Introduction to gas analysis
BiofuelsGS
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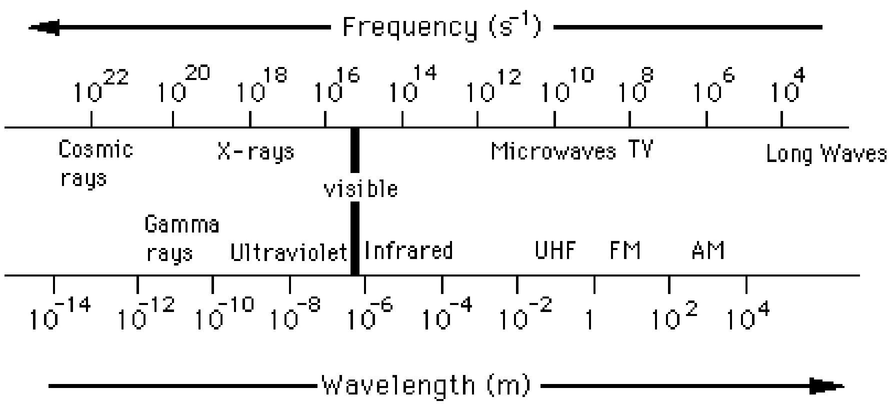
2004-20??

Measurement of gas compounds

- Principle of FTIR measurement
- Calibration of FTIR
- Principle of GC measurement
- Calibration of GC

FTIR spectroscopy

FTIR spectroscopy is an analytical method based on the interactions between IR light and matter.



The light spectra

Molecular Energy State

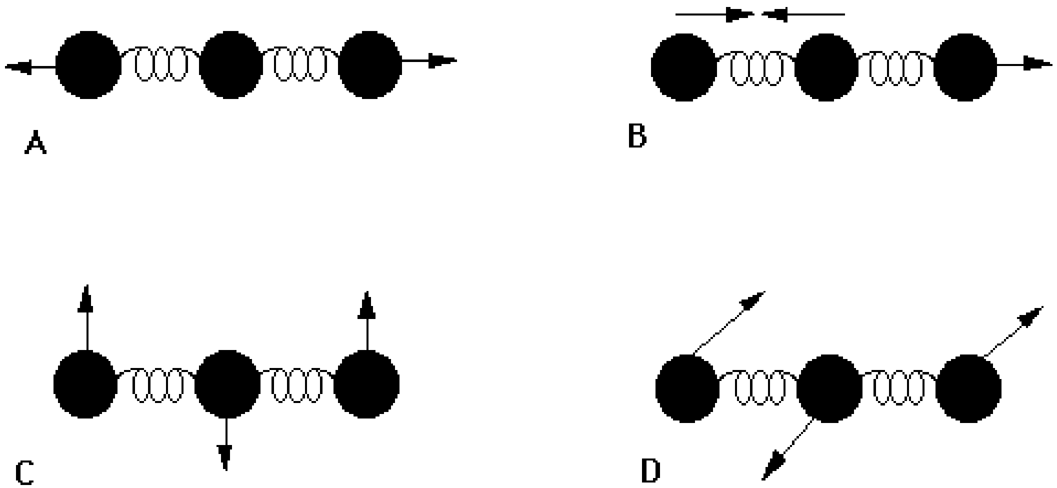
The energy state of a molecule can be written as:

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

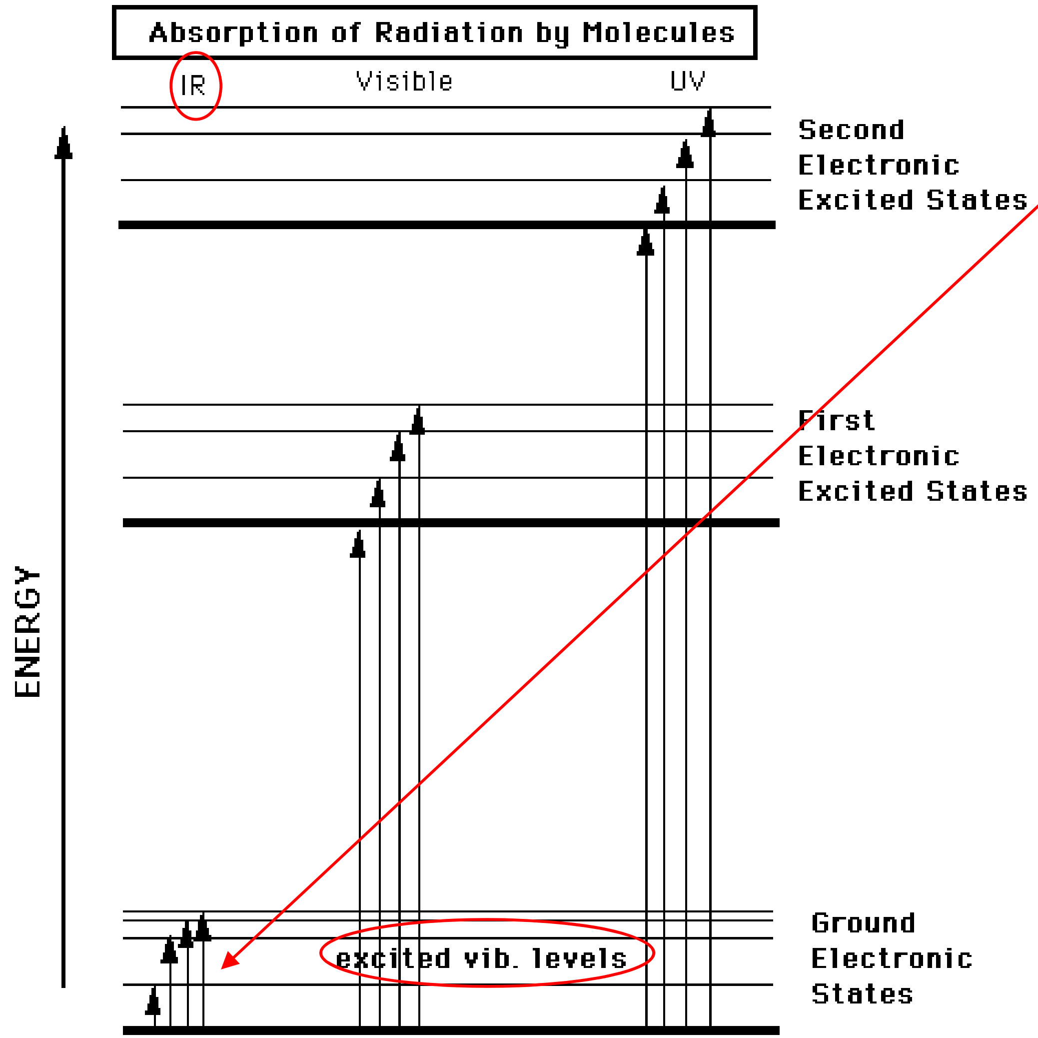
IR spectroscopy

Vibrational spectroscopy

CO_2 vibration modes:



How are IR light and molecules interacting?



IR light absorbed

Excitation of the molecule

- Absorption of IR light by a molecule follow rules
- Absorption of IR energy at characteristic frequencies (resonant frequencies)
- Energy expression:

$$E = (n + 1/2)h\nu$$

Transitions are *quantified*

FTIR spectroscopy

- Only the vibrational transitions inducing a change in the dipole moment of the molecule will be ”IR active” (visible during FTIR spectroscopy)

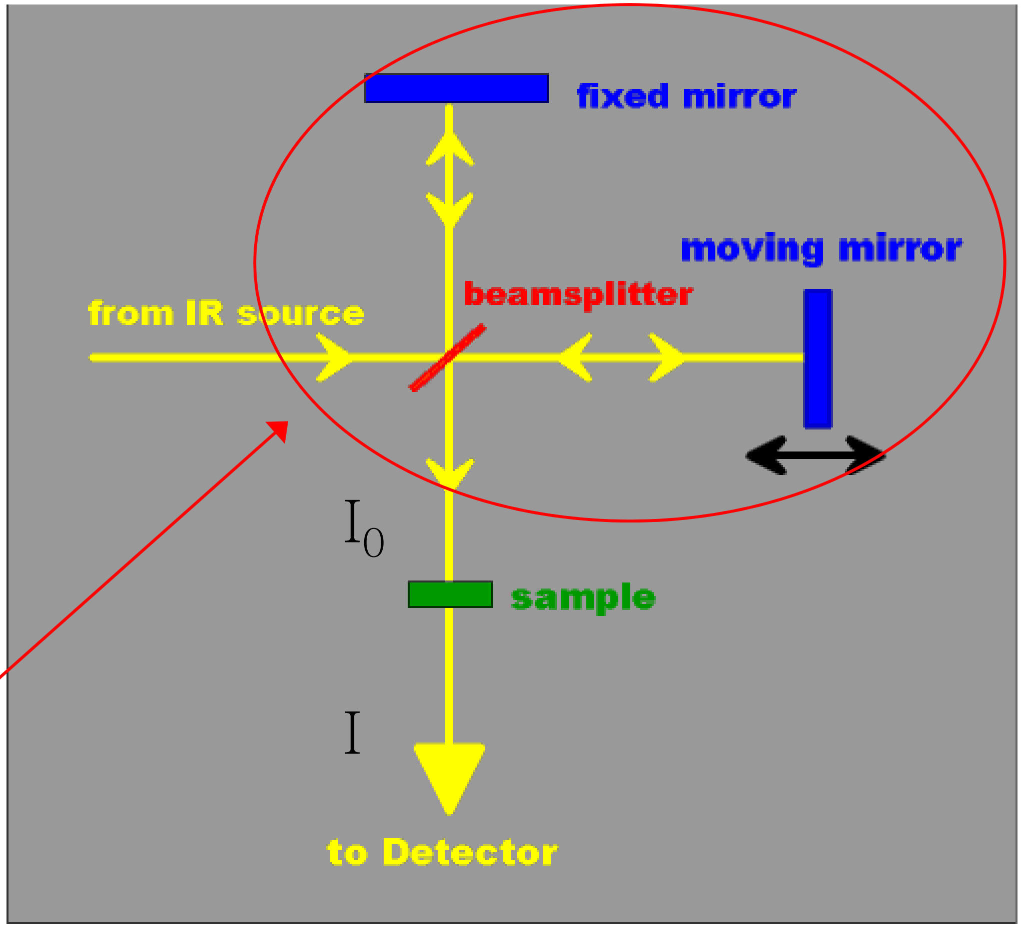
>>> Mononuclear molecules (Ar, Ne...) and symmetrical molecules (O_2, N_2...) will not be detectable by FTIR

- Absorption pattern (frequencies absorbed and intensity of the absorption) is unique for a given molecule

>>> Qualitative analysis is possible

>>> Quantitative analysis is possible

FTIR spectrometer: the interferometer



From IR radiation with many waves to a single wave varying over time (interferogram)

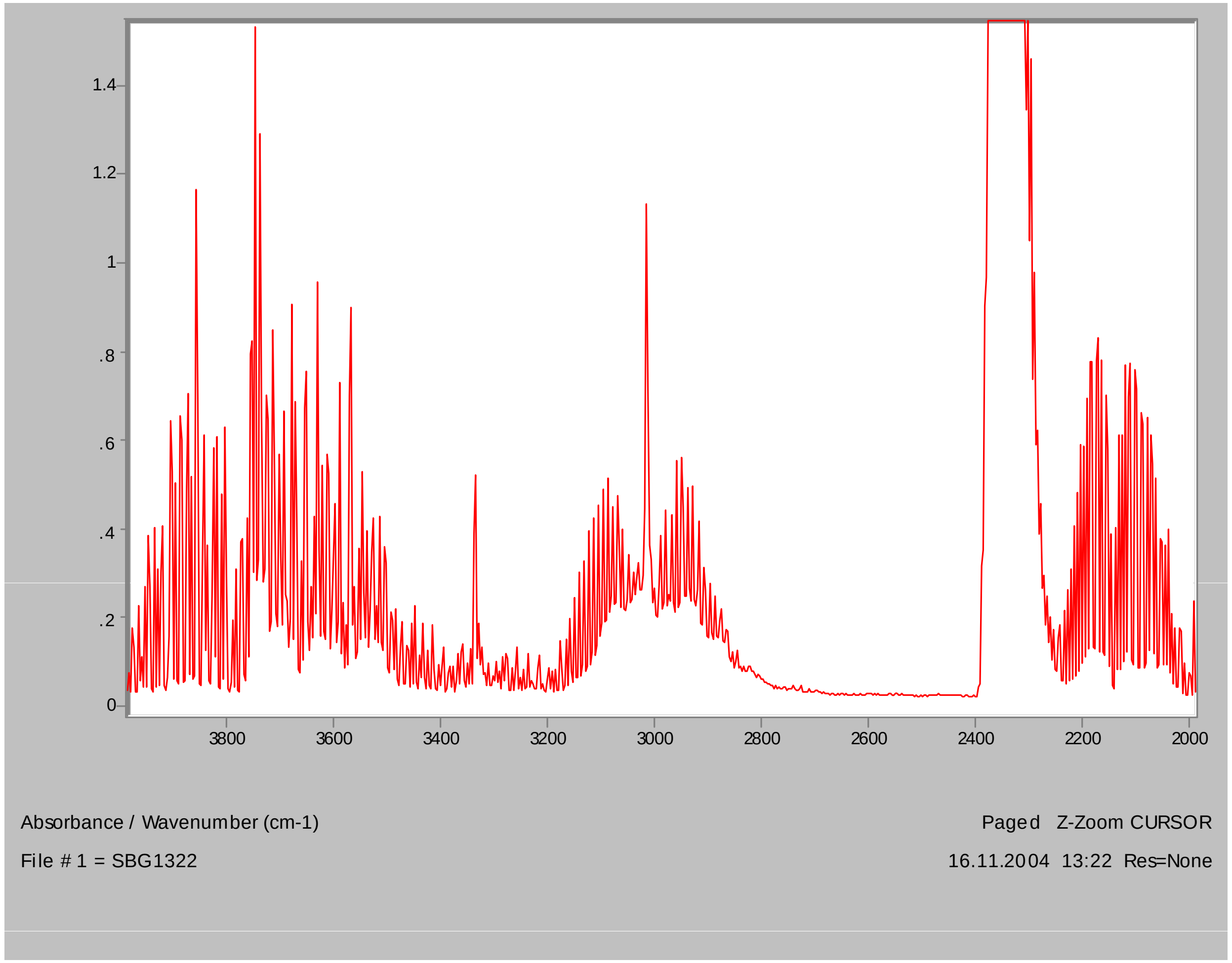
>>> FTIR can analyse all frequencies simultaneously!

FTIR spectrometer: the other components

- The IR source: IR lamp (spectral region 2.5 to 10 µm)
  - Visible range is under 1 µm
- The interferometer: modulation of the IR light
- The sample cell: 2 heated cells depending on the application
- The detectors: DTGS (Deuterated Triglycine Sulfate)
  MCT (Mercury Cadmium Telluride)
- The Fourier Transform $f(t) = \mathcal{F}^{-1}(F)(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} \, d\omega.$

Interferogram >>>IR spectrum

IR spectrum and some notions



Absorbance:

$A = \log_{10} (I_0/I)$

Wavenumber:

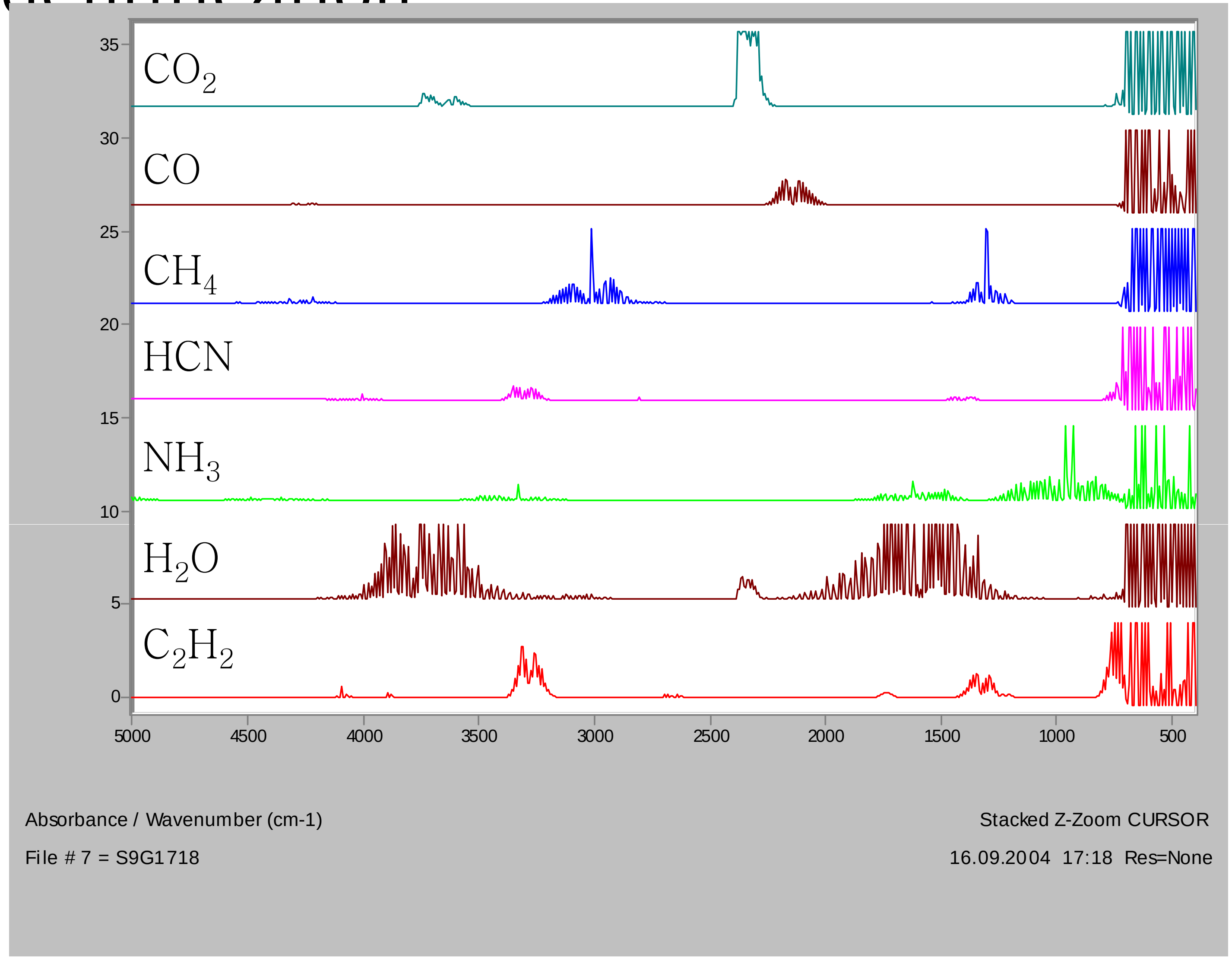
1 / wavelength

Transmittance:

$T = I / I_0$

Absorbance (no unit) against wavenumber (cm^{-1})

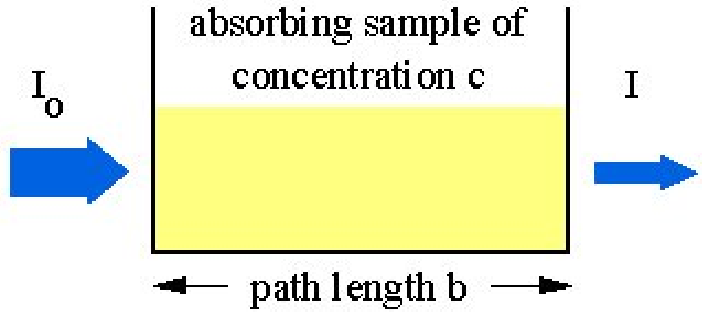
What can we get from a spectrum? Identification



What can we get from a spectrum? Quantification

The Beer-Lambert law is the linear relationship between absorbance and concentration of an absorbing species:

$A = \varepsilon * b * c$



A: absorbance

T: transmittance; λ: wavelength

$A = \log_{10} (I_0/I)$

$A = \log_{10} (1/T)$; $A = \log_{10} (100/\%T)$

$T = I/I_0$

b: the path length of the sample, that is to say the distance the light has to perform through the sample

c: concentration of the sample

ε is the extinction coefficient (absorptivity coefficient)

ε is substance-specific and function of the wavelength

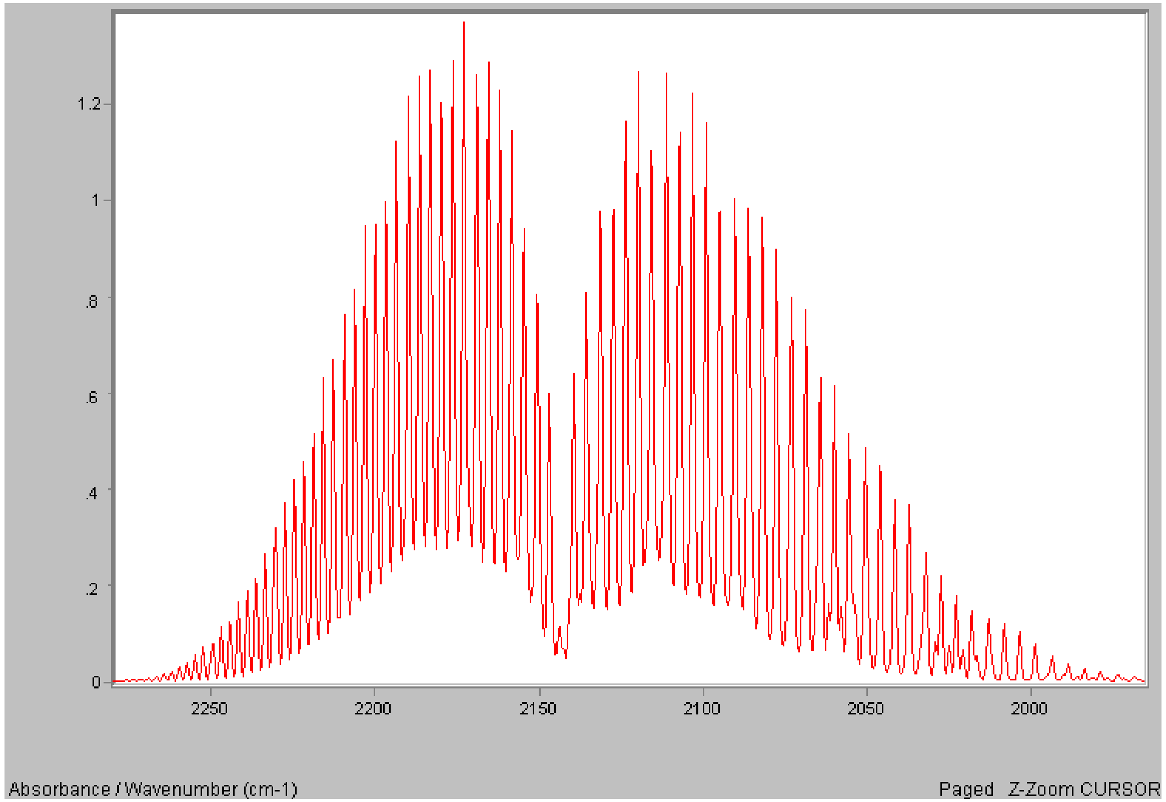
>>> Possible to build calibration curves

Our FTIR – BOMEM-9100

Data treatment from FTIR:

How to built a calibration method

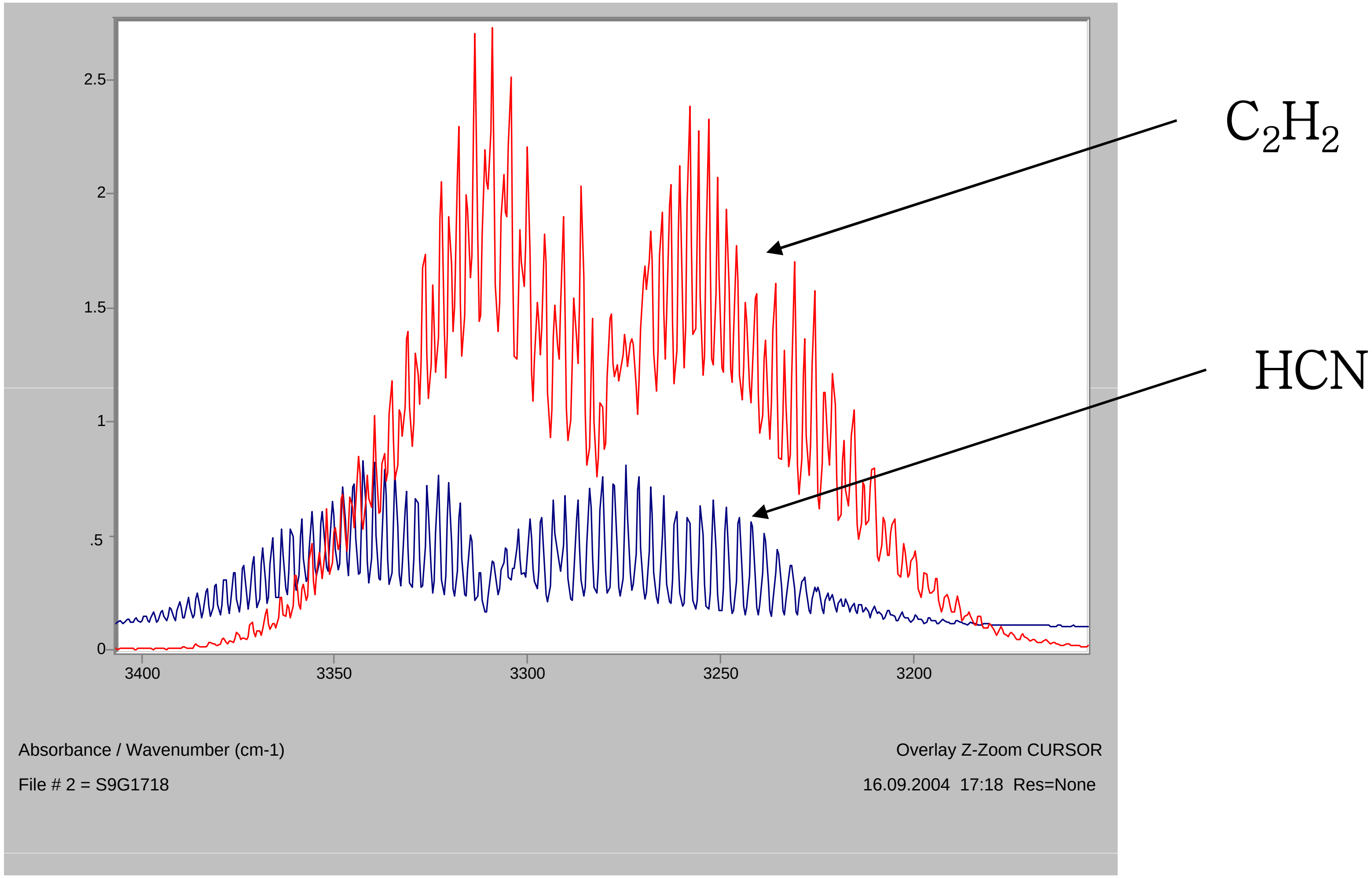
1. List of main expected compounds
2. Recording of single-compound spectra of all the expected compounds



Spectrum of CO at 1.21%

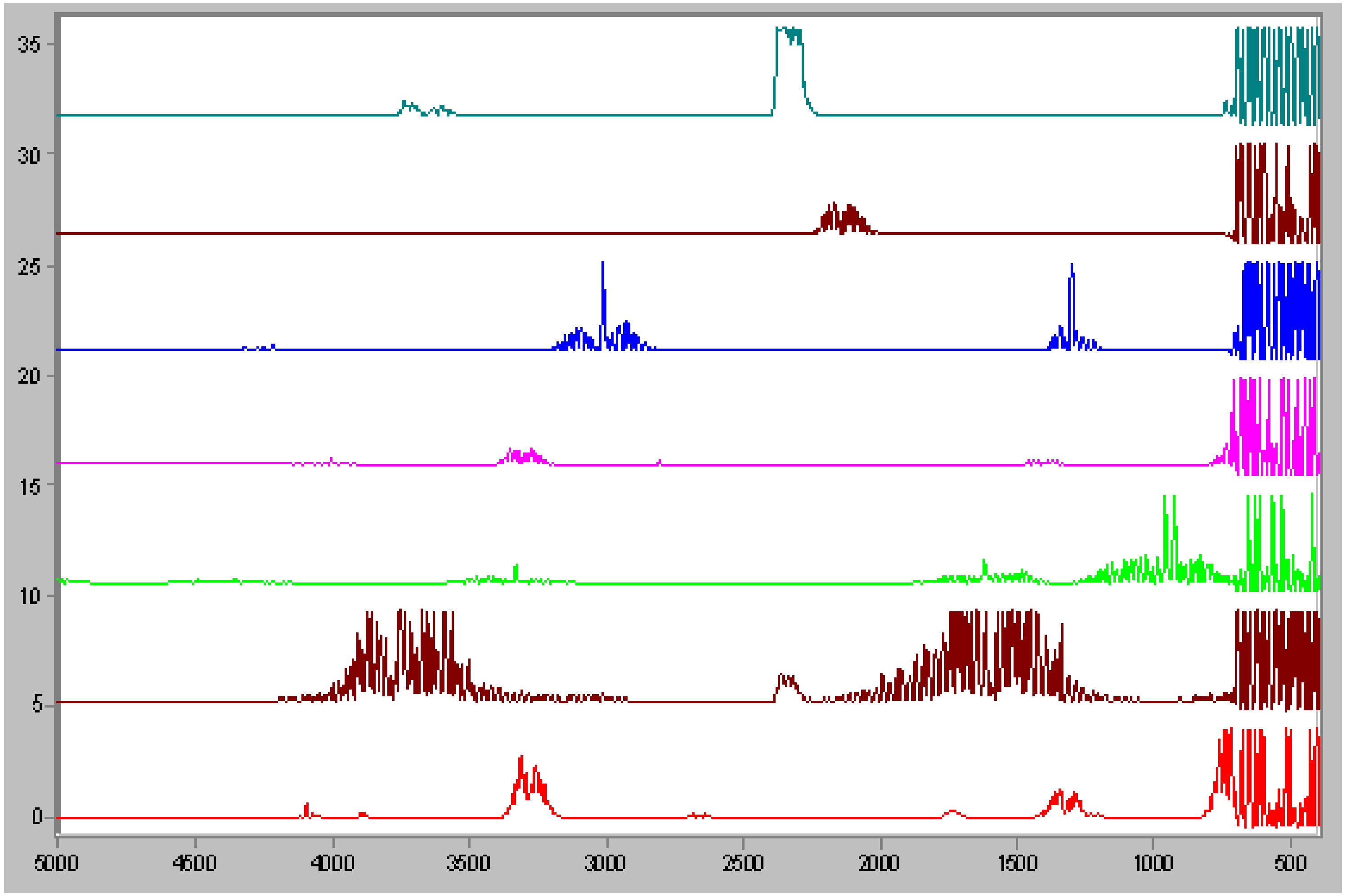
Data treatment from FTIR

3. Check for overlapping/interferences between the various compounds



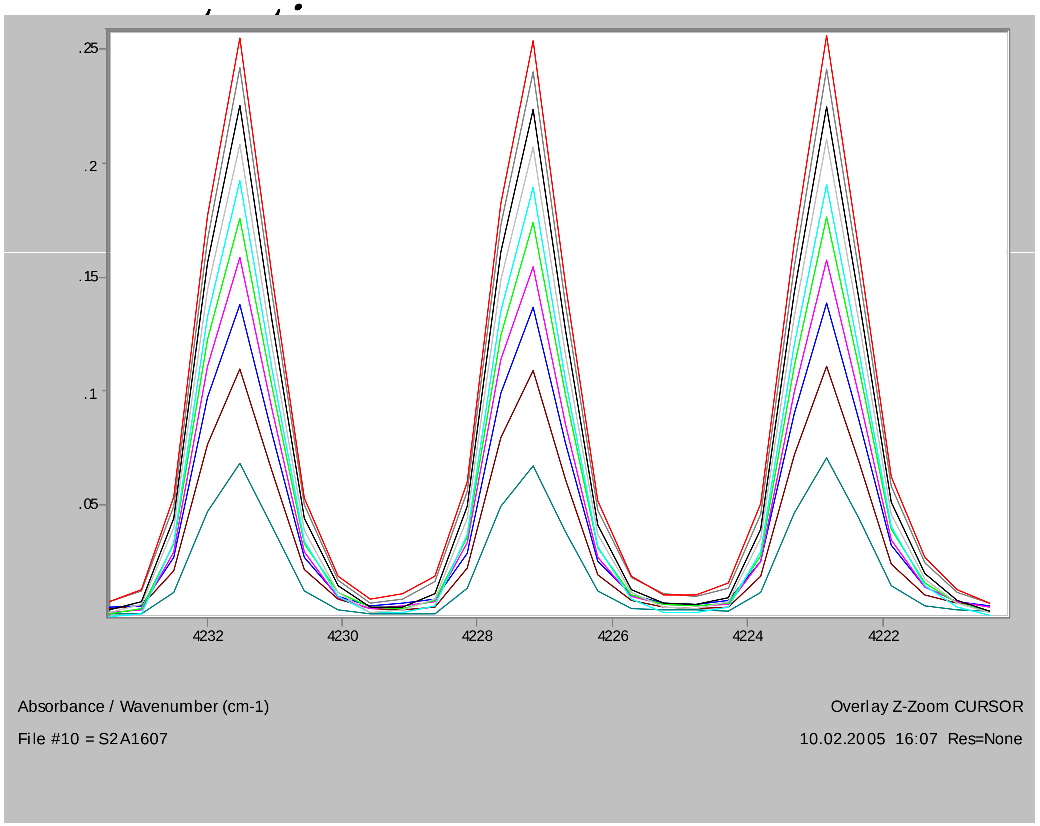
Data treatment from FTIR

4. Choice of wavenumber window where no interferences/overlapping are taking place => Only one compound is absorbing



Data treatment from FTIR

5. Recording single-compound spectra at various concentrations (highly pure calibration gases are needed). A sufficient number of calibration points (10 typically) over the whole working range are essential as the *Beer-Lambert law is not applicable at all concentrations*



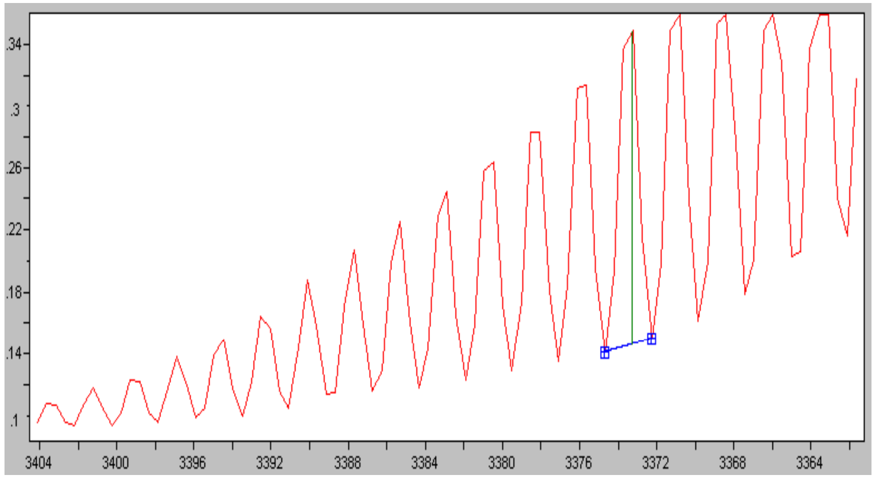
10 CO spectra ranging from 1.21 to 12.1%

Non-linearity is obvious

Obtained with a gas mixing/dilution rigg

Data treatment from FTIR

6. Recording of height of area of the selected peak(s) at the 10 concentrations



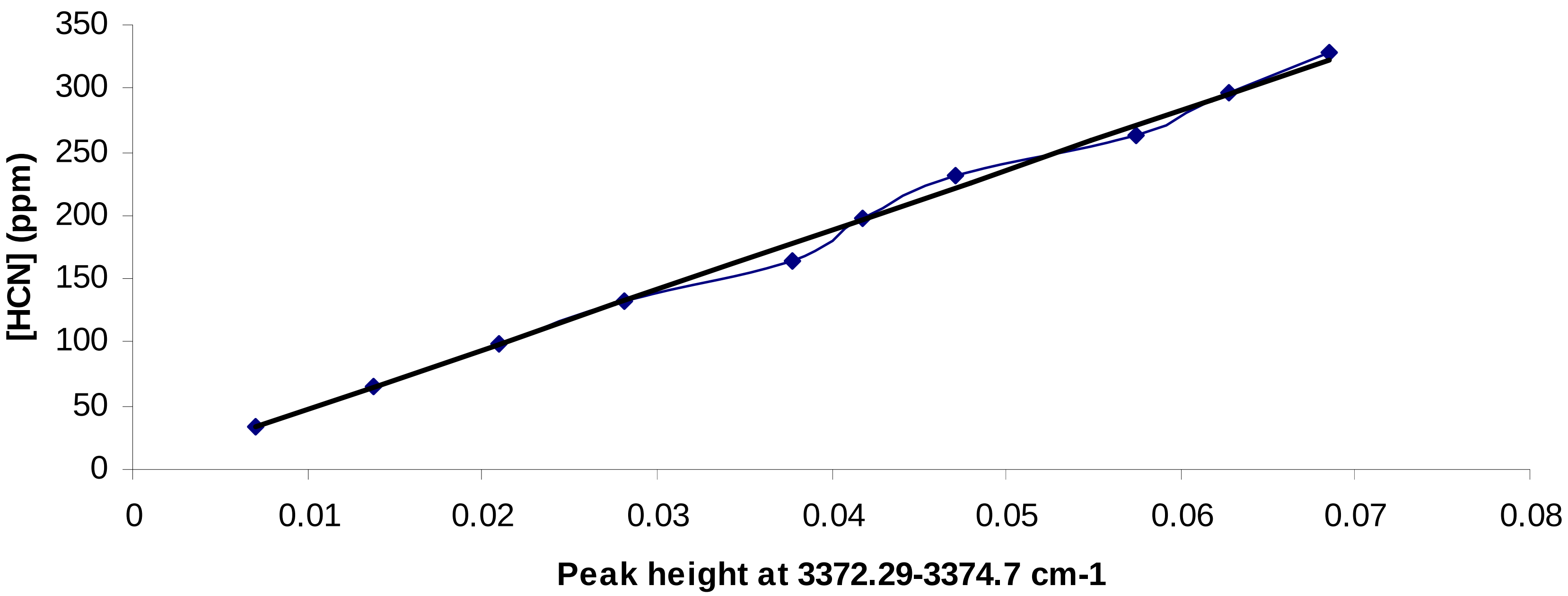
HCN: integration at 3374.7-3372.29 cm^{-1}

Our FTIR was calibrated for CO_2, CO, CH_4, C_2H_2, C_2H_4, NH_3 and HCN (pyrolysis conditions)

HCN (ppm)	area (3374.7-3372.29)	height (3374.7-3372.29)
198.637	0.0466047	0.0432997
396.96	0.0855833	0.080354
598.217	0.1172635	0.1107985
795.868	0.1437002	0.1360621
995.022	0.1657423	0.1577897
1194.349	0.1852855	0.1766663
1393.317	0.2033962	0.1944675
1593.039	0.2179309	0.2093923
1791.845	0.2295173	0.2209288
1990	0.2459953	0.2367647

Data treatment from FTIR

Example: HCN "low range"

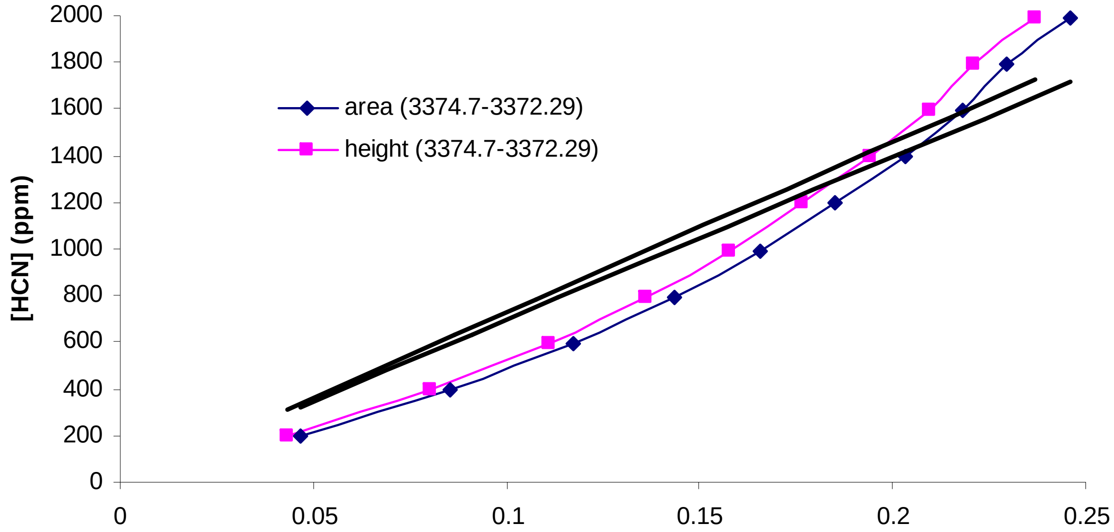


Linear relationship! Beer-Lambert law applicable

Data treatment from FTIR

HCN "high range"

Non-linearity!



The linearity of the Beer-Lambert law is limited by chemical and instrumental factors.

The most common causes of non-linearity are, amongst others:

- Deviations in extinction coefficients at high concentrations due to interactions between molecules in close proximity
- Scattering of light due to particulates in the sample
- Fluorescence or phosphorescence of the sample

Data treatment from FTIR

- After this calibrations, it is now time to treat the experimental results as described here:

1. Run a successful experiment

2. Collect the raw spectra recorded by the FTIR

3. With the help of the FTIR software, measure the height and area of the selected peak(s)

4. Using the calibration curve (best-fitting polynome), calculate the resulting concentrations

5. These data can be now integrated to determine C-conversion to gas species, total mass of gas produced…

Data treatment from FTIR

Some important limitations:

- A > 1 not suitable for quantification analysis

  Absorbance above 1 can not be used for quantification as this reflects the fact that all the light has been absorbed by the sample. Therefore one should choose a peak with an height less than 1 for the whole measuring range. This problem may of course occur at high sample concentrations.

- The non-linearity may have serious consequences at high concentrations. At high concentration, the correlation between area/height value and concentration is such that a minor increase in absorbance is leading to a substantial increase in concentration. This very high sensibility makes quantification difficult as the slightest shift/fluctuation/discrepancy can influence dramatically the calculated concentration.

Data treatment from FTIR

Some important limitations (continued)

- It is sometimes NOT possible to find a proper analysis window for a compound. It this case it is necessary to manipulate the raw spectrum in order to ”remove” the interferences caused by another species ”X”.

  This operation is called ”spectral subtract” and can be written as:

Result file = Sample file – (Subtrahend file x Subtraction factor)

”clean spectrum”

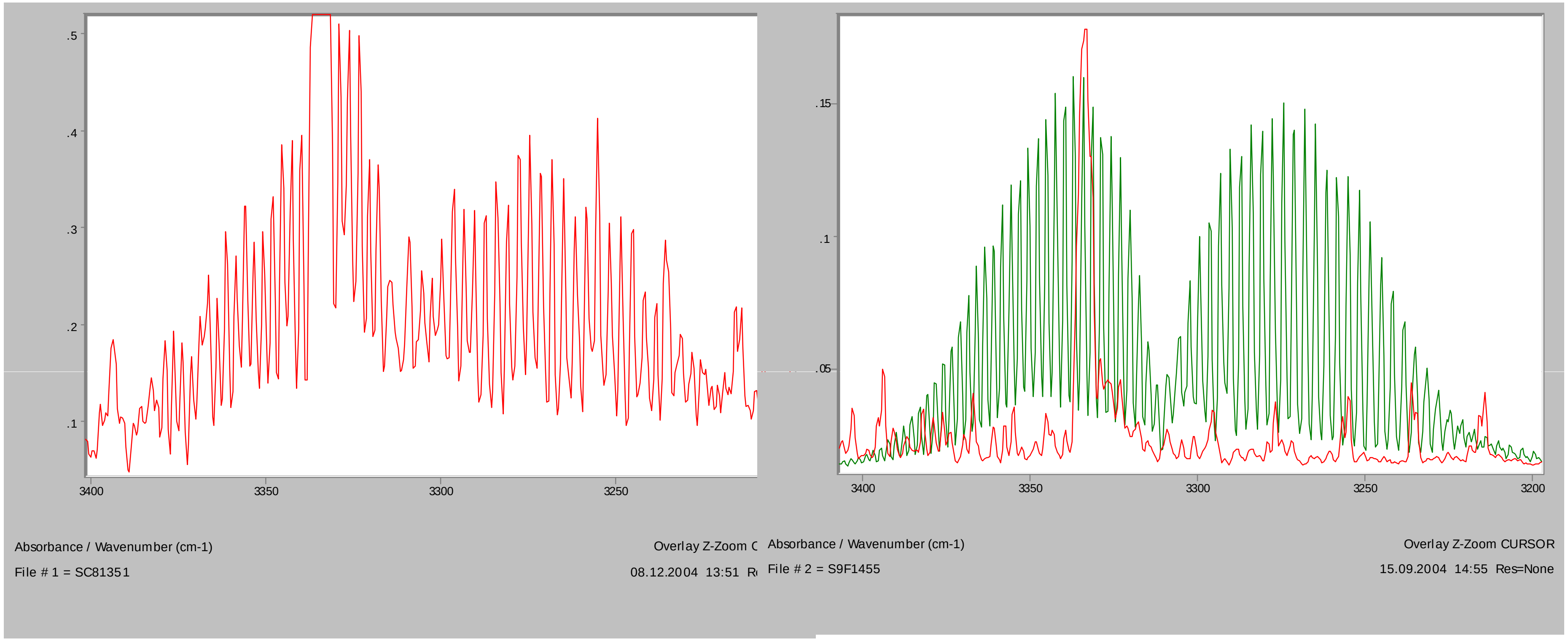
Interfering species X spectrum (known concentration $[X]_0$)

Raw spectrum
(calculated [X])

$[X] / [X]_0$

Data treatment from FTIR

- Spectral subtract: an example

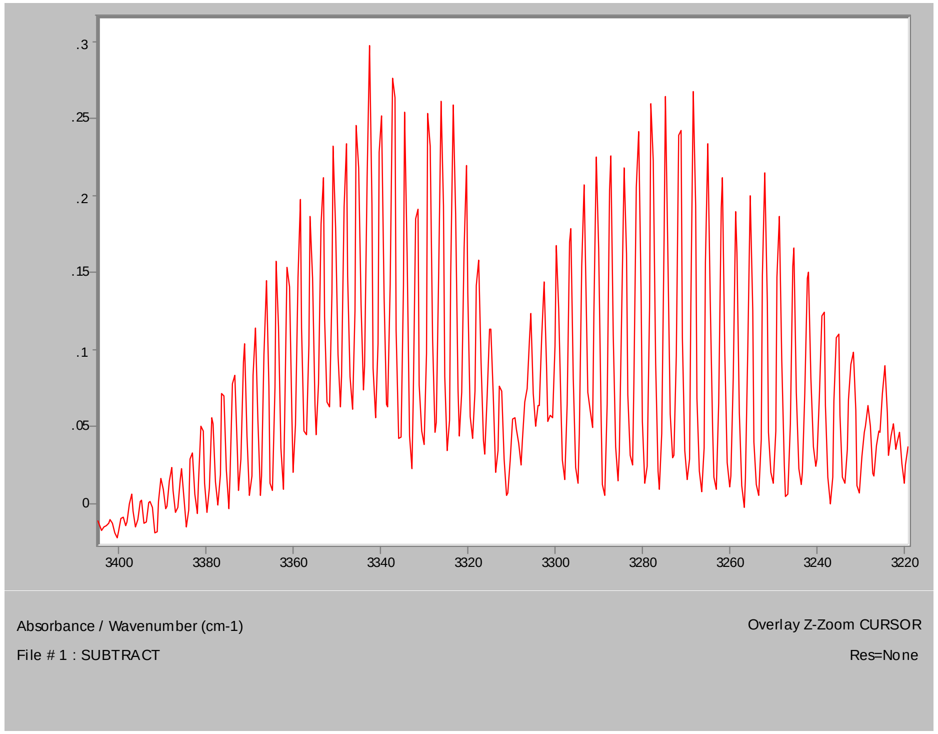


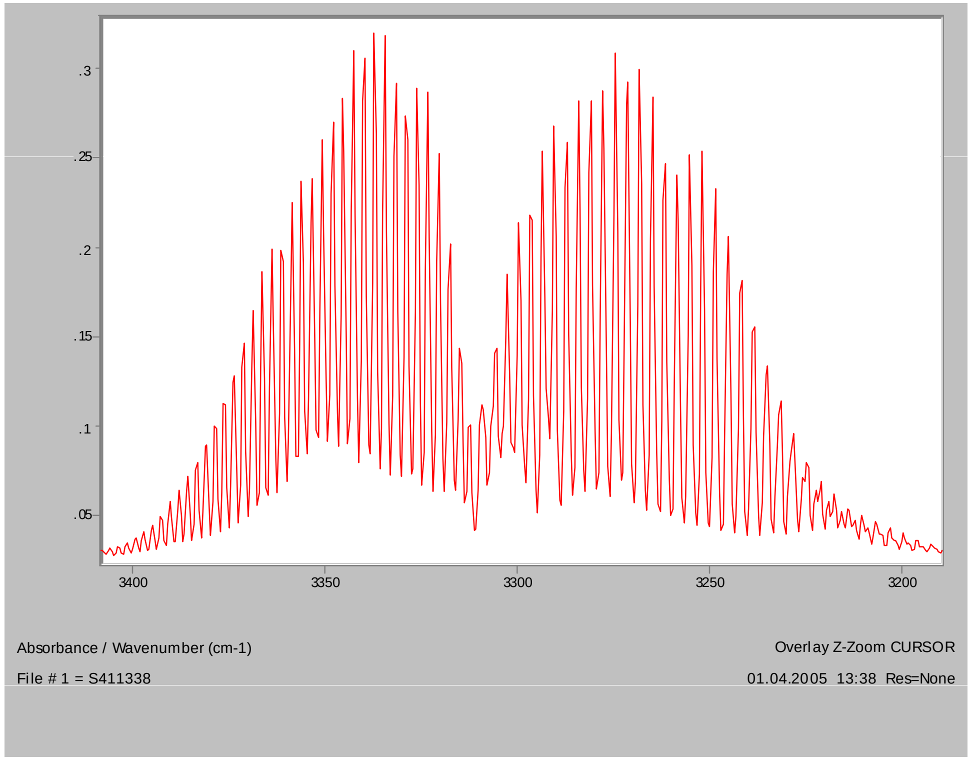
Raw data: pyrolysis of brewery waste

Spectra of HCN (green) and NH_3 (red)

Data treatment from FTIR

HCN AFTER spectral subtract >

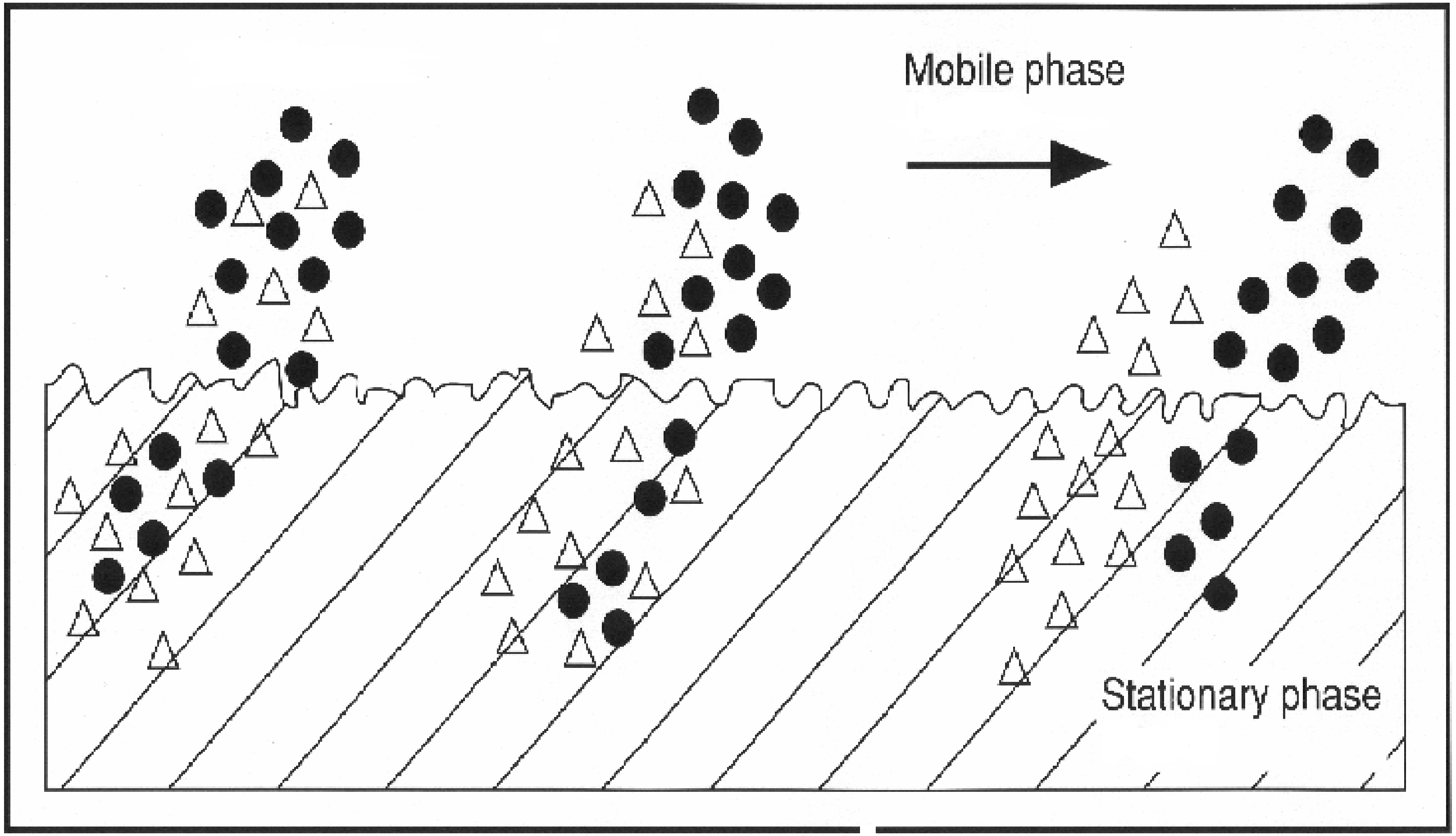




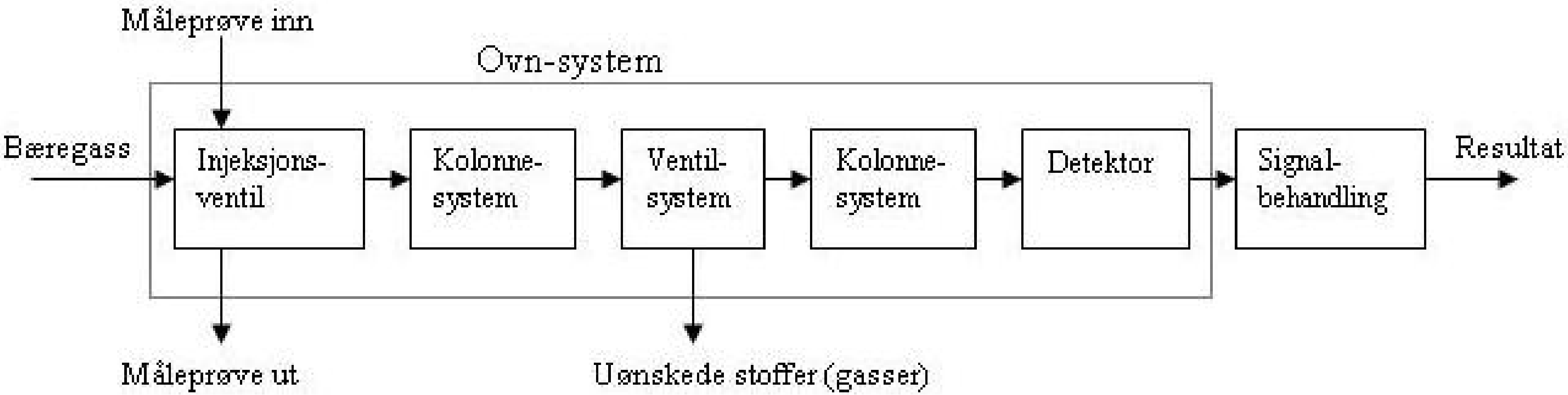
<HCN calibration spectrum (0.04%)

Gas Chromatography

Gas chromatography is an analytical method which separates complex mixture of chemicals by their distribution between two phases: a stationary phase (solid or liquid) and a mobile phase (gas).



A Gas Chromatograph



•Injeksjonsventil spyler prøvegass sammen med bæregassen gjennom et lite indre volum før kolonnen

•Kolonnen har den evnen til å separere de forskjellige molekyltypene

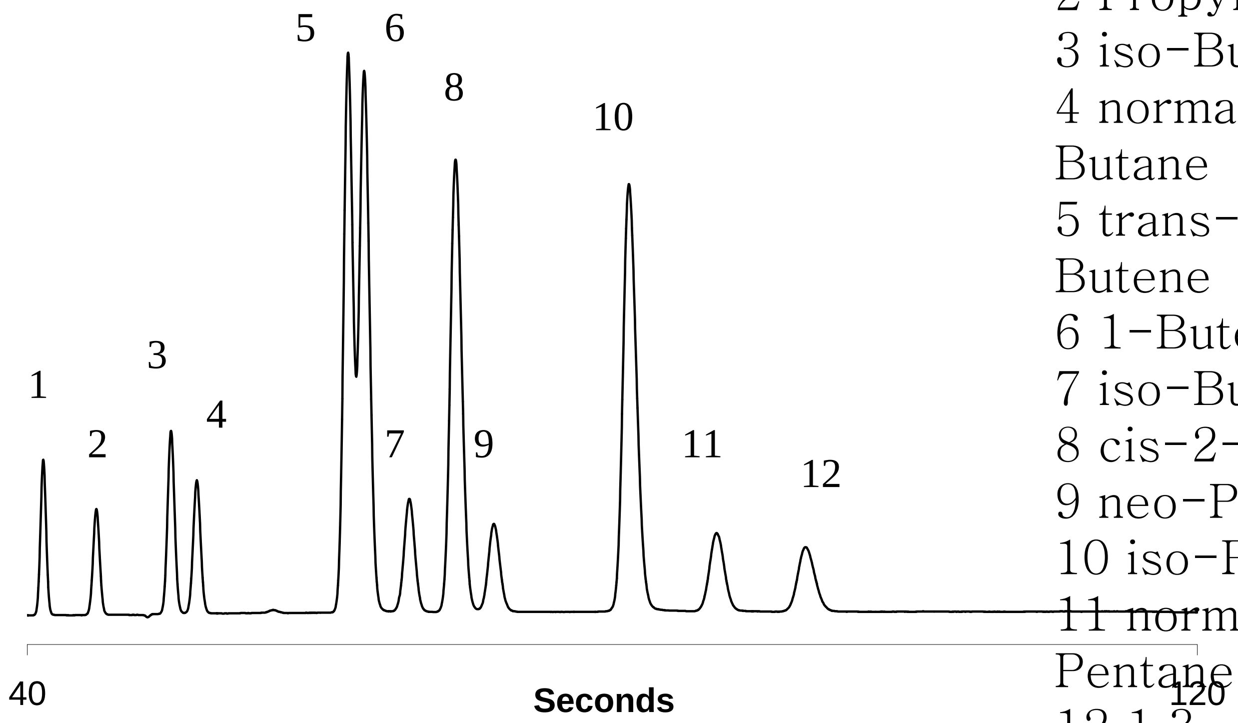
•Ventilsystem er den eneste bevegelig del i en GC. Den bestemmer hvilken retning gassen skal gå i et system med flere kolonner

•Ovn sørger for stabile temperaturomgivelser rundt de forskjellige komponentene

•Detektor omgjør konsentrasjon til et signal som kan tolkes av en datamaskin. Det finnes flere typer som bruker forskjellige metoder for å kvantifisere gassmengden

- •TCD–Thermal Conductivity Detector
- •FID–Flame Ionisation Detector

A chromatogram



1 Propane
2 Propylene
3 iso-Butane
4 normal-Butane
5 trans-2-Butene
6 1-Butene
7 iso-Butene
8 cis-2-Butene
9 neo-Pentane
10 iso-Pentane
11 normal-Pentane
12 1,3-Butadiene

•Elution time is characteristic of a compound

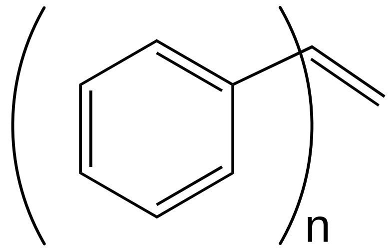
>Qualitative analysis

•Area/height of the peak is proportional to the amount of product

>Quantitative analysis

Our GCs: CP 4900 micro GC

- High resolution/ High speed
- On-line (sampling pump)
- Portable (field measurements)
- 1-4 independent channels per GC
- Columns: MS5, PPQ and PPB
- Detectors: TCD (Thermal Conductivity Detector)
  DMD (Differential Mobility Detector)
- Compounds measured: CO_2, CH_4, C_2H_2+ C_2H_4 and C_2H_6
  H_2, O_2, CH_4, CO and N_2
  H_2S, COS and more!



In order to optimise separation/measurement of compounds:

- Type of column (material, length, diameter…)
- Column module parameters: temperature, pressure, gas carrier
- Detector (detection limit, compound response…)

NTNU

NTNU

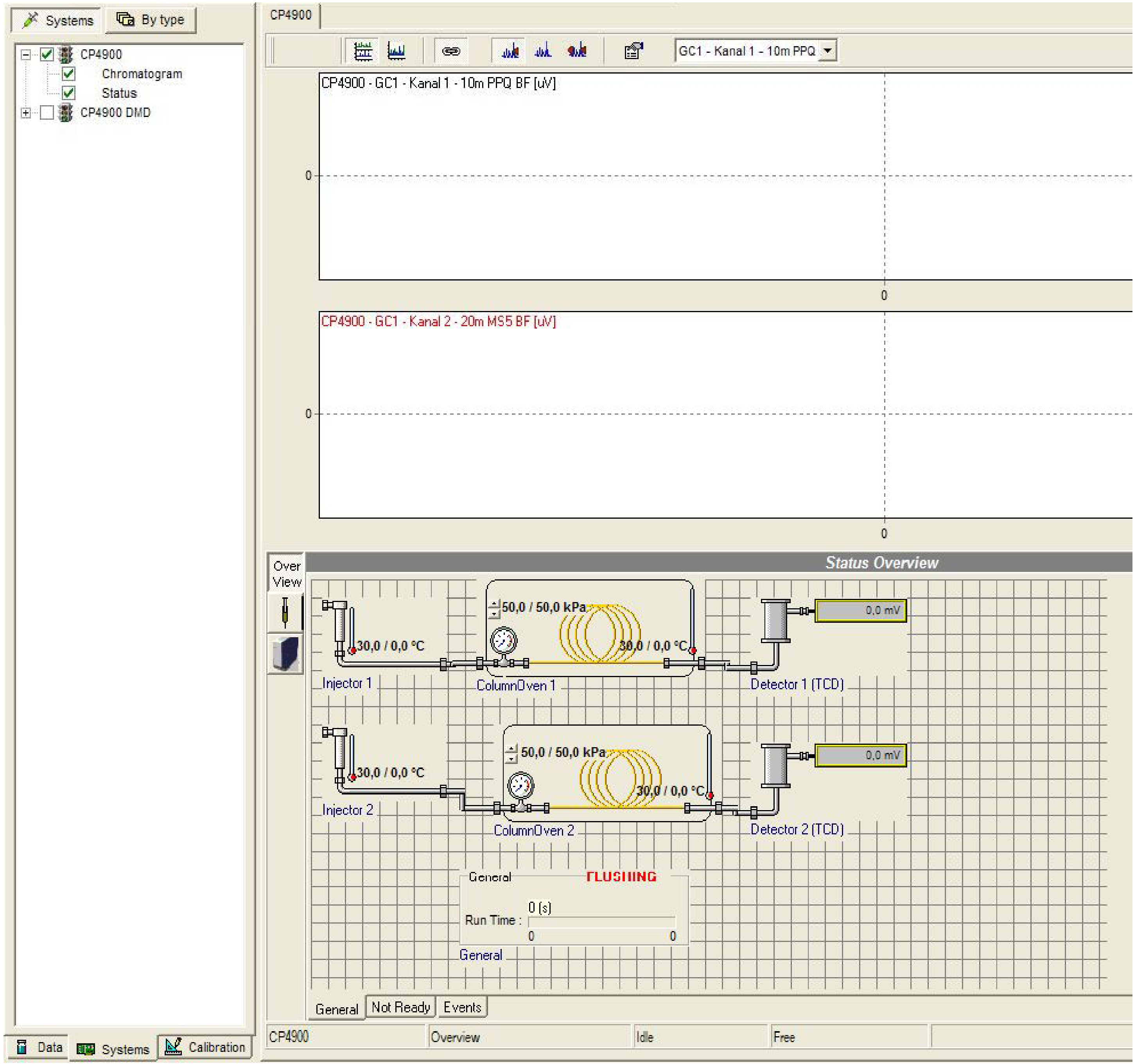
How can we influence compound separation I

- Column dimension
  - Increasing the length and decreasing the diameter will guarantee better component separation but it means also that the different components will take more time to go through the column
  - The type of column is important as well, for instance a Molseive column is good at separation of compounds such as H_2, O_2, N_2, CO and CH_4. Higher hydrocarbons will take quite a long time to go through the column and will disturb measurement in case the GC is set to continuous operation mode. In worst case it could ruin the column. A solution for this is to have a small column before that will roughly separate hydrocarbons from the rest of the compounds. A system with back flush will prevent hydrocarbons from entering the column.
  - The PoraPlot column is better suited for light hydrocarbons (up to C5 can be separated with this column) but will not be able to separate H_2, O_2, N_2, and CO. Such compounds will go straight through and will show up as a large top at the beginning of the chromatogram.

How can we influence compound separation II

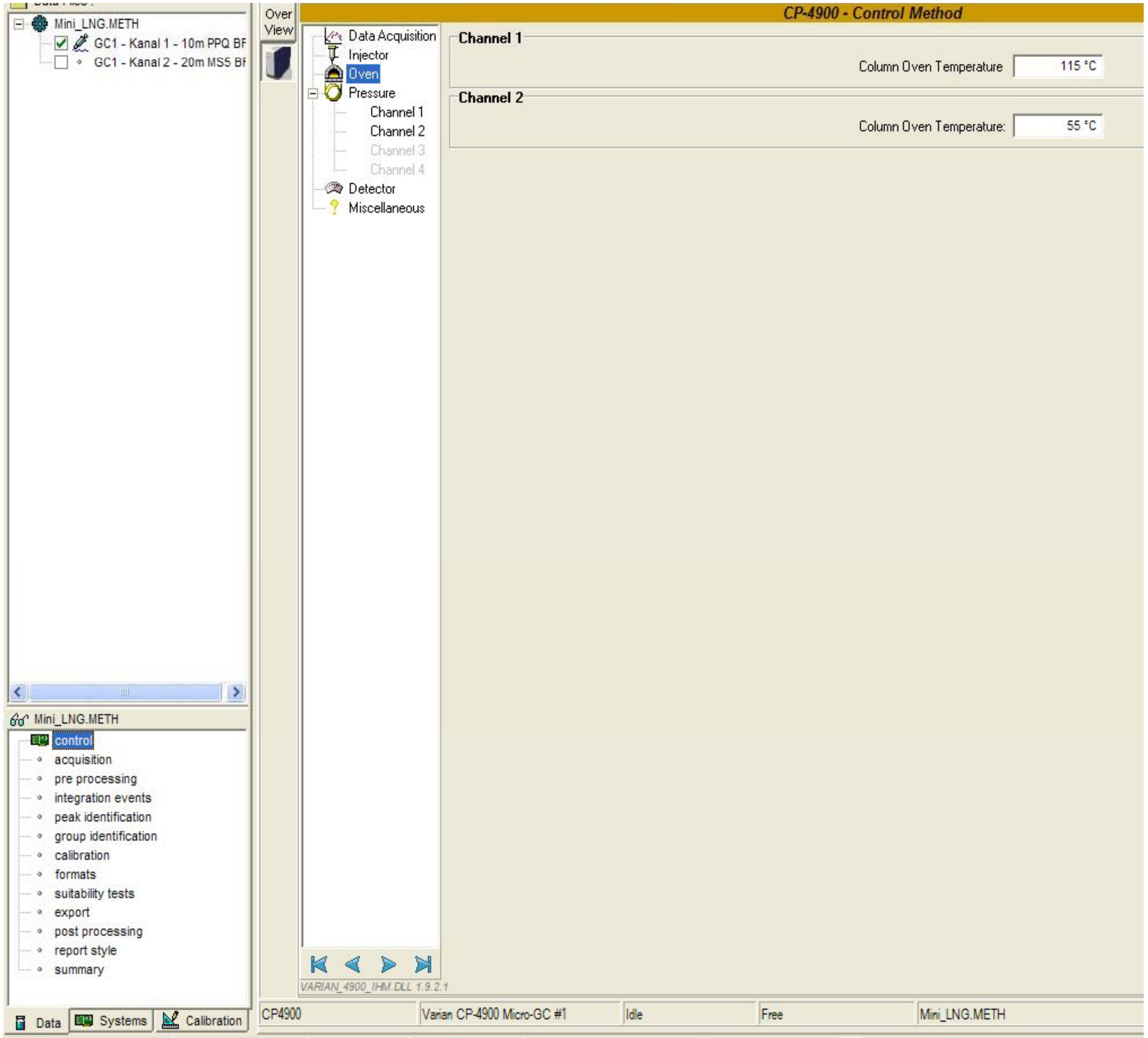
- Column temperature [ºC]
  - Increasing the temperature will result in higher tops (better in case of short tops that can be disturbed by signal noise), less separation and shorter sampling time
- Injection time [ms]
  - This decides how long a valve will open to allow the sample gas into the column
  - Increasing the injection time will result in less separation and higher tops. It also has a small effect on sampling time
- Column pressure [kPa]
  - An increase in pressure will make the compounds go much faster through. Distance to the neighbor top does not change. The tops are a little higher

- The Software used to control the GC and to process the data is called Galaxie.
- As the GC is running the Chromatogram will be drawn continuously in the window to the upper right
- Several GCs can be controlled at the same time
- The window to the right shows schematically the status of the instrument along with the current and set point of the different parameters



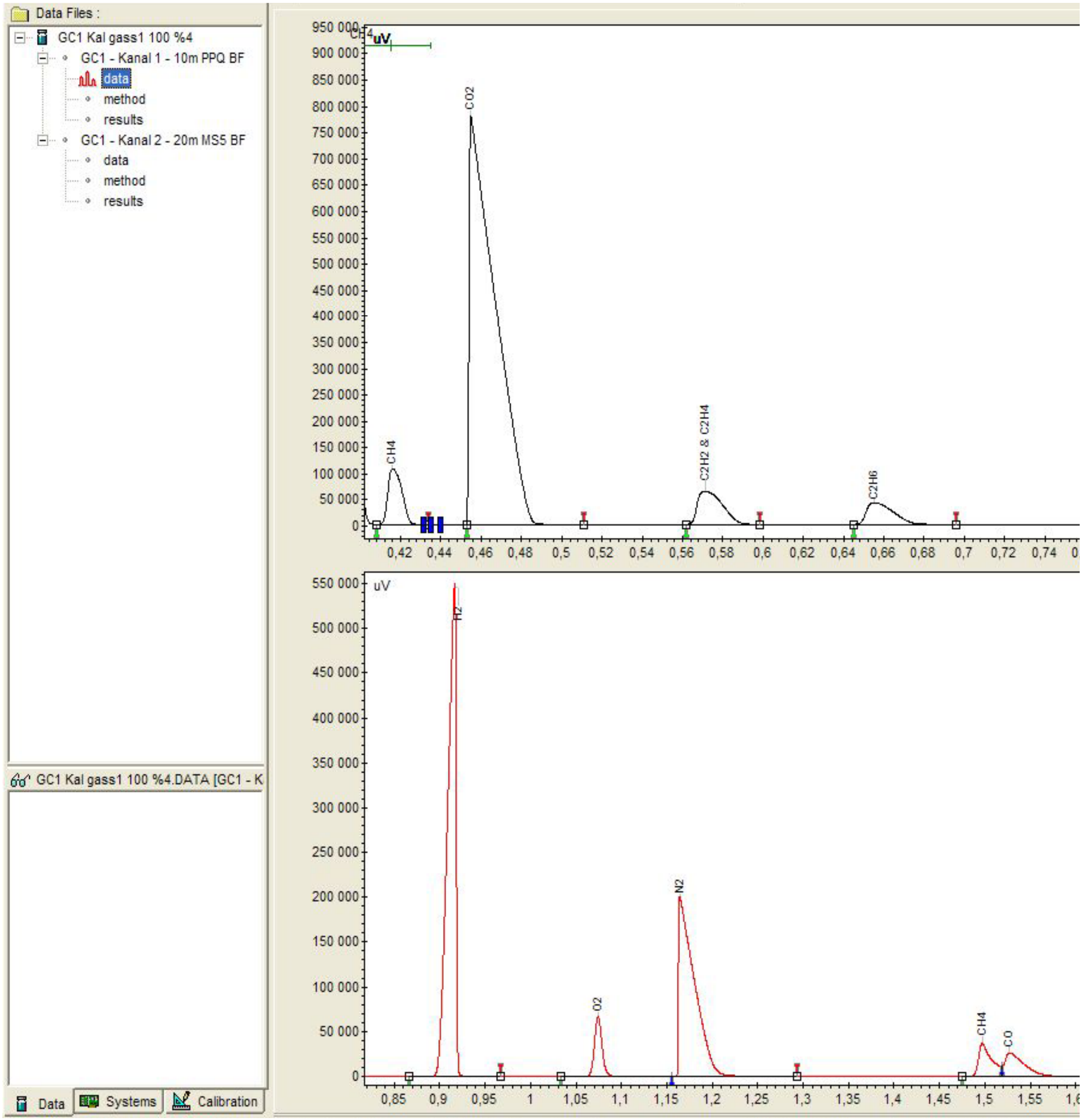
A method is used to control all the aspects of the GC. Within the method one can do the following:

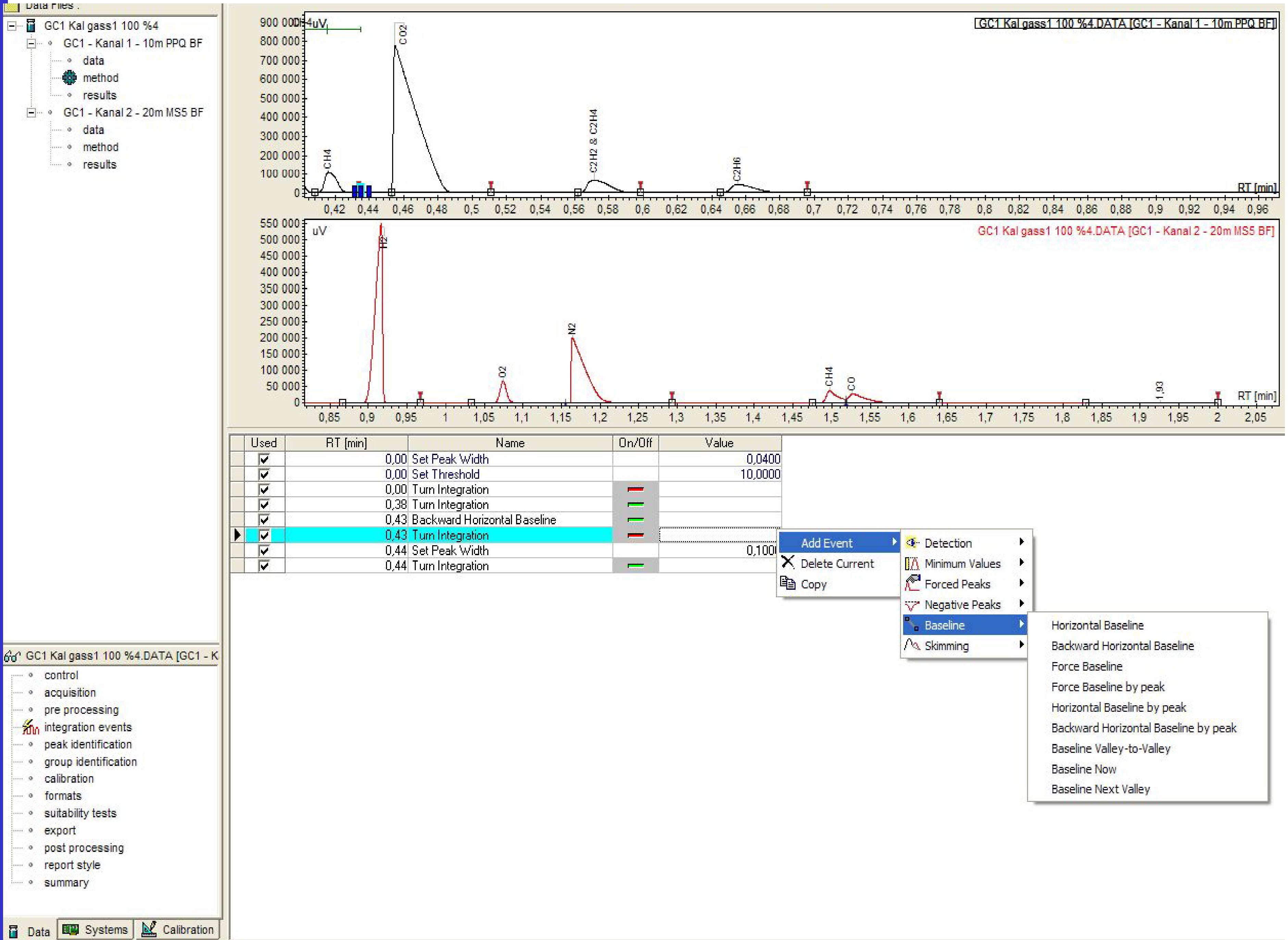
- Change the GC parameters
- Decide how and where the data will be saved
- Control the looks of the report file
- Set integration events
- Identify the different tops
- Use some kind of mathematical pre- or post processing to the chromatogram
- and other …



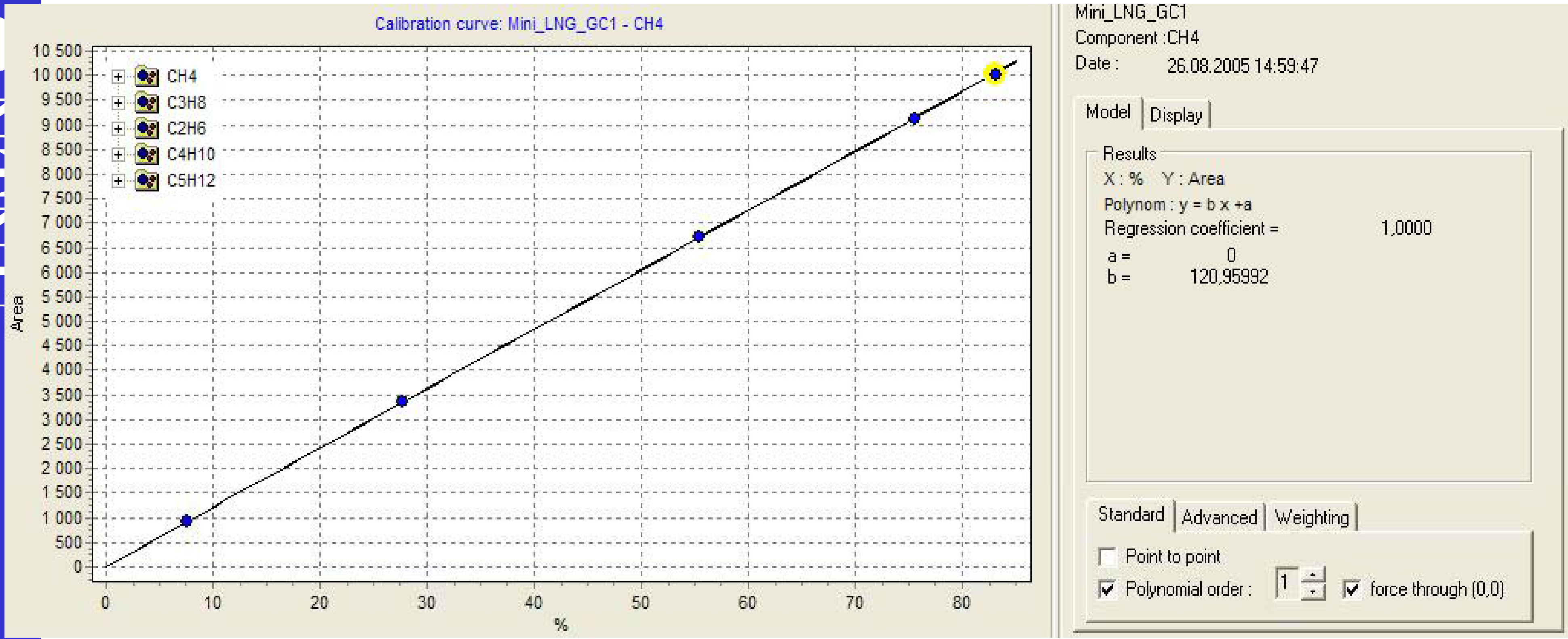
- The method is downloaded to the memory of the instrument after the optimization is complete

- When a chromatogram is recorded, it can be opened for post processing in Galaxie
- Identification of the different tops is based on experience, but data bases of several instrument types and “GC-conditions” are available
- The method should be optimized in a way so that we get the shortest sampling time and no overlapping
- In this example we see that the limitation here is the separation of CH4 and CO

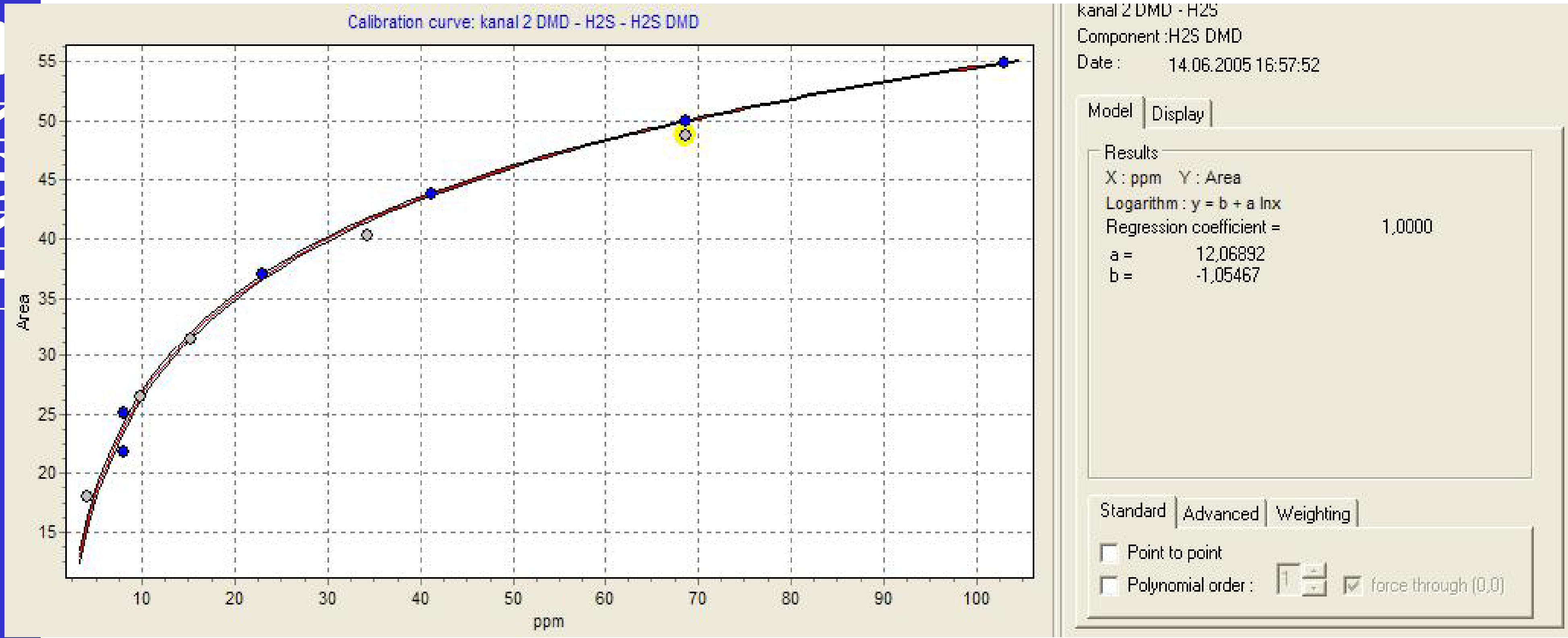




Used	RT [min]	Name	On/Off	Value
☑	0,00	Set Peak Width		0,0400
☑	0,00	Set Threshold		10,0000
☑	0,00	Turn Integration		
☑	0,38	Turn Integration		
☑	0,43	Backward Horizontal Baseline		
☑	0,43	Turn Integration		
☑	0,44	Set Peak Width		0,100
☑	0,44	Turn Integration		



- When the integration events are decided and the baseline is drawn. The area for the different tops can be calculated.
- When we record a chromatogram with known concentration the area can be related to this concentration and a calibration curve can then be constructed
- For a TCD detector the relation between the gas concentration and the area is as we can see quite linear.



- For the DMD detector the relation is not that linear.
- As we can see the DMD detector will get saturated and will not be able to detect higher concentrations
- The developers of this detector claim that it is quite linear in the lower range of the scale

Some differences between how a GC works compared to a FTIR

- A FTIR takes a snap shot of the absorbed laser intensity of the sample. This snap shot contains all the information needed to determine the gas concentration of the sample.
- The FTIR has fixed parameters; cell temperature or laser strength are predefined.
- This means that with a FTIR one can wait for the calibration until after the experiment.
- Because of overlapping between the different molecules in the absorption of the laser intensity the calibration of an FTIR is more complicated.
- Depending on the cell length the sampling time can vary from 20 to 60s.
- The FTIR needs large quantity of sample gas (5 Nl/min)

- A GC needs to pre-treat the sample in order to be able to measure any concentration.
- The GC has several parameters that can be varied depending on gases that are present in the sample
- With the GC one needs to ensure a total component separation before the experiment.
- In fact depending on the gas types of interest, one should make decisions prior to the purchase of the instrument.
- For example the type of column to buy, the length of the column and the diameter are important factors to consider.
- Sampling time of the GC depends on column type and dimension and other variables like column temperature and pressure. It can vary from 30 s to 30 min.
- The GC does not need more than 30 ml/min for the gas sampling