bijlagen voor tabellen meetresultaten.

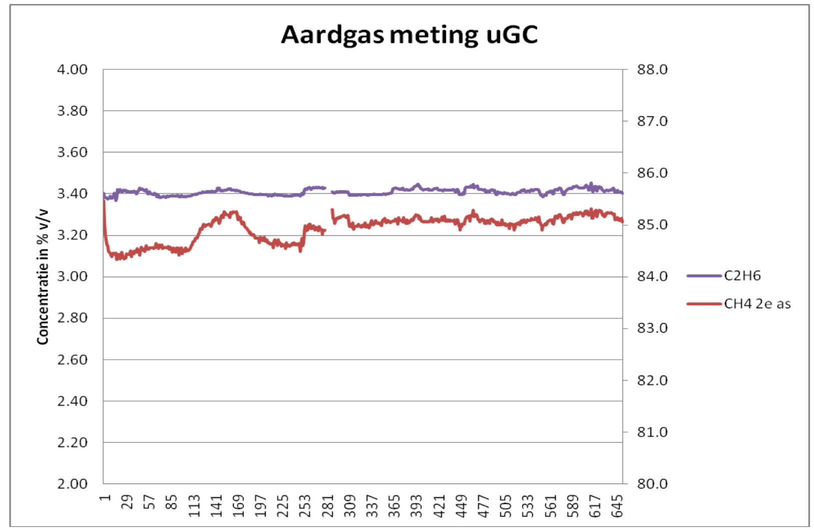
Tabel 3.1 *Prestatiekenmerken EDGaR sensor test opstelling*

| Component | Range | | Herhaalbaarheid | Juistheid | Respons tijd | |
|---|---|---|---|---|---|---|
| | | | | | $T^{95}$ | $T^{99}$ |
| | van % | tot % | rsd % | rsd % | sec | sec |
| $H_2$ | 0 | 20 | 1.7 | 3 | 90 | 240 |
| $N_2$ | 0 | 80 | 0.1 | 1 | 90 | 240 |
| $O_2$ | 0 | 25 | x | x | x | X |
| $CO_2$ | 0 | 30 | 0.1 | 1 | 90 | 240 |
| $CH_4$ | 0 | 50 | 0.3 | 3 | 90 | 240 |
| CO | 0 | 20 | 0.2 | 1.5 | 90 | 240 |
| $C_xH_y$ | 0 | 20 | x | x | x | X |

Energy Delta Gas Research

# Micro GC




| Field test | | Ne (ppmv) | | H2 (ppmv) | | CO (% v/v) | | CH4 (ppmv) | |
|---|---|---|---|---|---|---|---|---|---|
| | | in | out | in | out | in | out | in | out |
| **GC1 - BS #03** | mean | 66.9 | 66.8 | 401 | 568 | 0.803 | 0.843 | 105.0 | 23.0 |
| | **rsd %** | **0.5** | **0.5** | **2.8** | **2.0** | **0.2** | **0.2** | **0.2** | 4.4 |
| | n | 270 | 1389 | 270 | 1391 | 261 | 1336 | 270 | 1383 |

# Optical $CO_2$ sensor Vaisala

VAISALA

QUICK REFERENCE GUIDE

Vaisala CARBOCAP© Carbon Dioxide Module GMM111

- Compact flow aspirated CO2 measurement module
- CO2 measurement range options of 0 ... 5 % CO2, 0 ... 10 % CO2 or 0 ... 20 % CO2
- For OEM applications



## GENERAL

Vaisala CARBOCAP® Carbon Dioxide Module GMM111 measures $CO_2$ concentrations up to 5, 10, or 20 % depending on the choice of measurement range. The module features flow-through aspiration and is intended for applications such as incubators and bioreactors. GMM111 powers up from 24 VDC/VAC and provides both voltage and current analog outputs. The module also supports digital RS485 communication.

## ELECTRICAL CONNECTIONS

Make the connections according to the table below. See Figure 1 below the table for wire terminals.

| | |
|---|---|
| mA | Signal 4 ... 20 mA |
| V | Signal (+) 0 ... 10 V |
| 0 | Signal (-) |
| B | RS485 Signal B |
| A | RS485 Signal A |
| 0 | Power supply (-) |
| 24V | Power supply (+) 24 VDC/VAC |

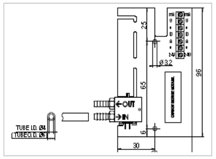


*Figure 1 Module Connections and Dimensions*

### Powering

The module requires a nominal 24 VDC/VAC power supply maintaining a voltage of 18 ... 30 VDC or 20 ... 26 VAC for all load conditions and all mains voltages. Although the power input includes a half-wave rectifier, it is recommended to use a DC supply to avoid current peaks.

### Connections to 24 VAC Power Supply

Connecting more than one module to a single 24 VAC transformer forms a common loop and increases the risk of a short-circuit. Therefore, a separate floating supply for each module is recommended (see Figure 2).

If several modules share a common transformer, the phase (~) must always be connected to the 24 V connector in each module (see Figure 3).

## GAS SAMPLE CONSIDERATIONS

The unit has been designed for strictly non-condensing conditions. If the gas sample is drawn from humid conditions, special care must be taken to prevent condensation from occurring in the sensor. In practice this means lowering the dewpoint of the gas sample below the sensor temperature, for example by drying the sample gas.

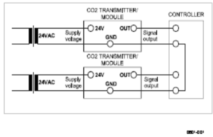



*Figure 2 Connection of Separate AC Supplies (Recommended)*

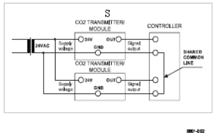
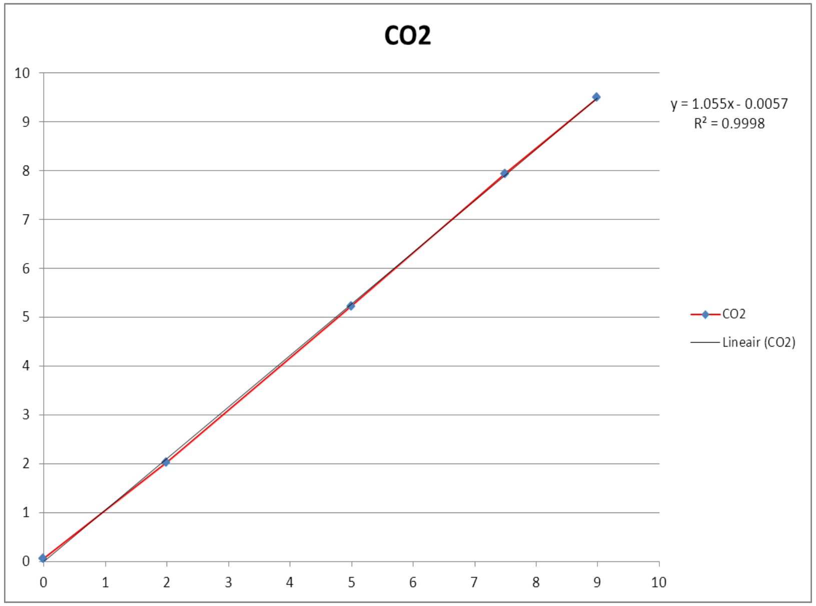
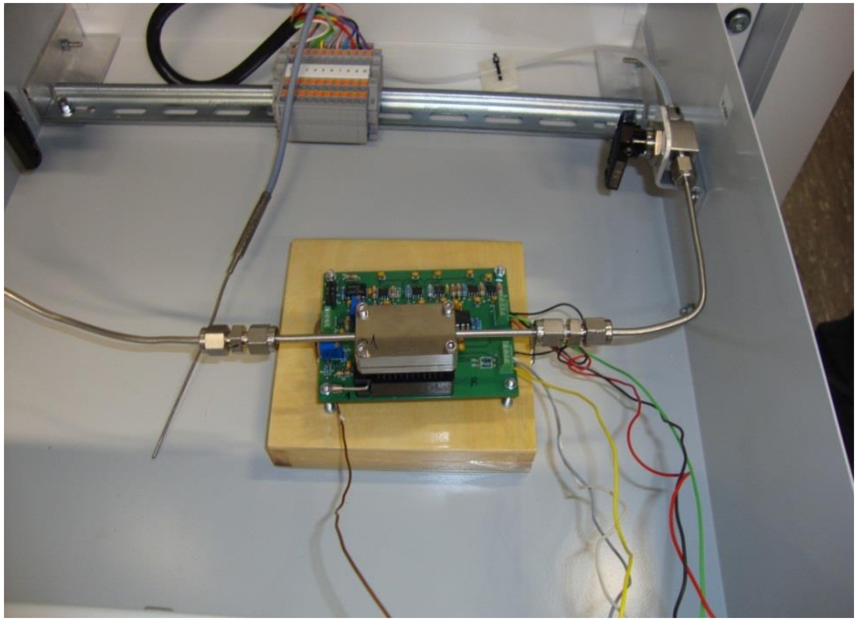
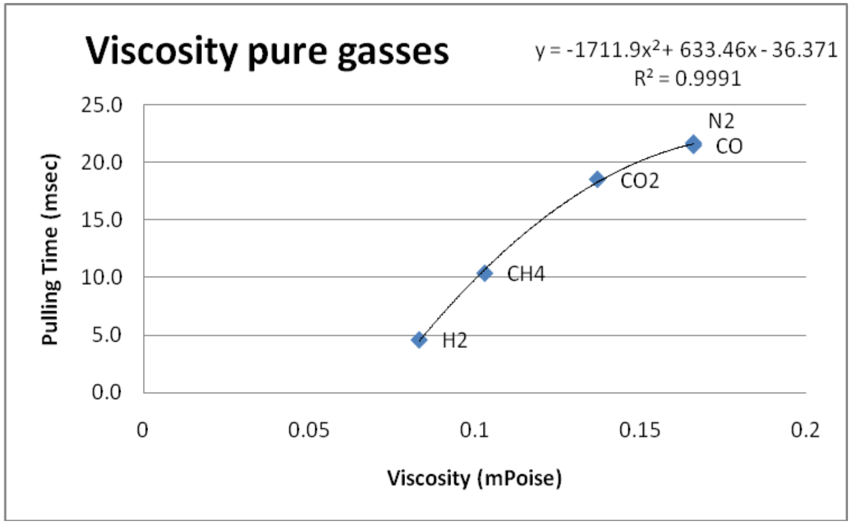



*Figure 3 Connection of Single AC supply to Several Modules*

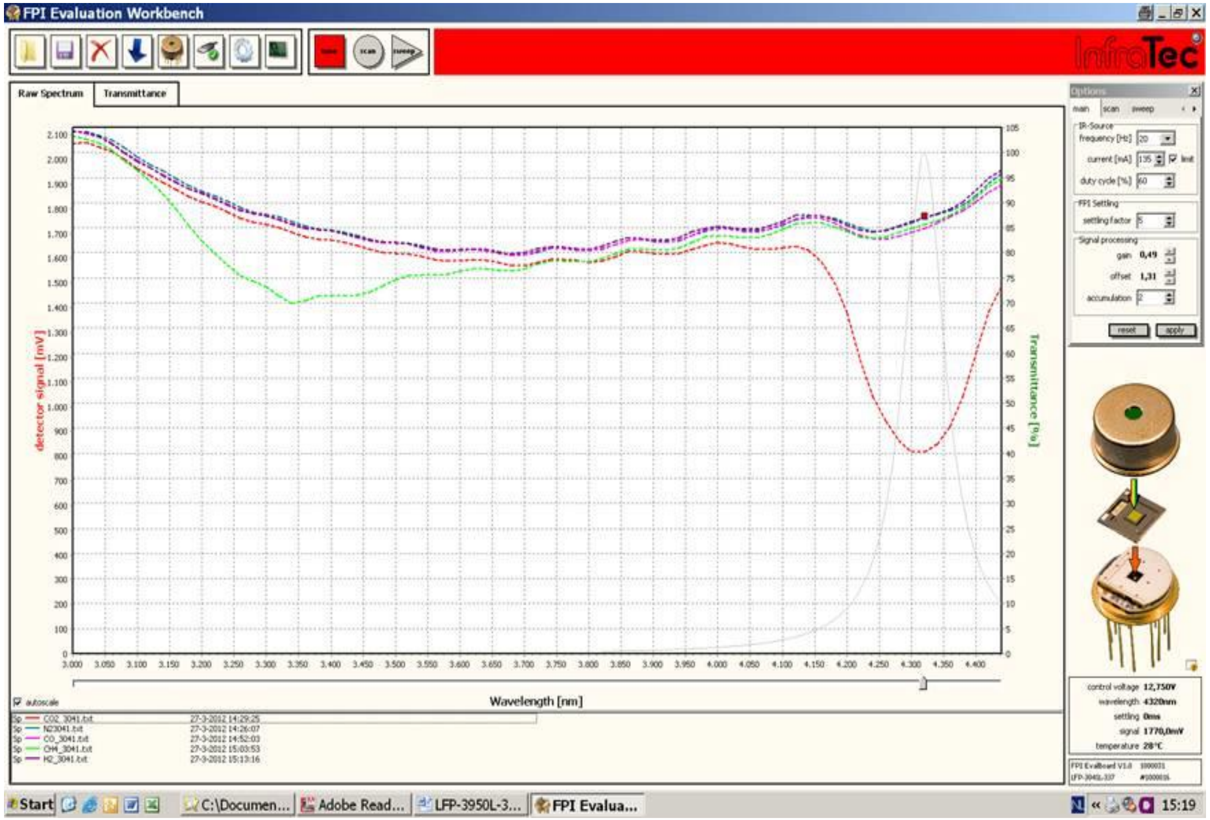


# Viscosity sensor TUD





# Tunable FP IR sensor



# TCD sensor TU Delft

TCD_Description_Report-2.pdf - Adobe Reader

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The response of the sensor to different typical gas compositions is shown in Figure 5.

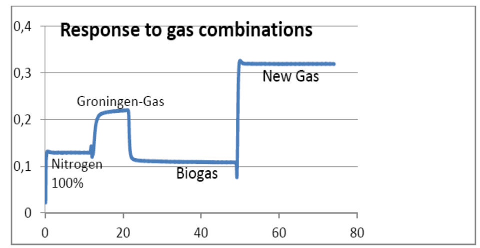
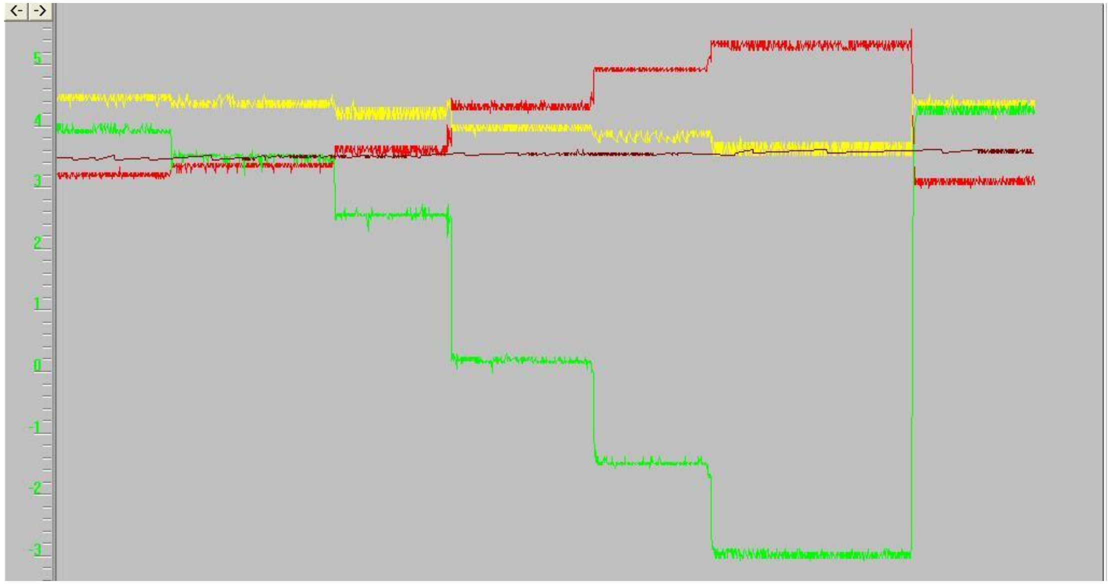



*Figure 5: Response of the ECN TCD prototype to some typical gas combinations.*

| Gas | Thermal conductivity [$Wm^{-1}K^{-1}$] * $10^{-3}$ | Sensor output Voltage [mV] |
|---|---|---|
| 100% $N_2$ | 24 | 129 |
| Groningen Gas 80% $CH_4$ + 10% $N_2$ + 10% $CO_2$ | | 219 |
| Biogas 80% $CH_4$ + 20% $CO_2$ | | 108 |
| New Gas 80% $CH_4$ + 10% $N_2$ + 10% $H_2$ | | 320 |

# Calorimetric sensor TU Budapest



# Summary sensor tests

| | uGC | $CO_2$ IR | Tunable FP | TCD | Viscosity | Calorimeter | Hydrogen |
|---|---|---|---|---|---|---|---|
| Range | oooo | ooo | oo | oooo | ooo | oo | oo |
| Linearity | oo | oooo | oo | oooo | oo | o | ooo |
| Accuracy | oooo | ooo | oo | oooo | oo | o | ooo |
| Response | oo | oooo | oooo | oooo | oooo | oooo | ooo |
| Selectivity | oooo | oooo | ooo | oo | oo | o | oooo |
| Stability | oo | oooo | oo | oooo | o | o | ooo |
| Maintenance | o | oooo | oo | oooo | oo | oo | oo |
| MEMS ready | o | oo | ooo | oooo | oooo | oooo | oooo |

o = poor, oooo = excellent

# DNV GL

Goal:

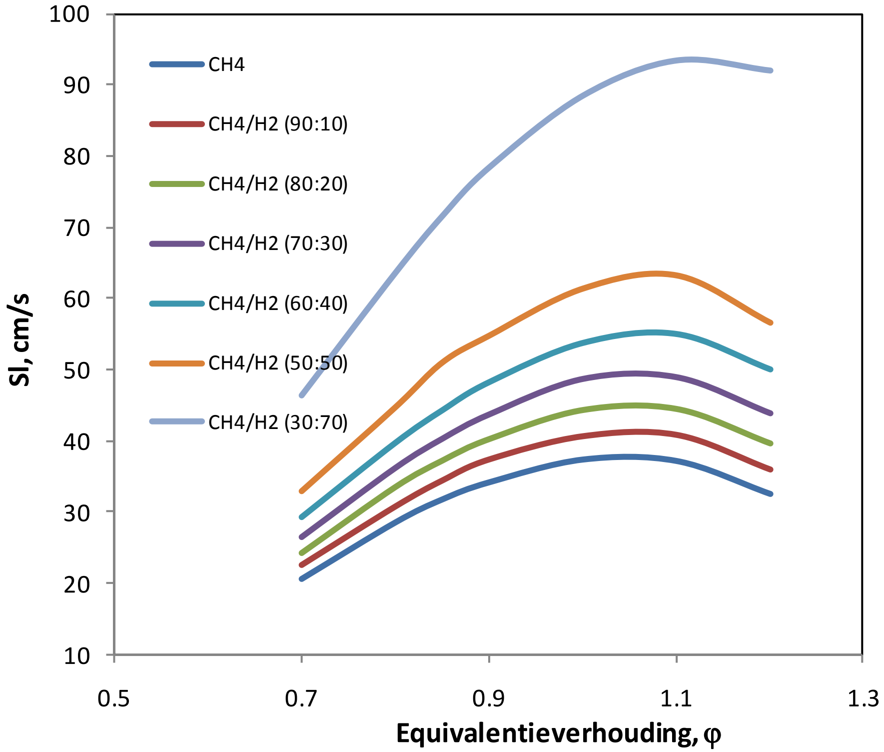
- Developing and demonstrate a novel type gas appliance ("New Gas Appliance") that can accept any type of gas

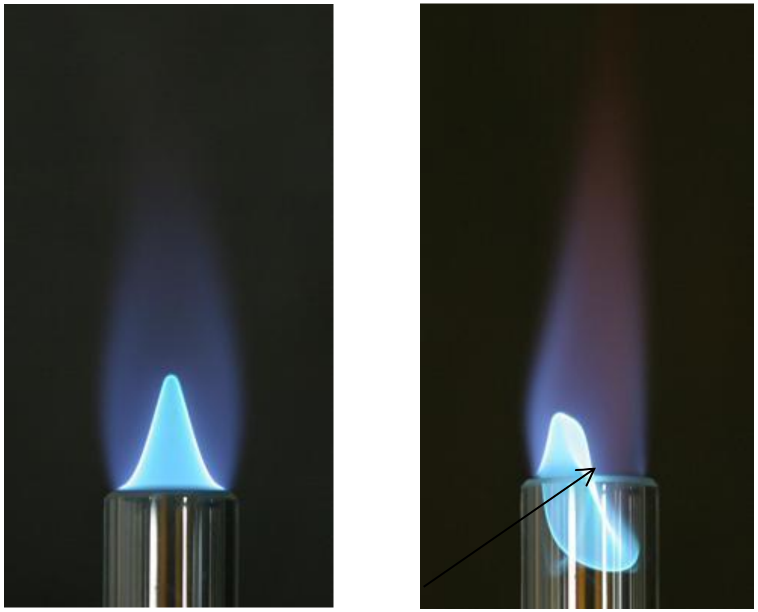
Why?

- Current used gas appliances are fit to traditional natural gas supplied ($CH_4$, $C_2H_6$, $C_3H_8$, and higher )

- Different composition can result in undesired behavior in end use appliances (related to combustion properties)

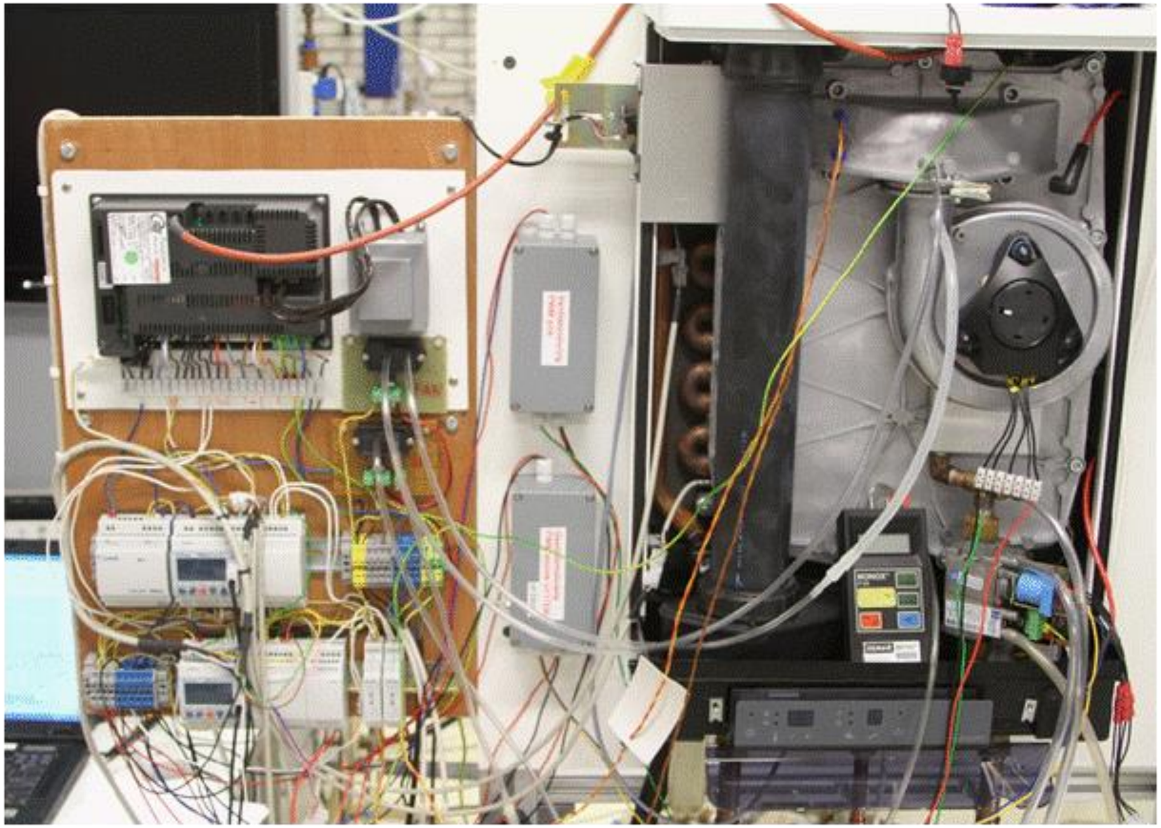
# Impact $H_2$ addition to $CH_4$ on the burning velocity



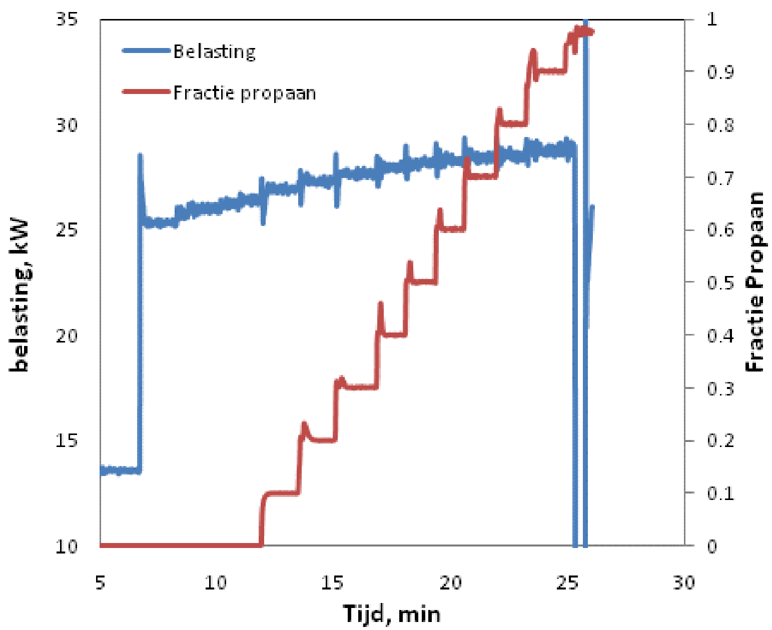



Flash-back

# Boiler and control system



# Effect of propane addition to methane (maximum load)



# Conclusion

- Boiler shows good performance for the following range of tested gaseous fuels
  - $CH_4/H_2$ up to 60% $H_2$
  - $CH_4/C_3H_8$ up to 100% $C_3H_8$
  - $CH_4/CO_2$ up to 50% $CO_2$

# Conclusion

- $H_2$ addition results in an increase in the temperature of the burner surface
- Addition of $H_2$, $CO_2$ and $C_3H_8$ results in a deviation between the air factor calculated by the algorithm and the measured air factor

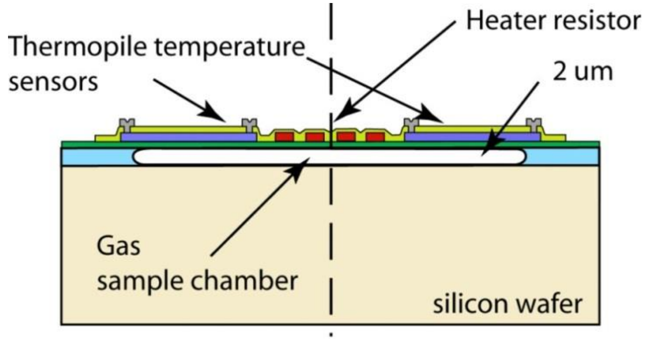
# TU Delft EWI

Thermal conductivity detector (Ger de Graaf

Viscosity sensor:  Luis Rocha, Rosana Dias (Univ. of Minho)

IR absorption:  LVOF (Arvin Emadi)

# Thermal conductivity detector




Cross section

Dedicated electronics has been built

AC modulation for high performance

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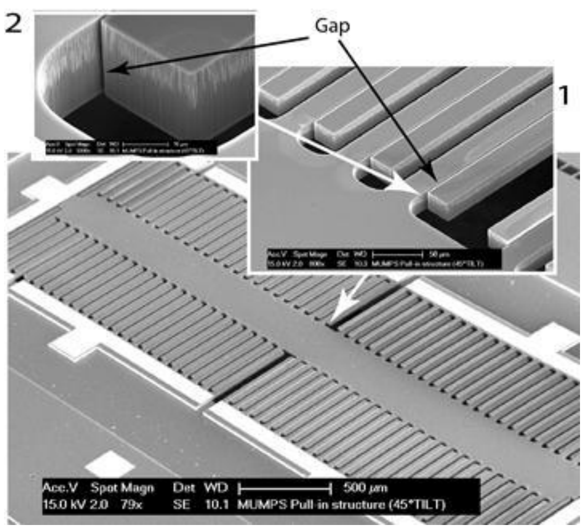
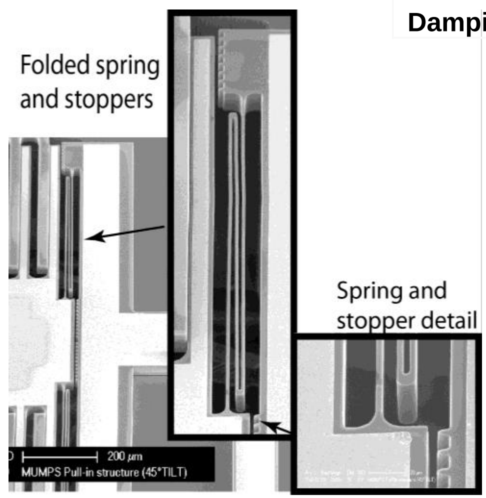
# Viscosity detector MEMS

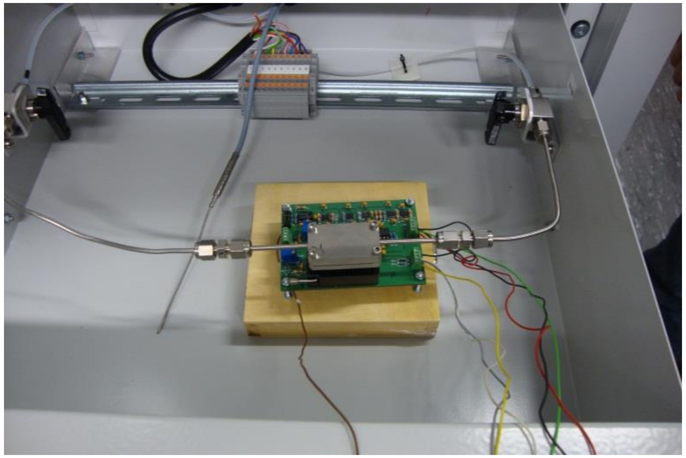


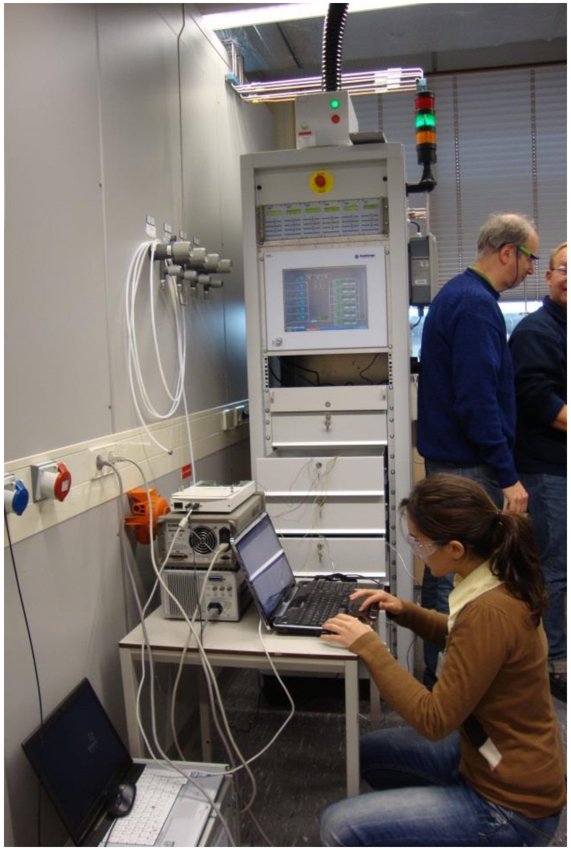




| | |
|---|---|
| **Mass (m)** | 0.249 mg |
| **Mechanical spring (k)** | 3.33 N/m |
| **Zero-displacement gap ($d_0$)** | 2.25 µm |
| **Natural resonance frequency ($f_0$)** | 582 Hz |
| **Zero-displacement actuation capacitance** | 0.66 pF |
| **Damping coefficient in air(b ; @ gap=2/3$d_0$)** | 1.73 mNs/m |

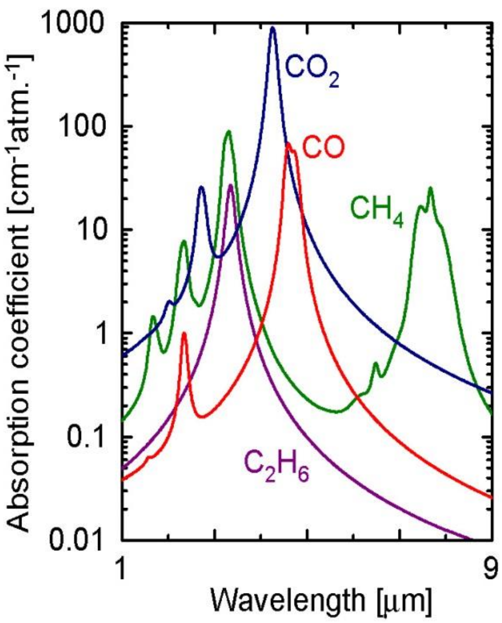
# Tests at ECN

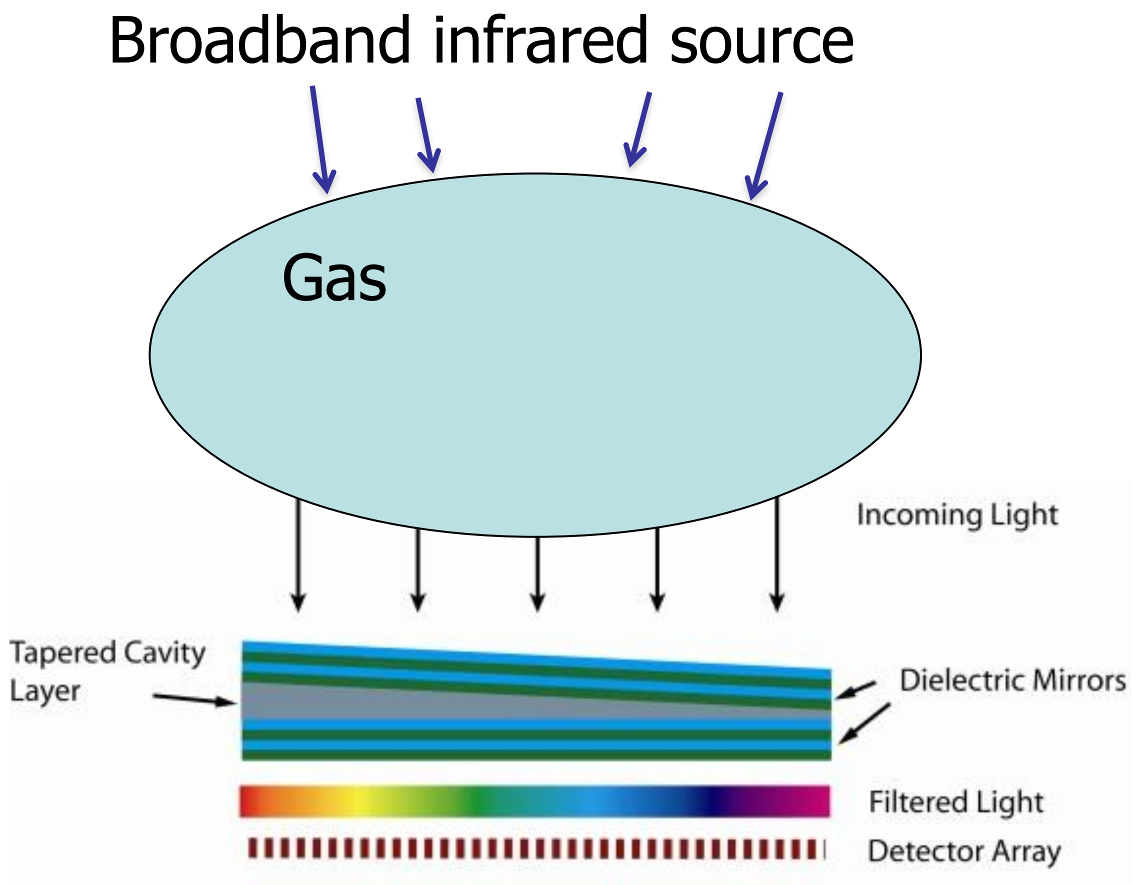
# October 2011





# LVOF Infrared Filter



# STW project

**STW 11476: Microsystem for Multi-Gas Analysis**

**Amir Ghaderi**

**Pelin Ayerden**

# TU Delft TNW

- Prepare optical hydrogen sensor for new gas application
- Perform field tests at ECN and DNV GL

# Project outline and goals TUDelft/MECS

- Develop an optical sensor for the required range of hydrogen pressures (1-300 mbar).
  - Various pressure threshold level detectors.
  - Single sensor material which shows a continuous optical change with increasing hydrogen pressure.

- Test and optimise the detector under realistic conditions.
  - Test the selectivity of the catalytic layer/sensor
  - Test the influence of other gas components/impurities: CO, $H_2S$, and $SO_x$, on the Pd-based layer
  - Test and optimise the developed protective coatings.

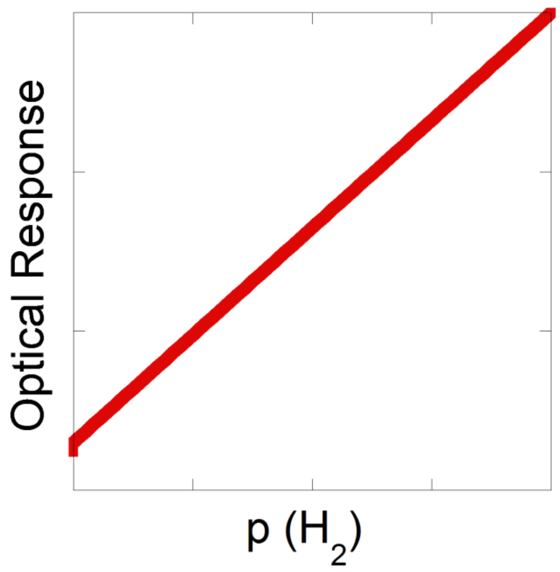
- A new design readout system should be made which is cheap and reliable and easily integrated without standard (PC) readout systems.

- An optimal sensor design should be tested under realistic conditions to determine the lifetime, accuracy and typical failure modes.

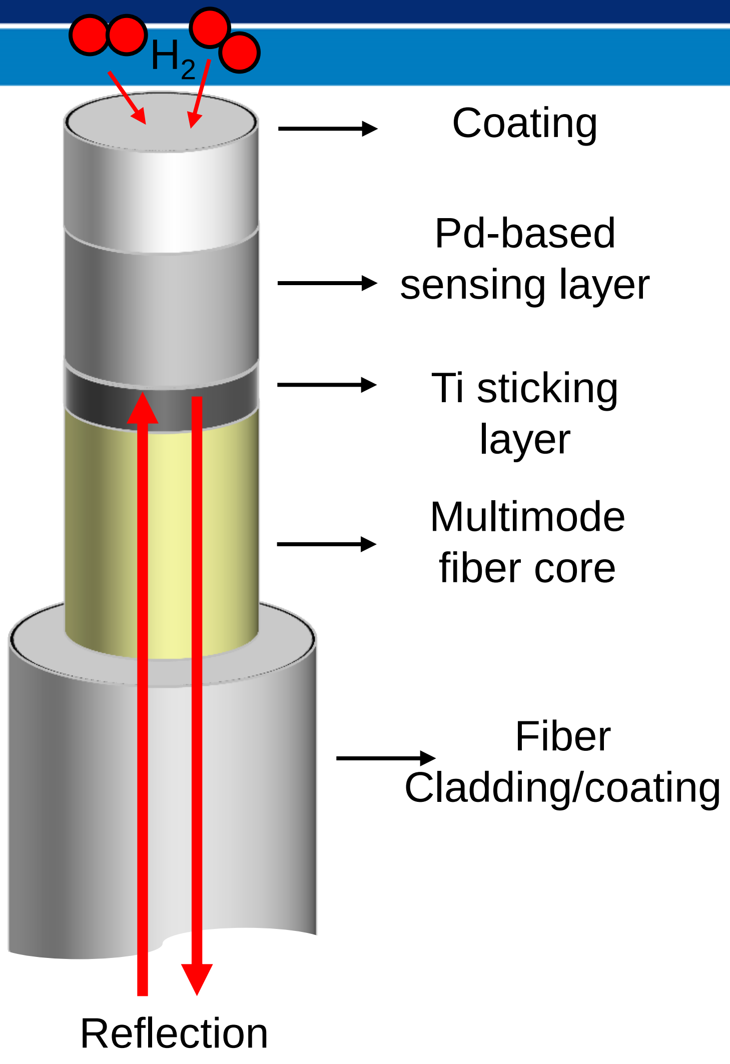
# Continuous hydrogen sensor: Pd-Ta

**Sensor → Quantitative information**

Continuous Sensor




Well-defined relationship between optical response and $H_2$ pressure



# Protective coating against CO contamination

Tested coating materials for the EDGaR project:

- PTFE (polytetrafluorethyleen, slows down CO blocking by diffusion)
- HDPE (high-density polyethylene, unable to deposit by sputtering)
- FEP (Fluorinated ethylene propylene, slows down CO blocking by diffusion, better than PTFE)
- Nanostructured $Al_2O_3$ caplayer (no improvement)
- Pd-PTFE composite (no improvement)*
- MOF (possible solution, but a suited pore diameter is required)
- PMMA (Promising but to be tested)

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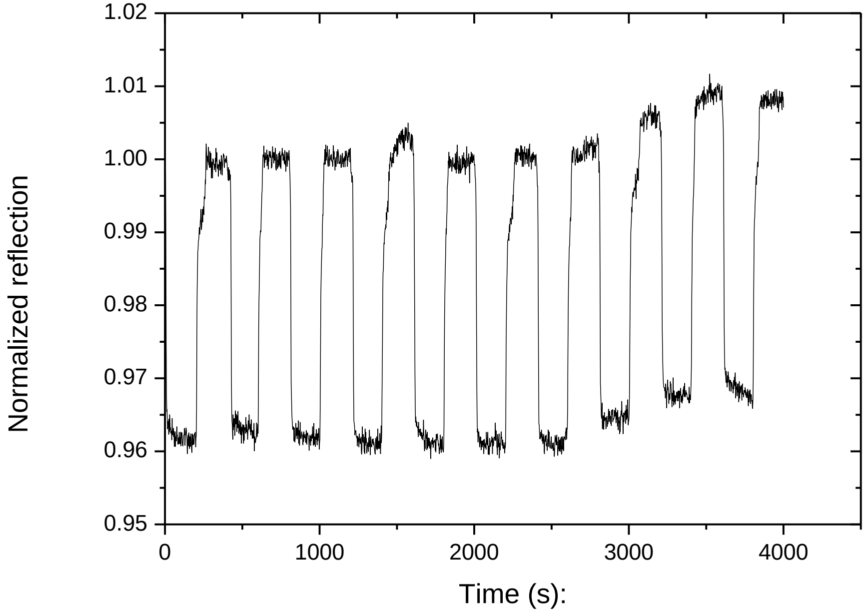
# A continuous $H_2$ sensor: Limitation CO influence

200 nm PTFE, 30 nm $Pd_{81.3}Au_{18.7}$ 200ml/min, RT




- Loading step 1% $H_2$+0.0018% CO
- Unloading step 1% $O_2$ in Ar
- **No influence of CO during cycling!**
- **$2CO+O_2 \rightarrow 2CO_2$**

- The influence of CO can be limited by the presence of $O_2$ in the feed flow
- It depends on the gas mixture if there is a large influence of CO.

# Conclusions $H_2$ sensor

- A linear $H_2$ sensor has been demonstrated (Pd-Ta: 300mbar, Pd-Au: 200mbar)
- These sensor materials show a high stability and reproducibility
- The sensor is able to operate in the presence of Ar, $O_2$, $CO_2$, $CH_4$
- The sensor is very sensitive towards CO and the tested coatings are unble to prevent contamination
- The influence of CO can be strongly reduced by the presence of $O_2$
- The sensor has been tested under the most realistic conditions we can apply

# Putting all together: Multi sensor scheme

- Tunable Fabry-Perot sensor ($CH_4$, $CO_2$, $C_2H_6$, $C_xH_y$, CO)
- Optical Hydrogen sensor
- Thermal Conductivity sensor

With this configuration it will be possible to calculate the energy content of the gas and predict the combustion behavior.
For high precision determination of the energy content a direct measurement principle is required, more work will have to be done to improve the performance of the calorimetric sensor that we tested. An alternative might be the use of a micro (solid oxide) fuel cell.

# In the meantime

Measuring viscosity of new gas and electrical properties (capacity measurements) are well possible with MEMS based devices. These parameters can contribute to the quality of measured values and might enable calculation of the nitrogen content of new gas.

An improved version of the tunable Fabry-Perot sensor system became commercially available. This version has been tested extensively at KEMA. They concluded that this version was able to determine $CH_4$, $CO_2$, $C_2H_6$ and higher hydrocarbons with sufficient accuracy.

# Valorisation

1. Road to value, ECN valorization study
    1. Gasunie
    2. TAQA

    Result; interesting but only relevant > 2020
2. Patent on multi sensor chip filed but not submitted
3. SBIR project H-gas sensor
    1. SBIR 1 part feasibility study granted, no follow up
    2. SBIR 2 not granted
4. EDGaR Parel ( capacity sensor ) granted

# Objectives

- ✓ Overview of suitable sensors for new gas metering
- ✓ Development of an innovative hydrogen sensor, geared towards the aimed multi sensor concept, based on inherent safe principles
- ✓ Performance characteristics of potential sensor systems (range, accuracy, stability)
- ✗ Proof of principle of the combination of the preferred new gas sensor lay-out and the intelligent boiler/burner concepts (done with individual components)
- ✗ Design of the sensor chip lay-out (on component level)

# New Gas Sensors project, conclusions

1. Suitable optical and physical ‘MEMS ready’ sensors are available
2. Optical hydrogen sensor successfully demonstrated
3. Gas boilers can be adapted to accept changes in gas composition
4. For industry too early to start development of new gas sensor chip

*Nederlands*

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Samenwerkingsverband Noord Nederland.
Dit project wordt medegefinancierd door het Europees Fonds voor Regionale Ontwikkeling en door het ministerie van Economische Zaken.
Cofinanciering vindt eveneens plaats door de Provincie Groningen.

*English*

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**ECN**

Westerduinweg 3
1755 LE  Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl