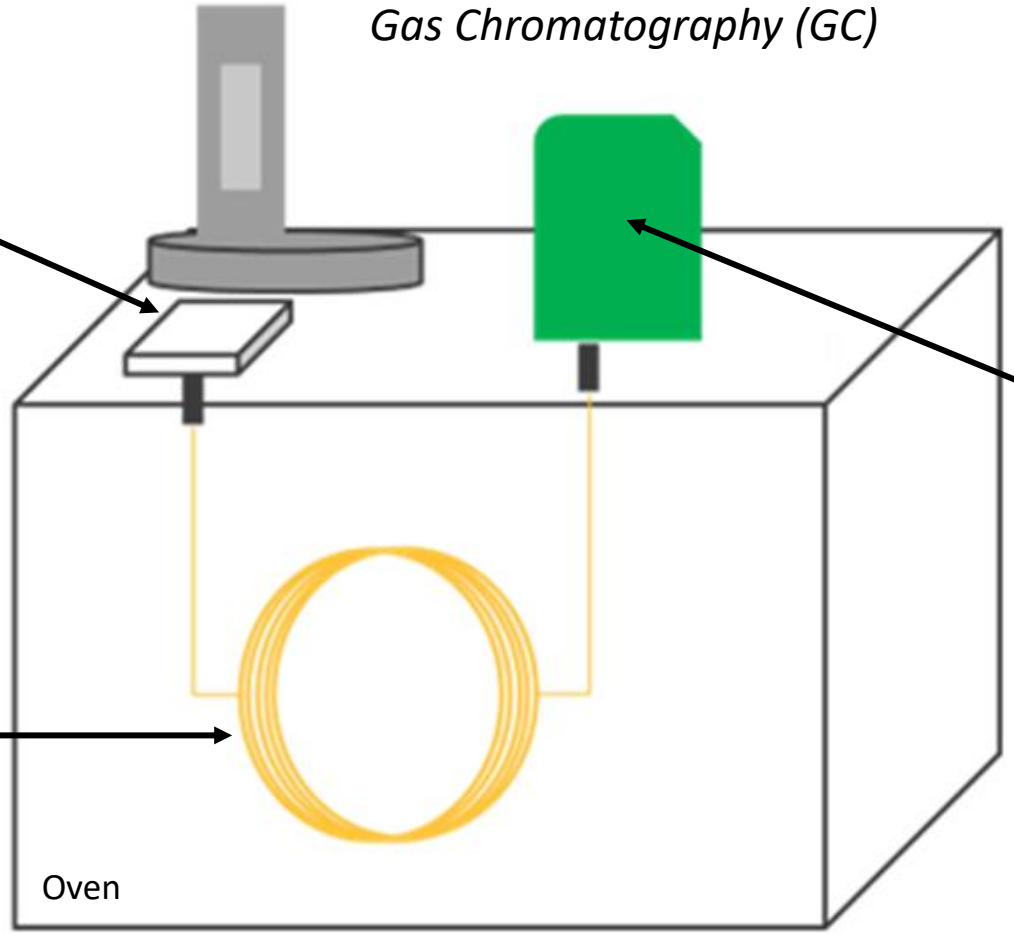
Cooled down nano-gravimetric detector to detect light molecules at ppb levels

David Sanz, Application Engineer

APIX Analytics

Gas Chromatography (GC) : key points

Gas Chromatography (GC)



1. Injector

2. Column

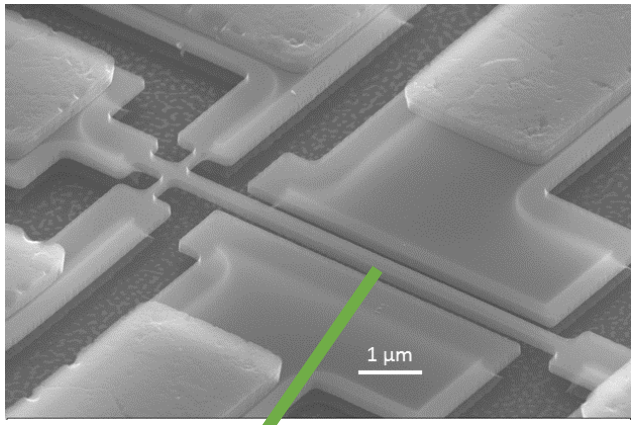
3. Detector

- FID : Flame ionization detector
- TCD : Thermal conductivity detector
- **NGD : nano-gravimetric detector**

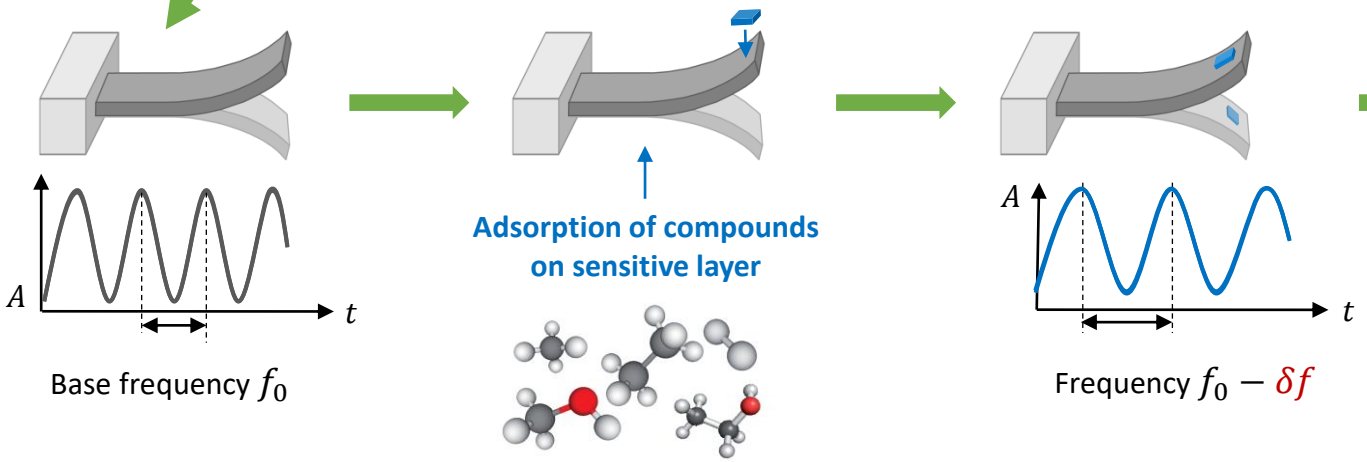
…

A unique technology: the NGD

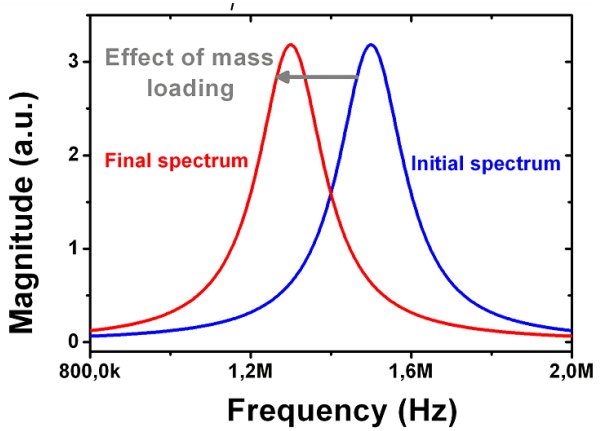
1. Resonating structure covered with a sensitive layer



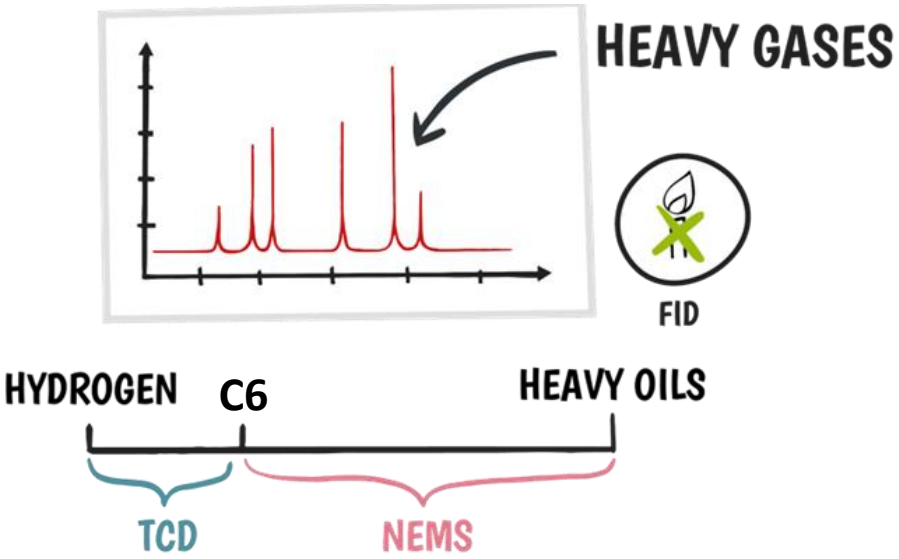
The NGD detector is a **small**, **sensitive**, **fast** and **universal** gas sensor



2. Adsorption of compounds causes resonance frequency shift



TCD-NGD coupling

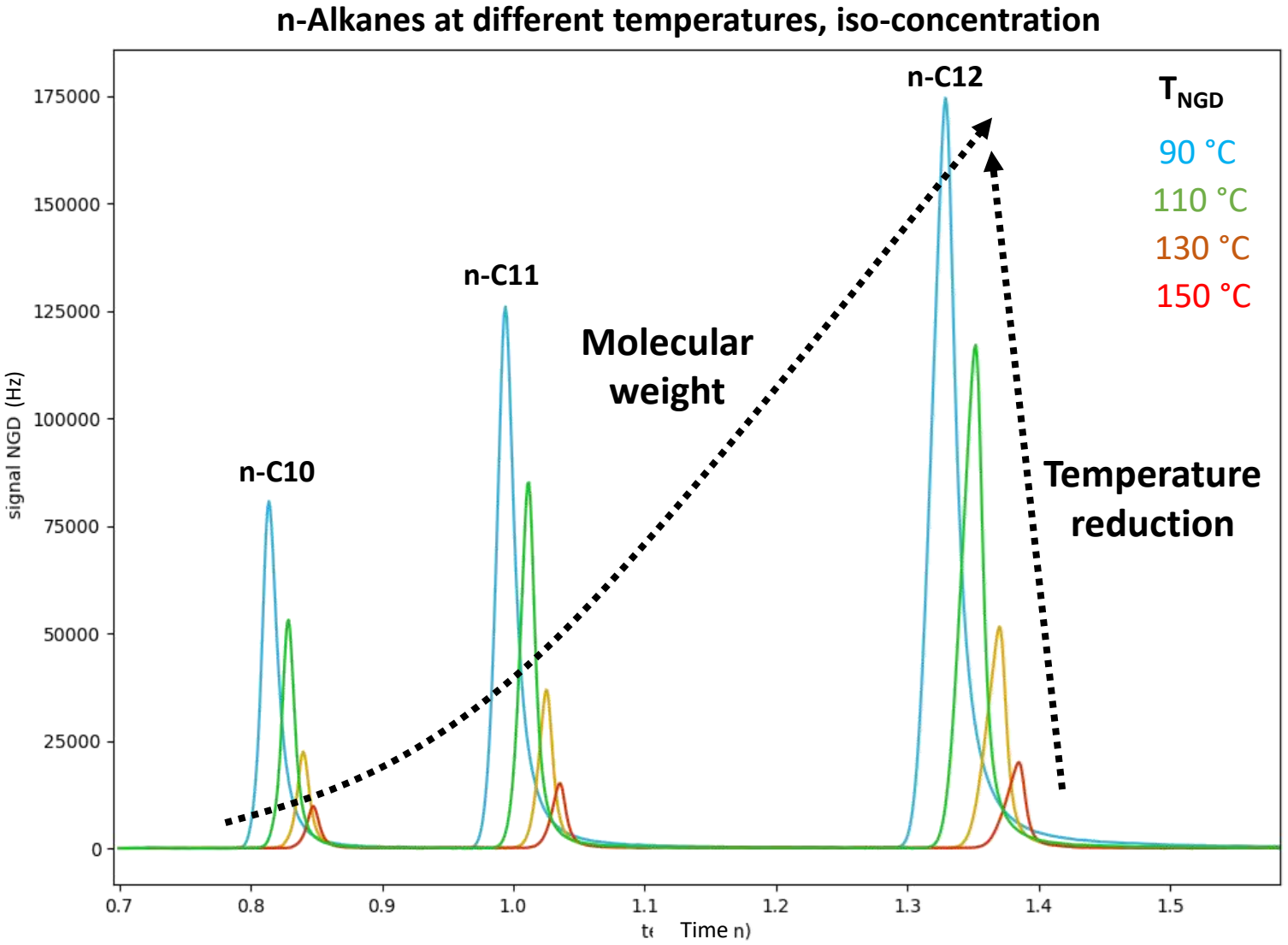


- TCD and NGD are concentration detectors, meaning they can be coupled together because they are **nondestructive**, unlike FID
- TCD is a universal detector, but can only detect **light molecules** from hydrogen to C6 (above, FID is typically used)
- Contrary to TCD, the NGD is very sensitive to **heavier compounds** (C6 to C32)
- **TCD-NGD coupling** covers a wide spectrum of analysis, from hydrogen to heavy oils, without FID

The NGD is also :

- **Insensitive** to carrier gas
- ATEX compatible (**no flame, no hydrogen**)

Sensitivity of the NGD : mass and temperature



NGD sensitivity :

- Increases exponentially with the number of carbons (**molecular weight**).
- Increases with a stronger **chemical affinity** on its surface, which increases with lower **temperatures**.

Conditions :
n-Alkanes standard, 100 µg/mL
Split/Splitless injection (1 µL)
Column : PDMS (15 m x 250 µm x 0.1 µm)
Pressure : 100 kPa (Helium)

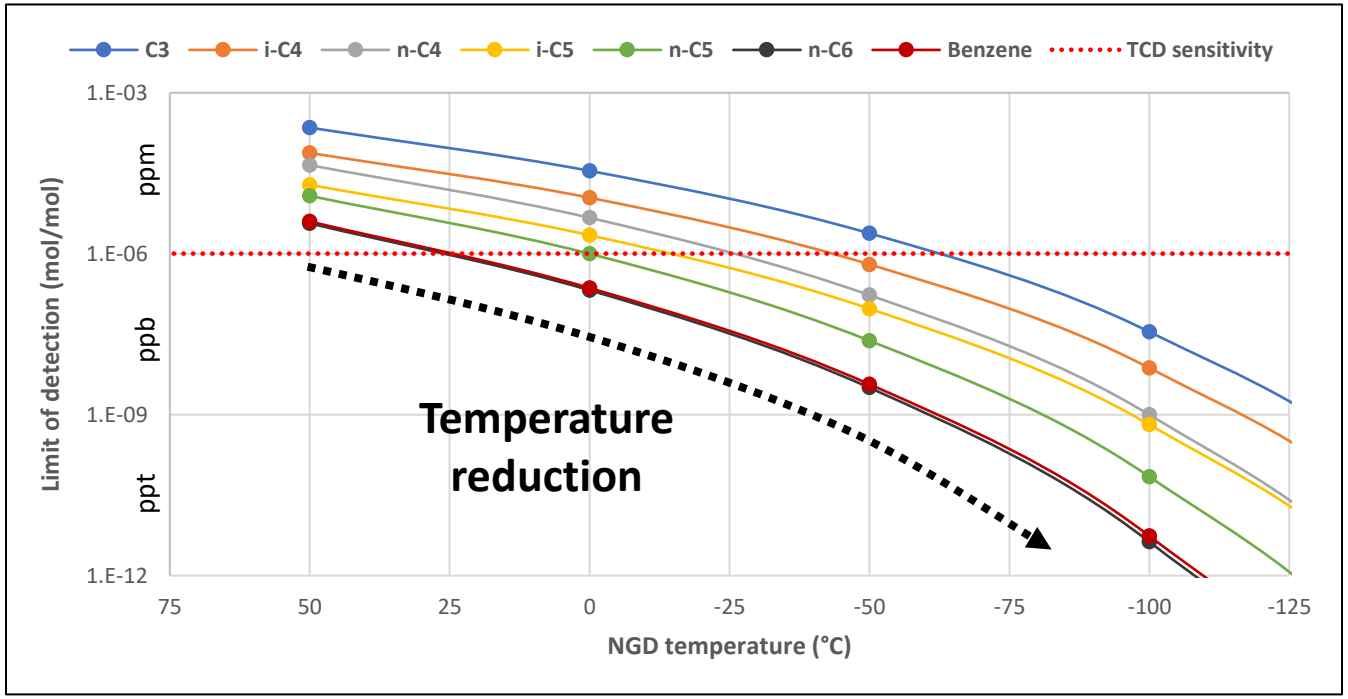
Characterization of Nano-Gravimetric-Detector Response and Application to Petroleum Fluids up to C_{34}
Laura Alonso Sobrado, Matthieu Loriau, Serge Junca, Christophe Tremaudant, Pierre Puget, Eric Colinet, and Jérôme Randon
Analytical Chemistry **2020** *92* (24), 15845-15853

Benefits of low temperatures

NGD response based on Langmuir adsorption model :

$$ln\left(\frac{A_p}{C_{inj}M_w}\right) = a + \frac{\Delta S°}{R} - \frac{1}{T}\frac{\Delta H°}{R}$$

- A_p is the peak area of the analyte
- $C_{inj}M_w$ is the mass concentration of the analyte in the injected solution
- a is a constant linked to the NGD geometry, flow and injected volume
- $\Delta H°$ is the standard enthalpy of adsorption for a given solute
- $\Delta S°$ is the standard entropy of adsorption for a given solute
- R is the universal gas constant



Limits of detection extrapolated from experiments at 50 °C

T_{NGD} (°C)	Limit of detection (ppm mol)						
	C3	i-C4	n-C4	i-C5	n-C5	n-C6	Benzene
50	223	75	45	19	12	3.7	4.0
0	35	11	4.7	2.2	1.0	**0.21**	**0.23**
-50	2.4	**0.63**	**0.17**	**0.094**	**0.024**	**0.0032**	**0.0037**
-100	**0.035**	**0.0074**	**0.001**	**6.5E-04**	**7.0E-05**	**4.3E-06**	**5.5E-06**
-150	**1.6E-05**	**2.3E-06**	**7.9E-08**	**8.0E-08**	**1.8E-09**	**2.8E-11**	**4.0E-11**
-200	**2.1E-13**	**1.2E-14**	**1.7E-17**	**4.5E-17**	**2.4E-20**	**1.4E-23**	**2.8E-23**

Cooling the NGD allows ppb (or better) levels of detection. The sensitivity of the TCD is challenged for C6 and below.

Cooled NGD chromatography test bench

Vacuum chamber with NGD

Transfer line

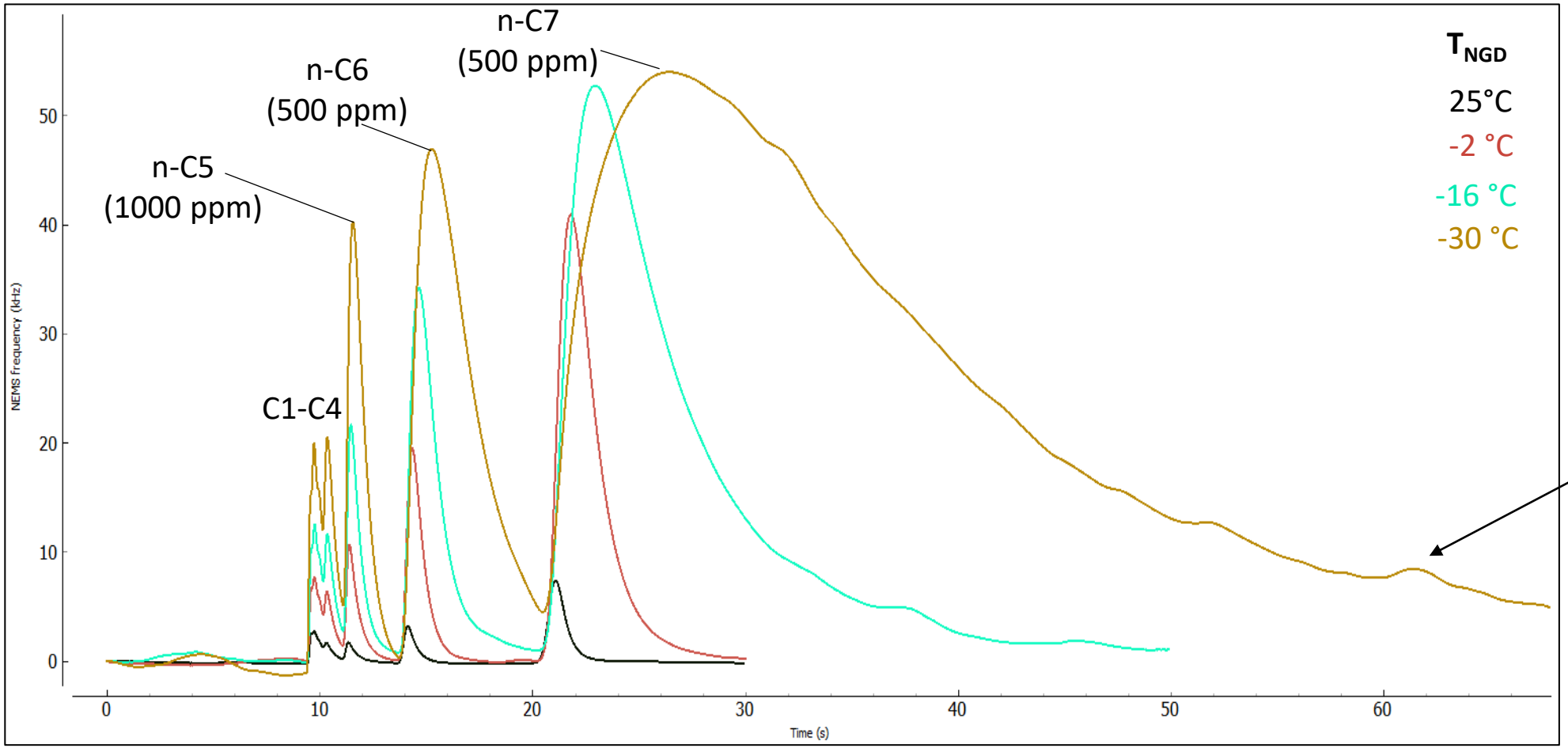
Micro GC

Stirling cooler

Cryogenic temperatures up to -140 °C (about 130 K) are achieved.

Effects of cooling the NGD

Natural gas standard



Nitrogen 5.0 :

- H2O < 3 ppmV
- CnHm < 0.5 ppmV

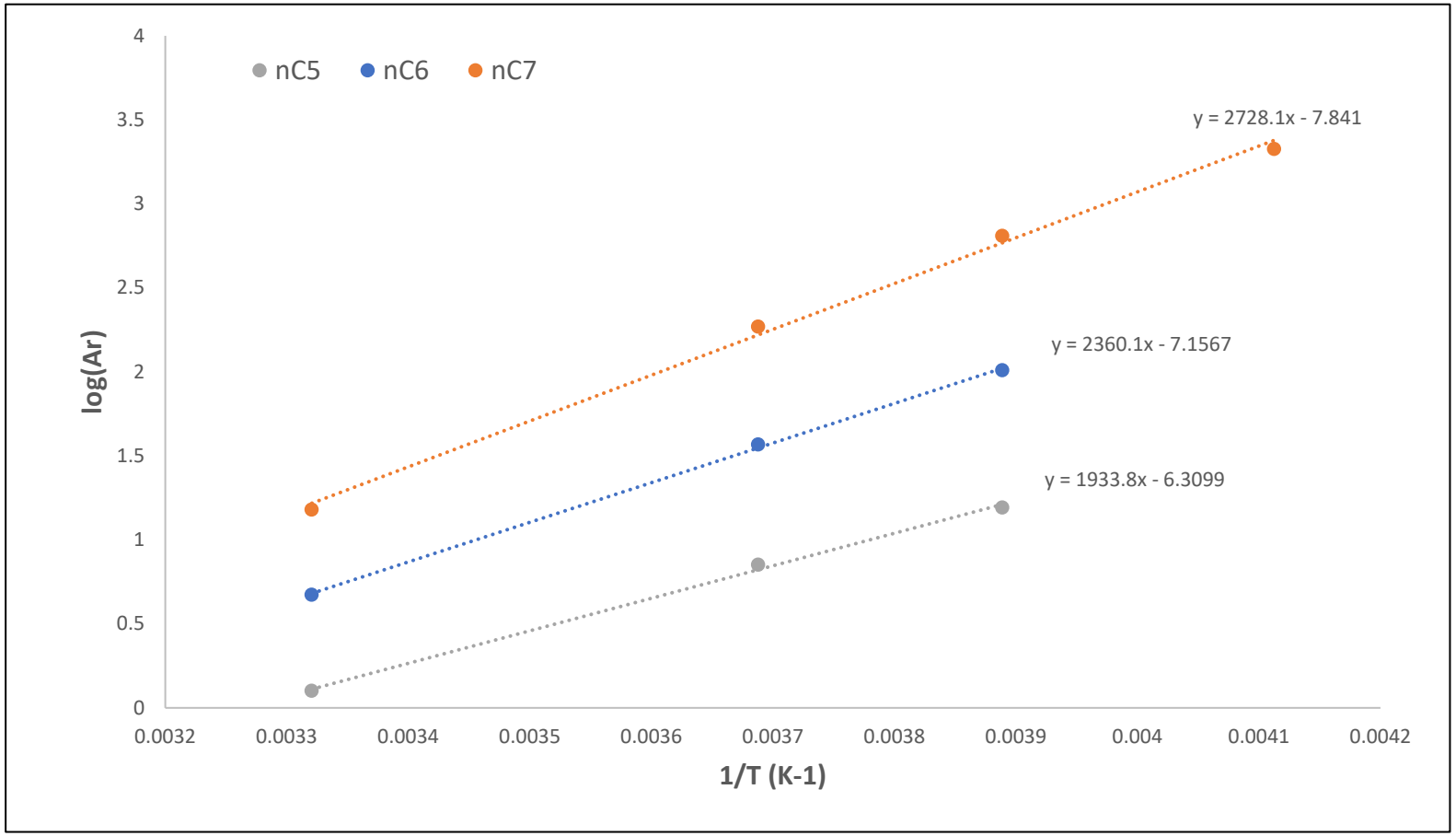
Noisy baseline (carrier gas impurities)

Conditions :
Column : PDMS (15 m x 250 µm x 0.25 µm)
Pressure : 300 kPa (Nitrogen)
Gas injection (10 µL)
GC temperature : 40 °C
NGD temperature : Variable

- **Sensitivity is improved, but…**
- **Peaks are broadened due to higher residency time in the detector**
- **Noisy baseline related to carrier gas purity**
- **Requirement to find a middle ground between great sensitivity and saturation**

Fitting of experimental cold NGD data

Normalized area models as a function of 1/T



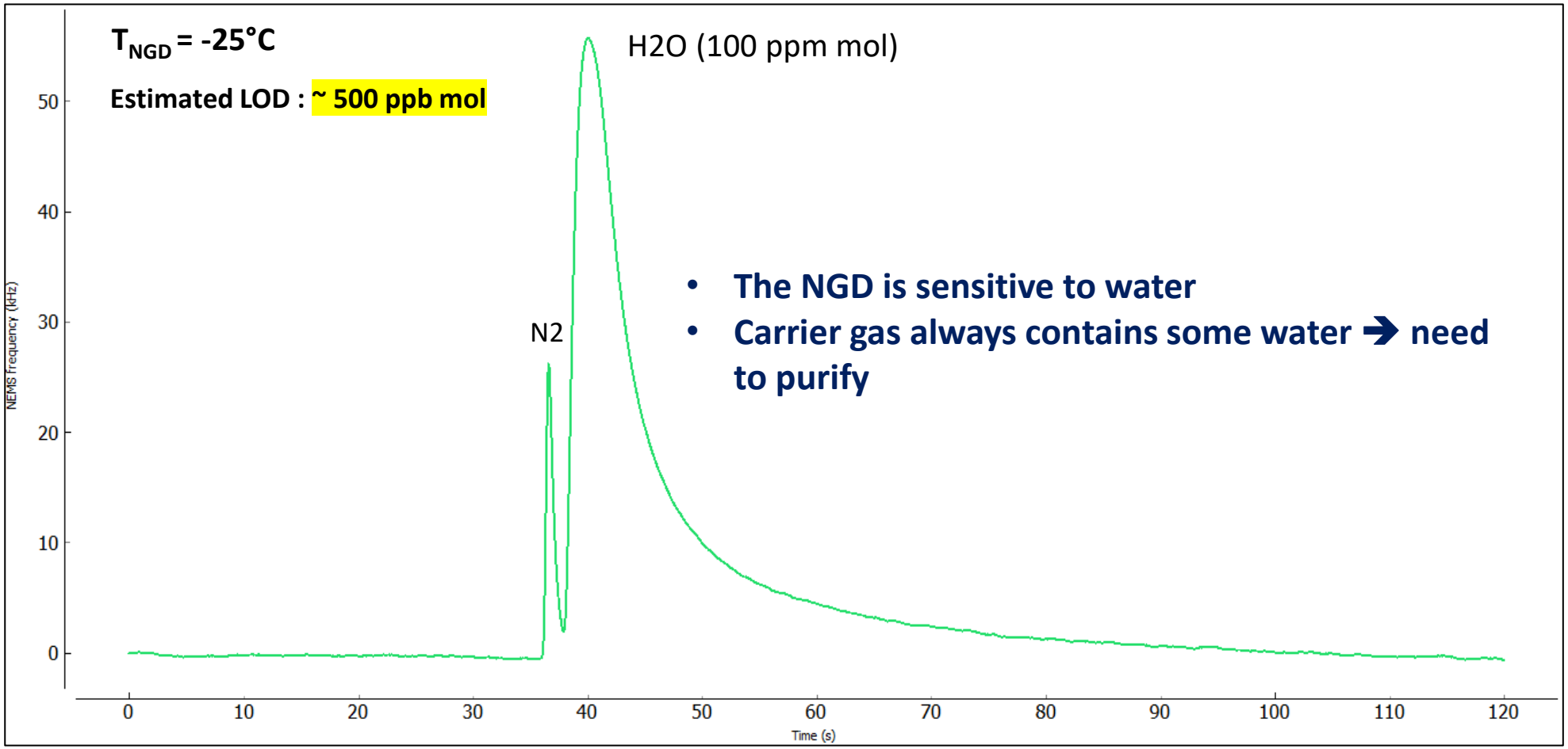
Reminder :

$$ln\left(\frac{A_p}{C_{inj}M_w}\right) = a + \frac{\Delta S°}{R} - \frac{1}{T}\frac{\Delta H°}{R}$$

Experimental data at sub-ambient temperatures fits the NGD response model.

H2O sensitivity

Water in N2 standard



- **The NGD is sensitive to water**
- **Carrier gas always contains some water ➔ need to purify**

Conditions :
Column : PDMS (15 m x 250 µm x 0.25 µm)
Pressure : 150 kPa (Nitrogen)
Gas injection (10 µL)
GC temperature : 40 °C
NGD temperature : -25 °C

High-purity gas filter

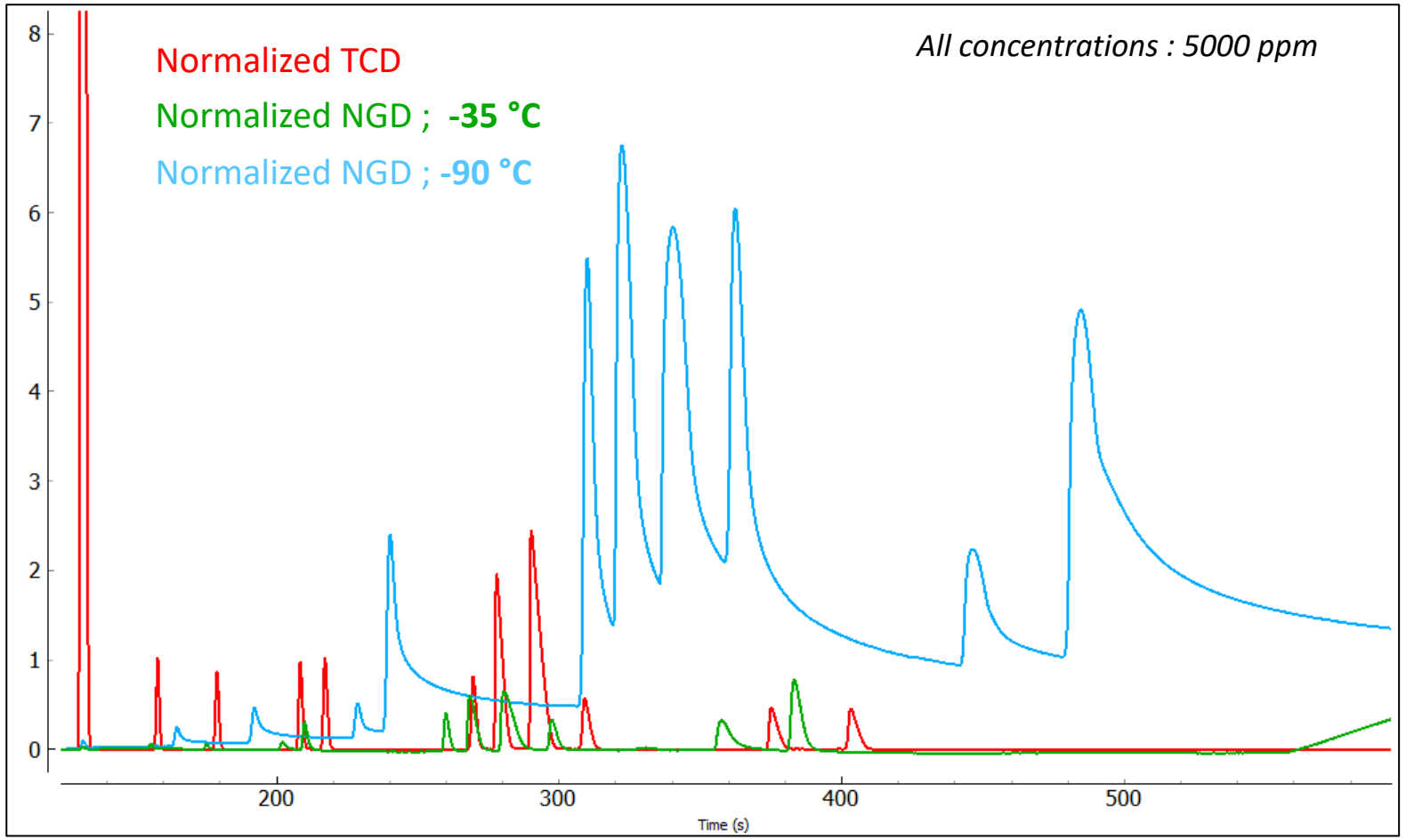
Helium 6.0 :
- H2O < 500 ppbV
- CnHm < 50 ppbV

GateKeeper® Gas Purifiers

High-purity Helium :
- H2O < 100 pptV
- CnHm < 100 pptV

TCD vs. cooled NGD with ultra-pure carrier gas

Refinery gas standard (alkenes)



C2-C3 | C4 isomers | C5 isomers

* Retention time shift due to chromatography effects

Helium 6.0 + high-purity filter :

- H2O < 100 pptV
- CnHM < 100 pptV

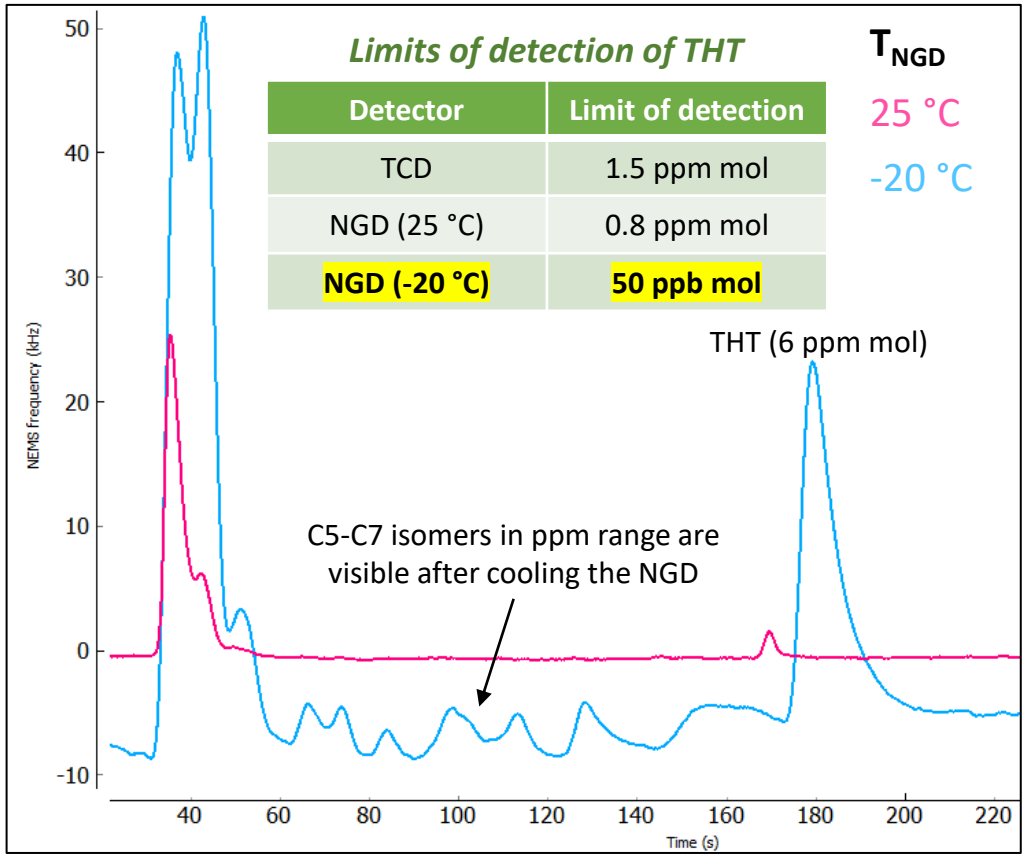
- **Highly pure carrier gas allows even lower temperatures to be reached without noisy baselines**
- **By cooling the NGD enough, it surpasses the sensitivity of the TCD in the C4-C5 range and approaches it in the C2-C3 range**

Conditions :
Column : Alumina (30 m x 250 µm x 4 µm)
Pressure : 150 kPa (ultra-pure Helium)
Gas injection (2 µL)
GC temperature : 120 °C
TCD Temperature : 50 °C
NGD temperature : Variable

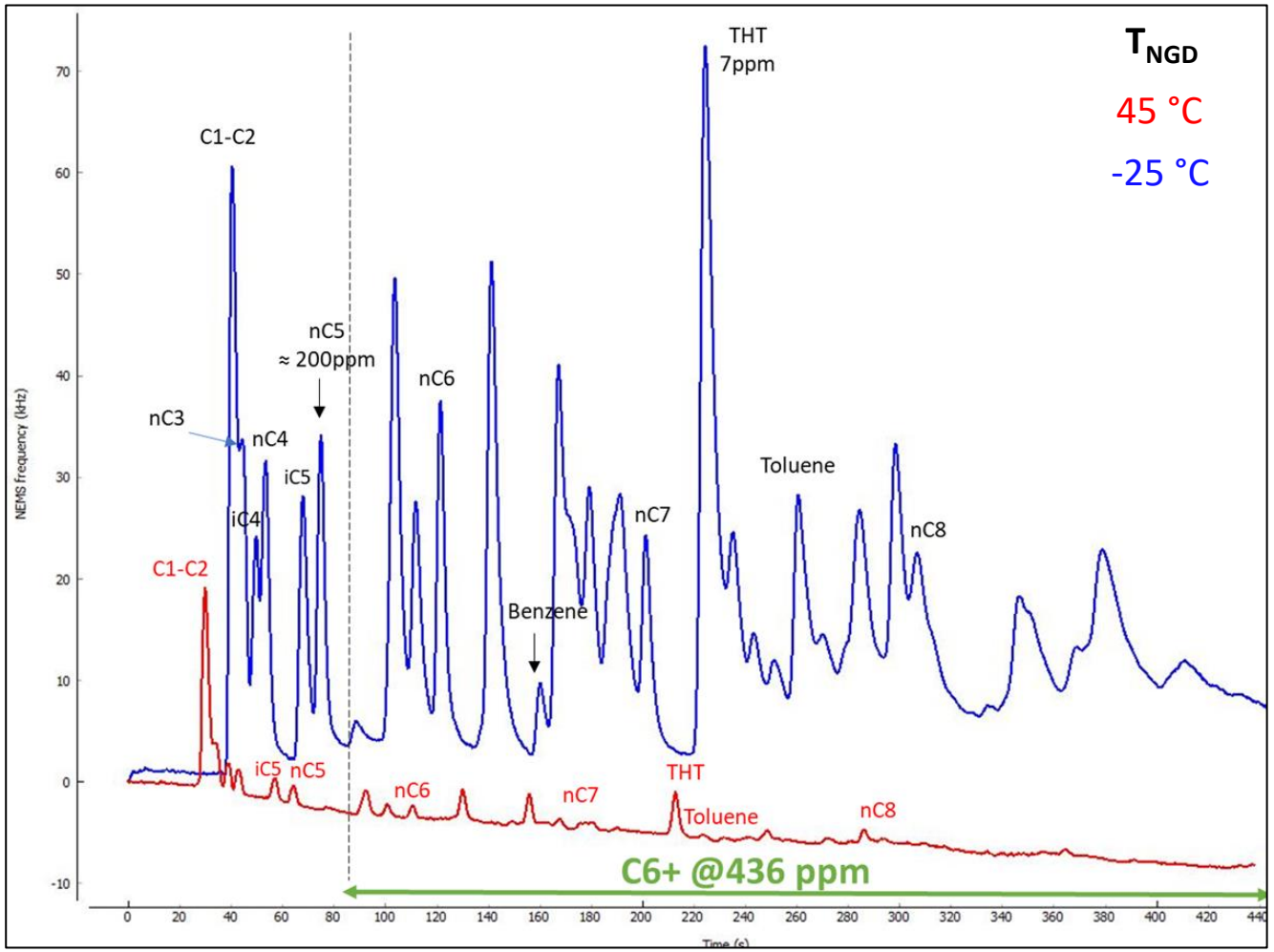
Focus on natural gas and THT

Conditions :
Column : PDMS (15 m x 250 µm x 0.25 µm)
Pressure : 300 kPa (Helium)
Gas injection (10 µL)
GC temperature : 70 °C (0.5 min), 170 °C at 10 °C/min (10 min)
NGD temperature : Variable

Light natural gas stream (city network)

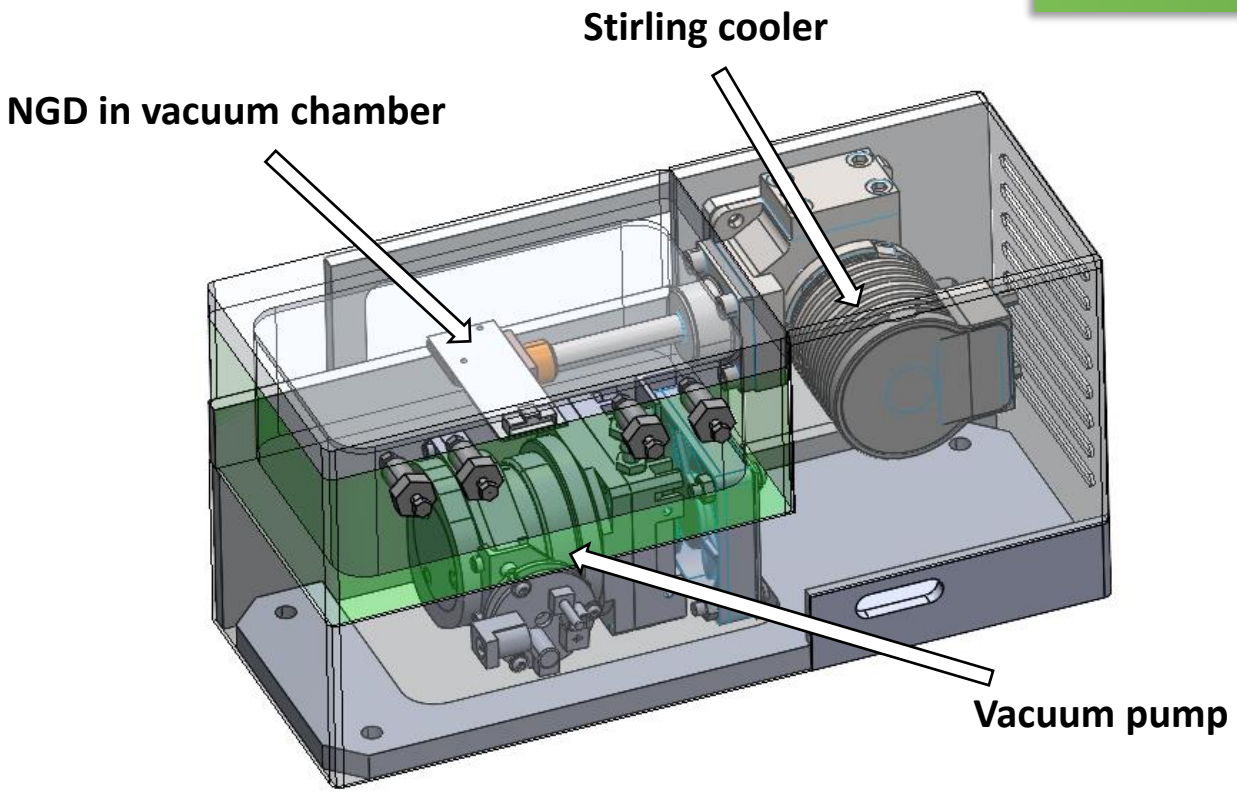


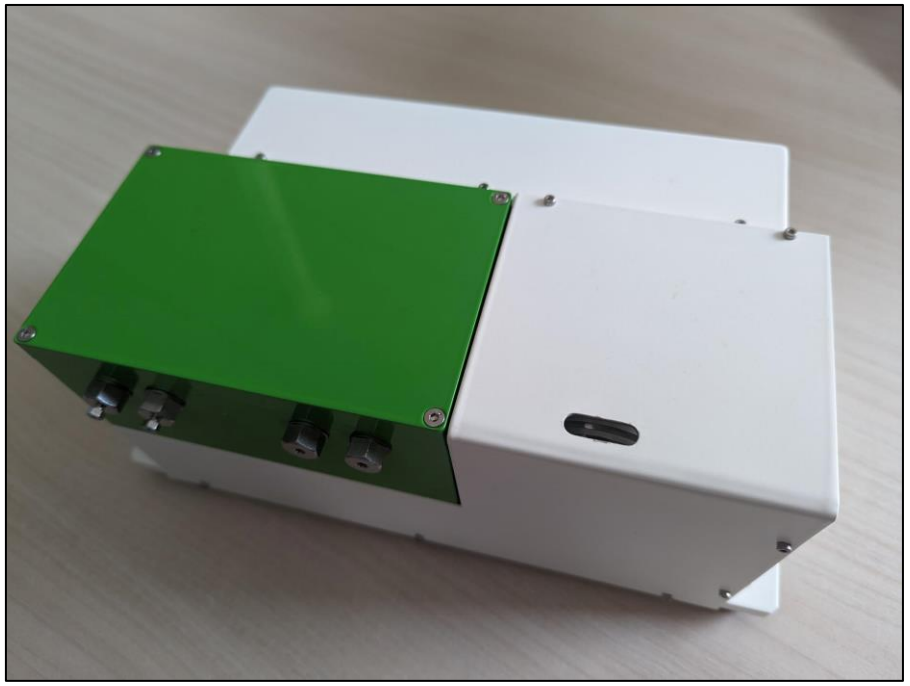
Heavy natural gas stream (city network)



- **Cooling the NGD down to -20 °C allows detecting THT at 50 ppb**
- **Under the right conditions, calorific value (BTU) measurement with N2 carrier gas is possible**

Towards compact cooled NGD system



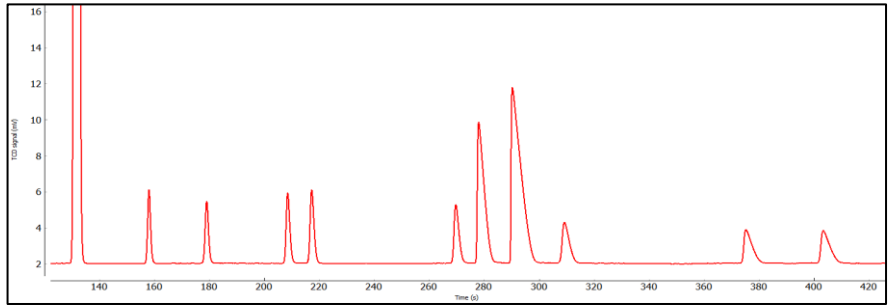


- Standalone compact system with an integrated pump, cooler, and electronics for data acquisition
- Runs on 24V DC
- Cryogenic temperatures up to -100 °C are achieved (about 170 K)
- Can be coupled with any GC

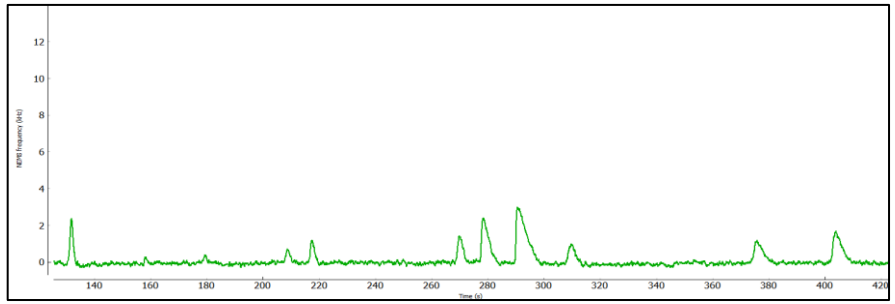
GC-NGD/TCD coupled with standalone cooled NGD

3 detectors in a single system

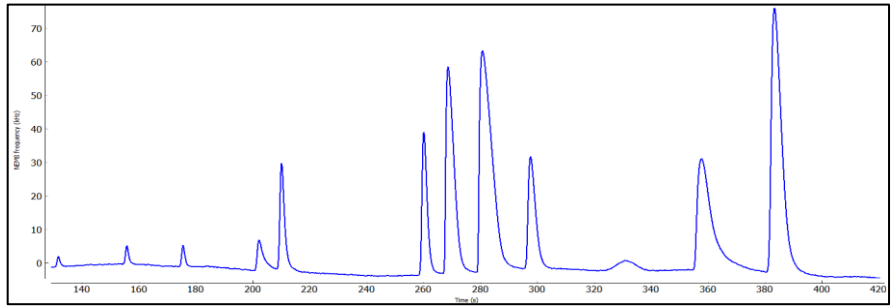
TCD



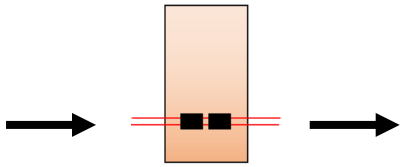
NGD



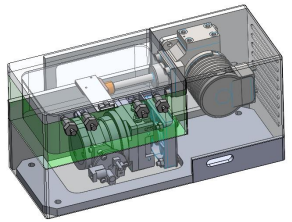
Cold NGD



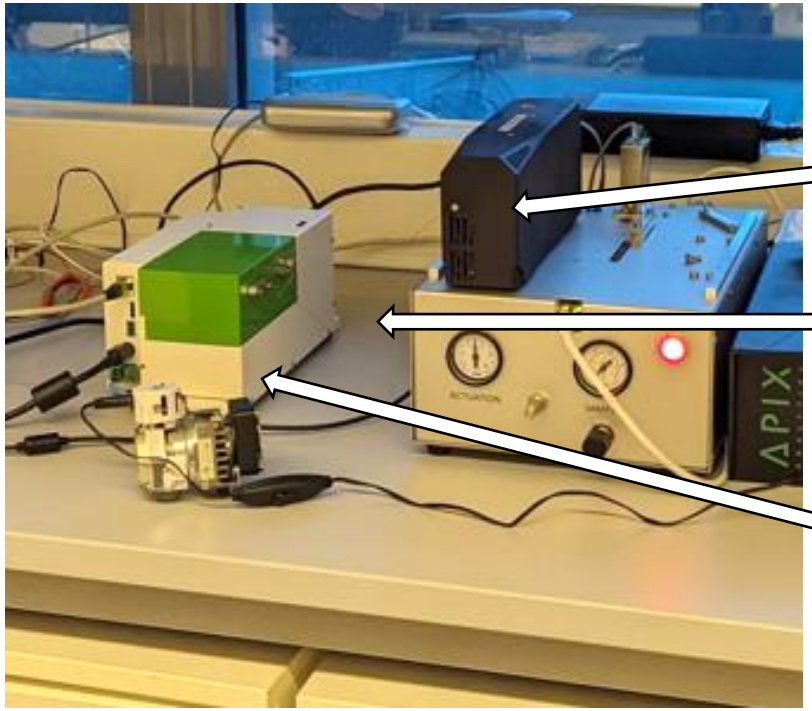
µGC



TCD/NGD dual detection



Cooled NGD



µGC with NGD/TCD dual detection (or any GC)

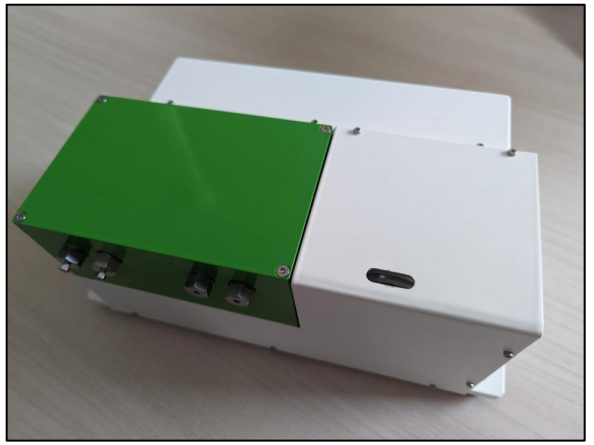
Transfer line

Standalone cooled NGD

Example installation in partnership with CNRS and ISA (Institut des Sciences Analytiques) in Lyon

Conclusions and perspectives

- Preliminary development shows that the NGD's sensitivity is greatly improved by cryogenic cooling, allowing ppb level limits of detection to be reached for light compounds.
- Experimental data at low levels of cold match the theory, but extreme limits of detection currently seem to be limited by other factors, such as carrier gas purity, condensation effects and peak tailing.
- Stability of the chromatography system (retention times) at high levels of cold was achieved by using ultra-pure carrier gas filters.
- When cold enough, performance can match the TCD, with the advantage of being insensitive to carrier gas
- Calorific value (BTU) measurement with cold NGD and Nitrogen carrier gas is possible.
- A compact, standalone system is available that can be coupled to any GC.



Thank you

Come see us at booth 4E45 !