Methoden der Validierung der FTIR-Spektrometrie in der Gasanalytik

Offen-Pfad- und passive Messungen

Klaus Schäfer

Forschungszentrum Karlsruhe GmbH

Institut für Meteorologie und Klimaforschung

Atmosphärische Umweltforschung

Garmisch-Partenkirchen, Germany

VDI Guideline 4211, part 1

Burner and calibration gases

Calibration flame

Hot calibration gas cell

Instrumental Line Shape determination

Relevant information from advisory standards

VDI Guideline "Atmospheric measurements near ground with FTIR spectroscopy. Measurements of gaseous emissions and immissions. Fundamentals" (VDI 4211, part 1)

CEN working group TC 264/WG 18 "Open path optical methods for the measurement of ambient air quality"

Use of reference spectra

CEN
Primary Calibration

IR gas cell with calibration gas in the radiation path of the spectrometer

Five concentration levels minimum, run through in 10 cycles according to VDI Guideline 2449 Part 1 or ISO standard 9169

Test gases are produced and metered into the gas cell statically or dynamically according to VDI Guideline 3490

Determination of calibration function with its confidence ranges in accordance with VDI Guideline 2449 Part 1 or ISO standard 9169

CEN
Control calibration

Determination of N_2O (340 ppb) and CH_4 (1.7 ppm) concentration in ambient air

Determination of H_2O concentration

Comparison with independent water vapour concentration measurements

CEN

Calibration by using spectral lines from data bases and determination ILS

Synthetic determination of calibration spectra with molecular spectroscopic database and quantitative ILS

Determination of actual ILS with measurement of laser or CO of known concentration (spectral resolution narrower than line width)

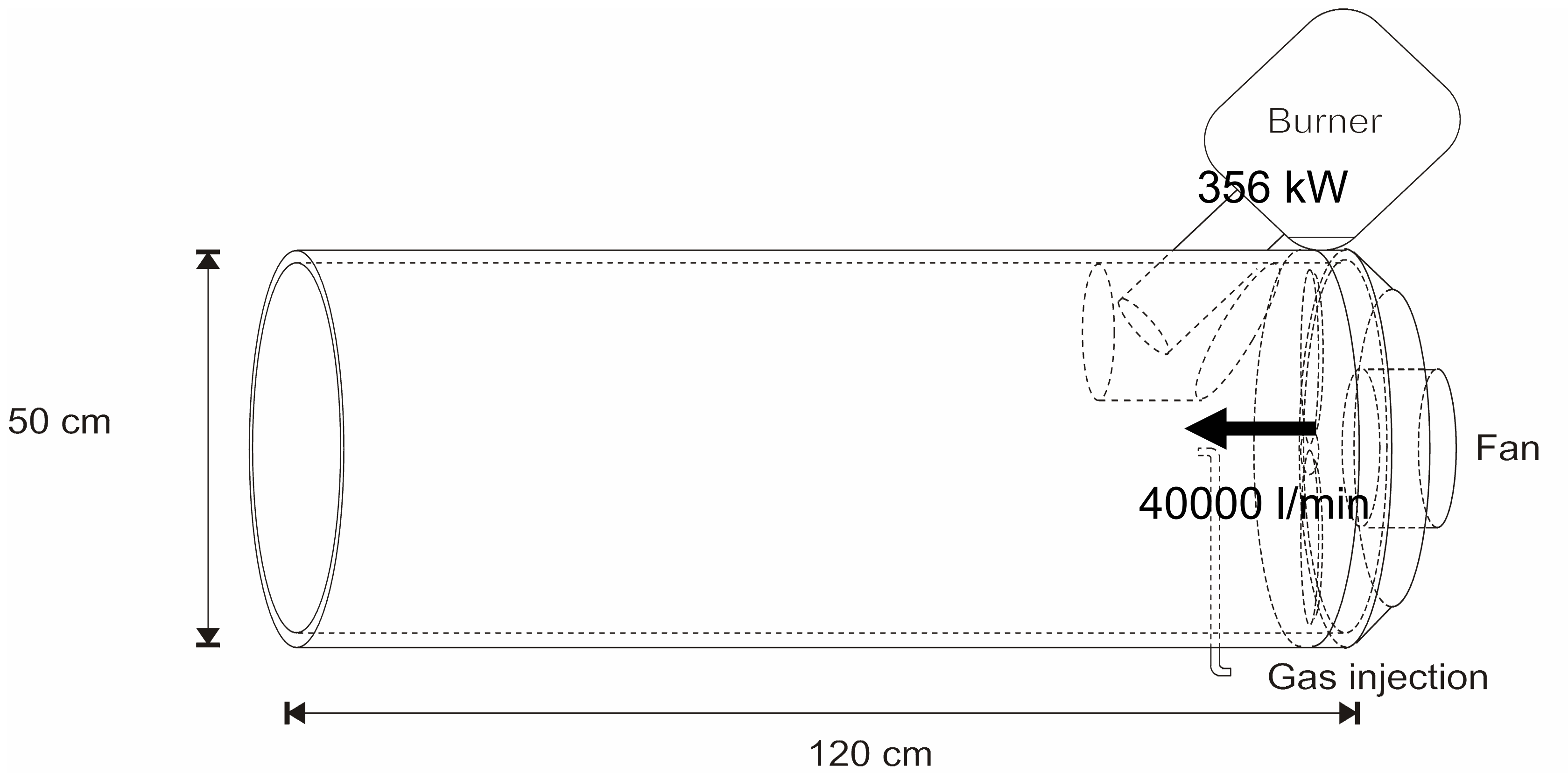
Evaluation of FTIR spectrometry applied for hot gas analyses

Evaluation of FTIR measurement results is necessary for routine application of the measurement method

Different methodologies and techniques for this task were considered:

- **calibration burner (high temperature gas producer),**
- **calibration flame,**
- **hot cell**

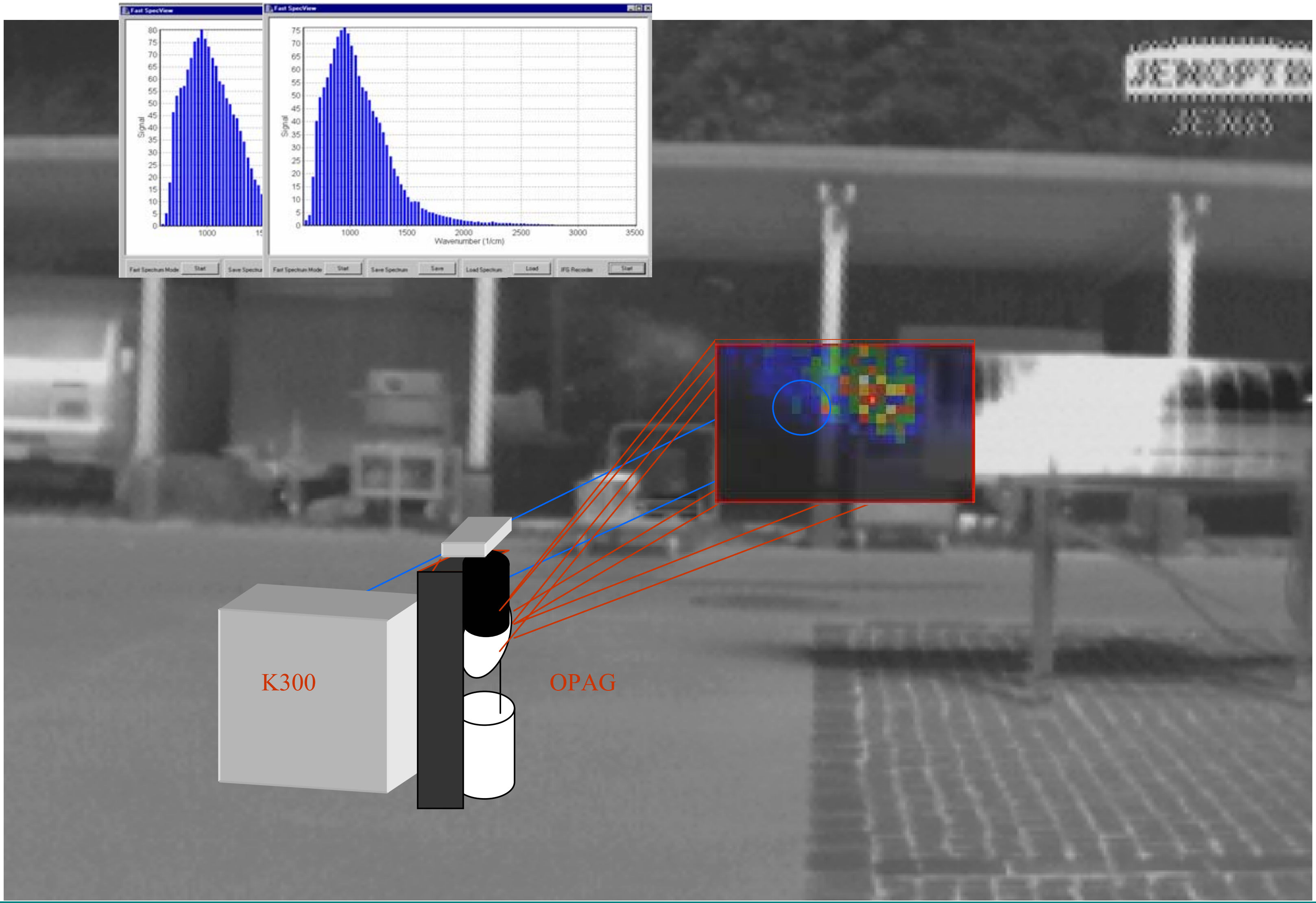
Calibration burner (high temperature gas producer)



Burner experiments

McKenna burner

Hot gas cell

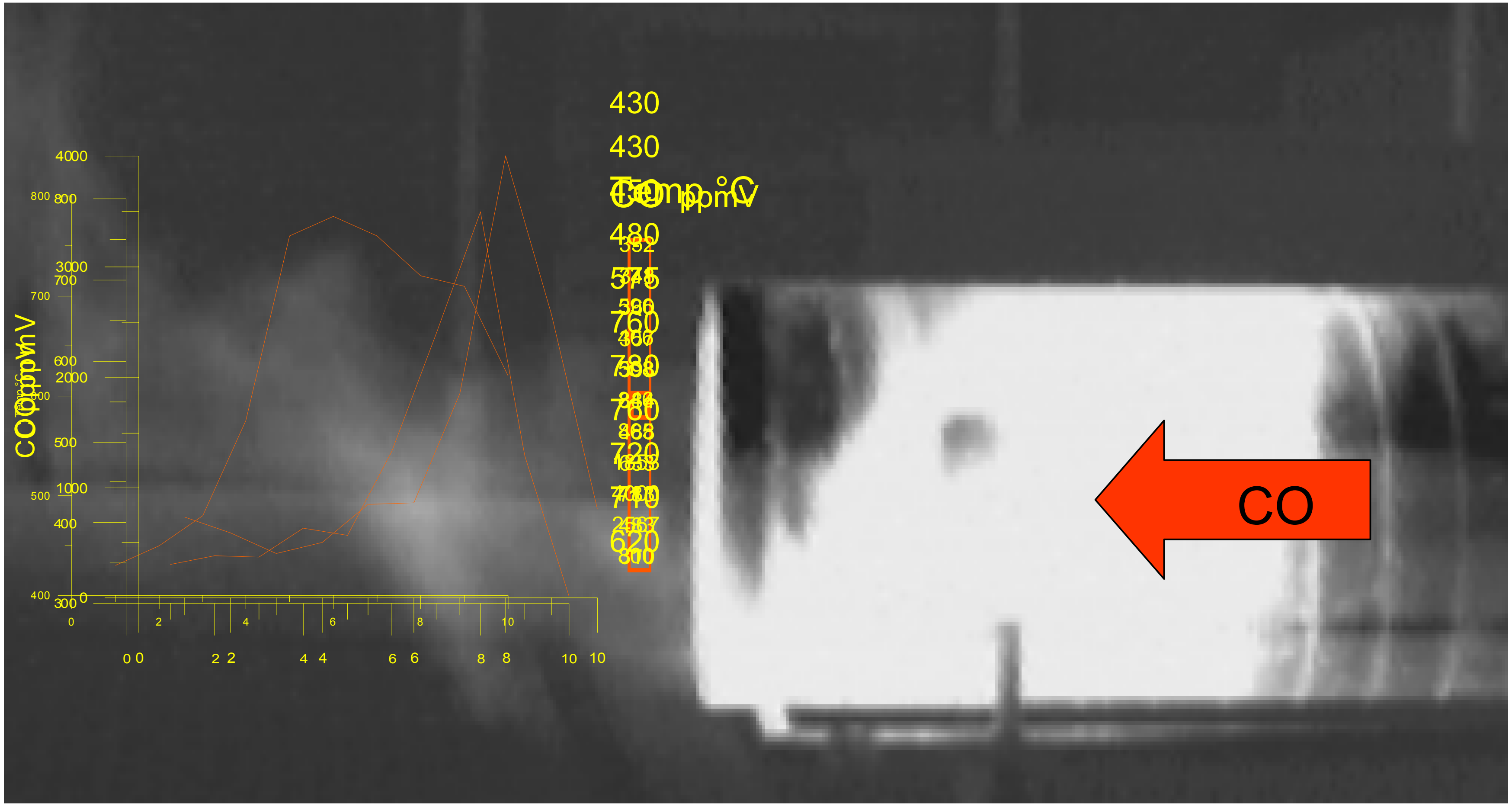


OPAG
CO injection

Burner experiments

McKenna burner

Hot gas cell



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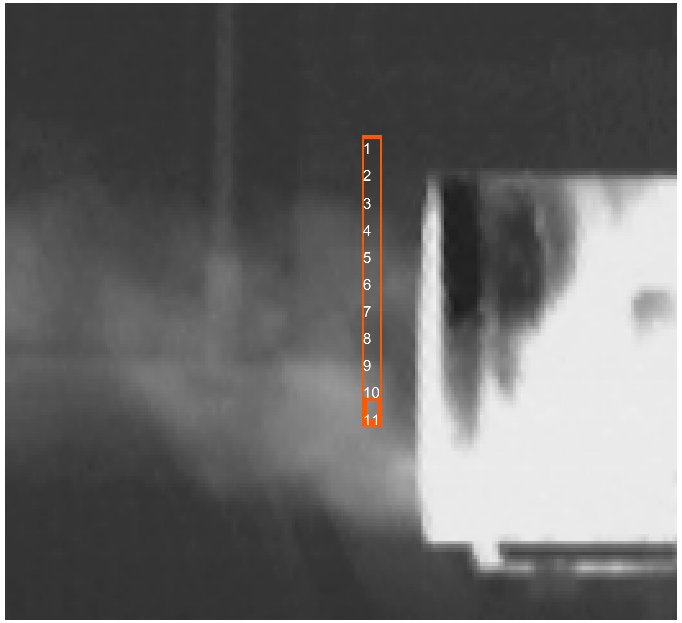
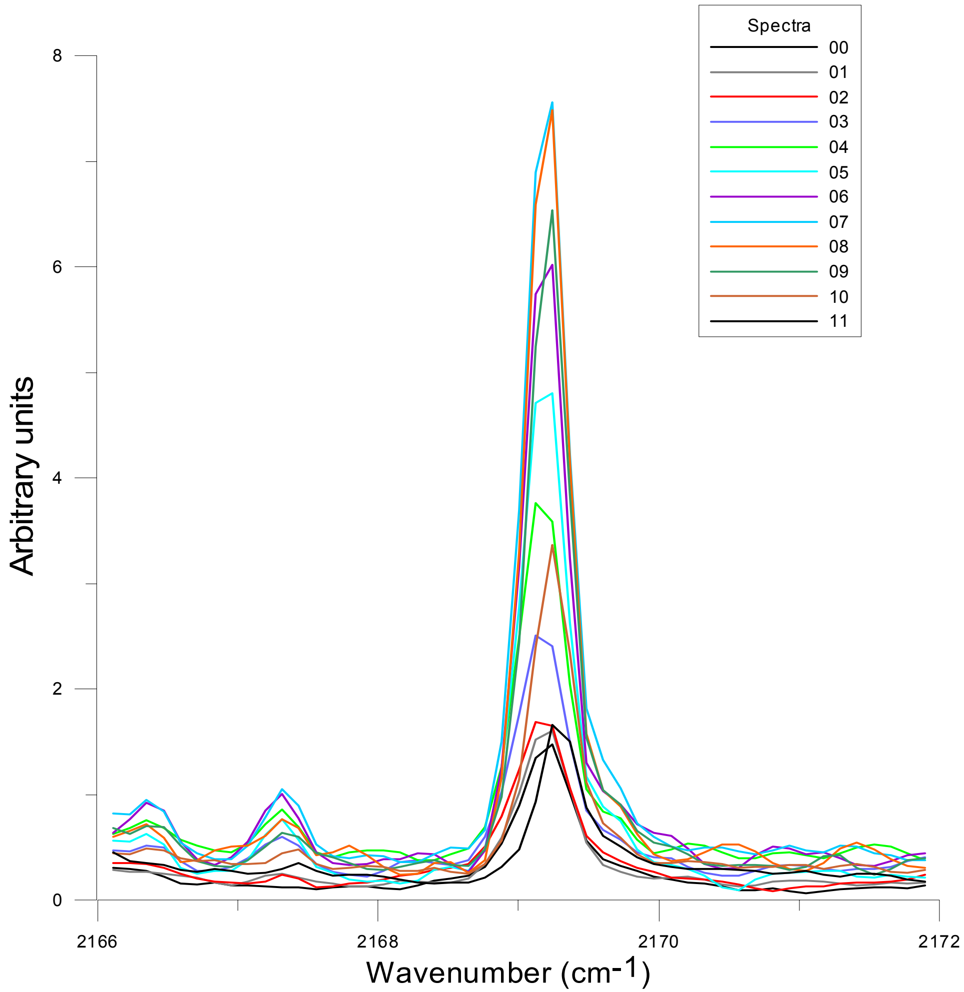
OPAG
CO injection

Burner experiments

McKenna burner

Hot gas cell



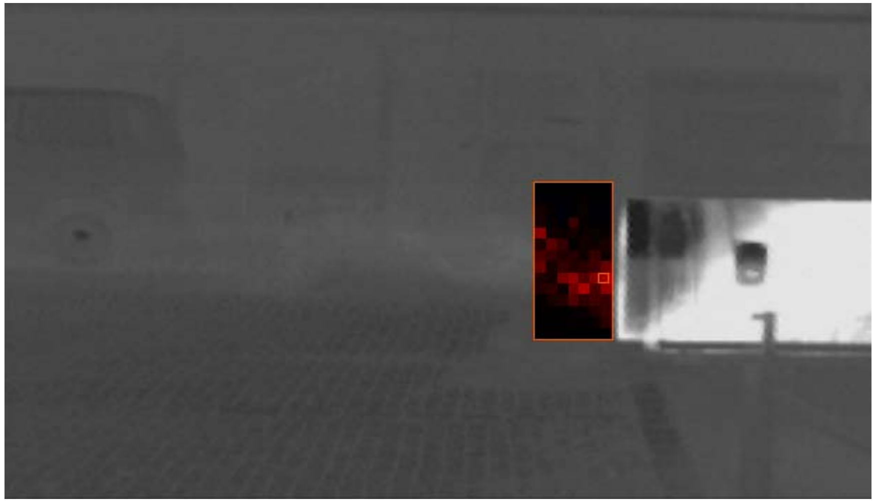


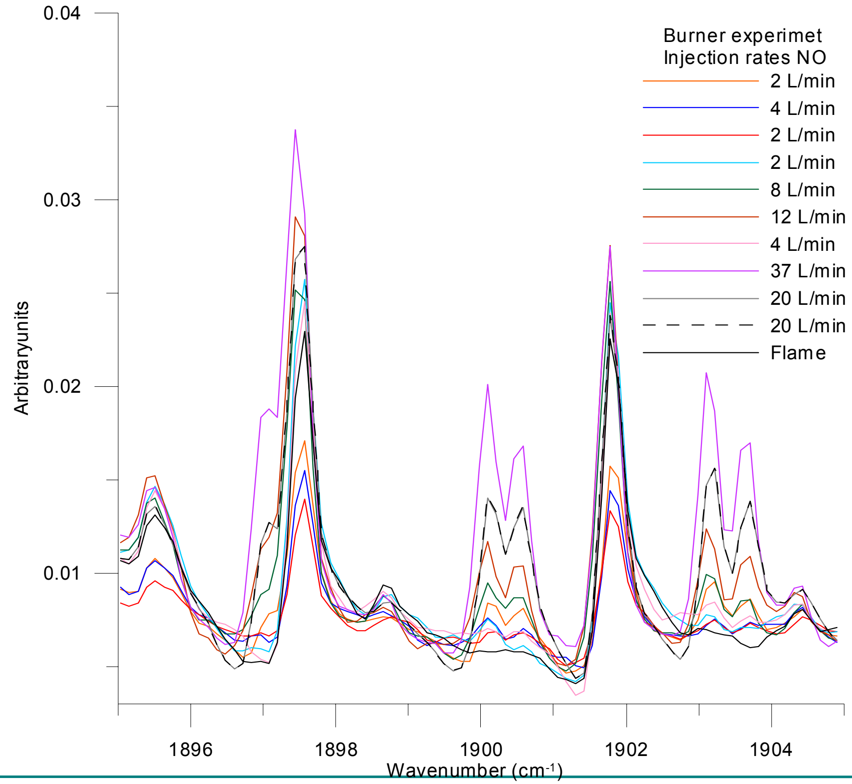
OPAG
NO injection

Burner experiments

McKenna burner

Hot gas cell

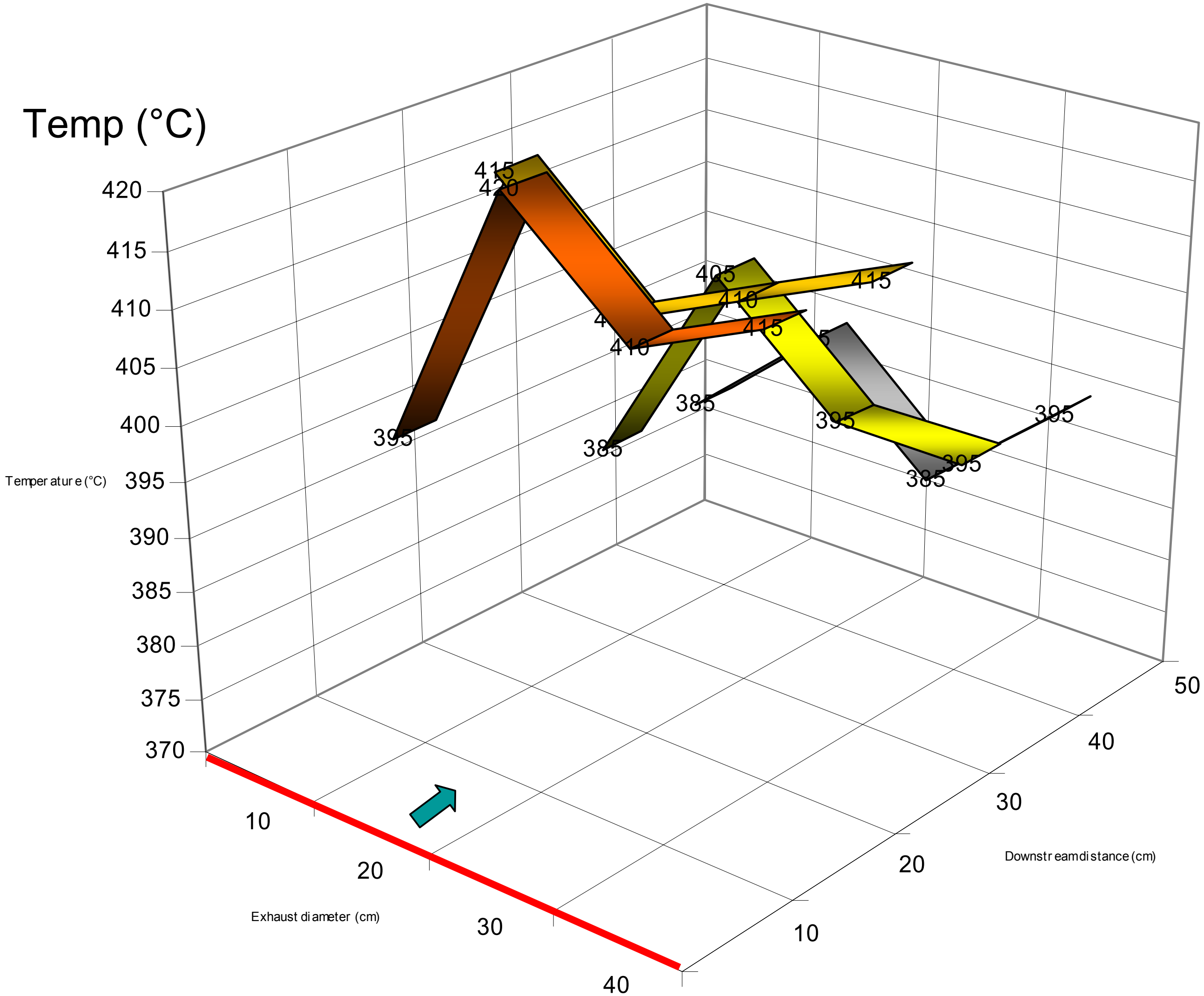




Burner experiments

McKenna burner

Hot gas cell

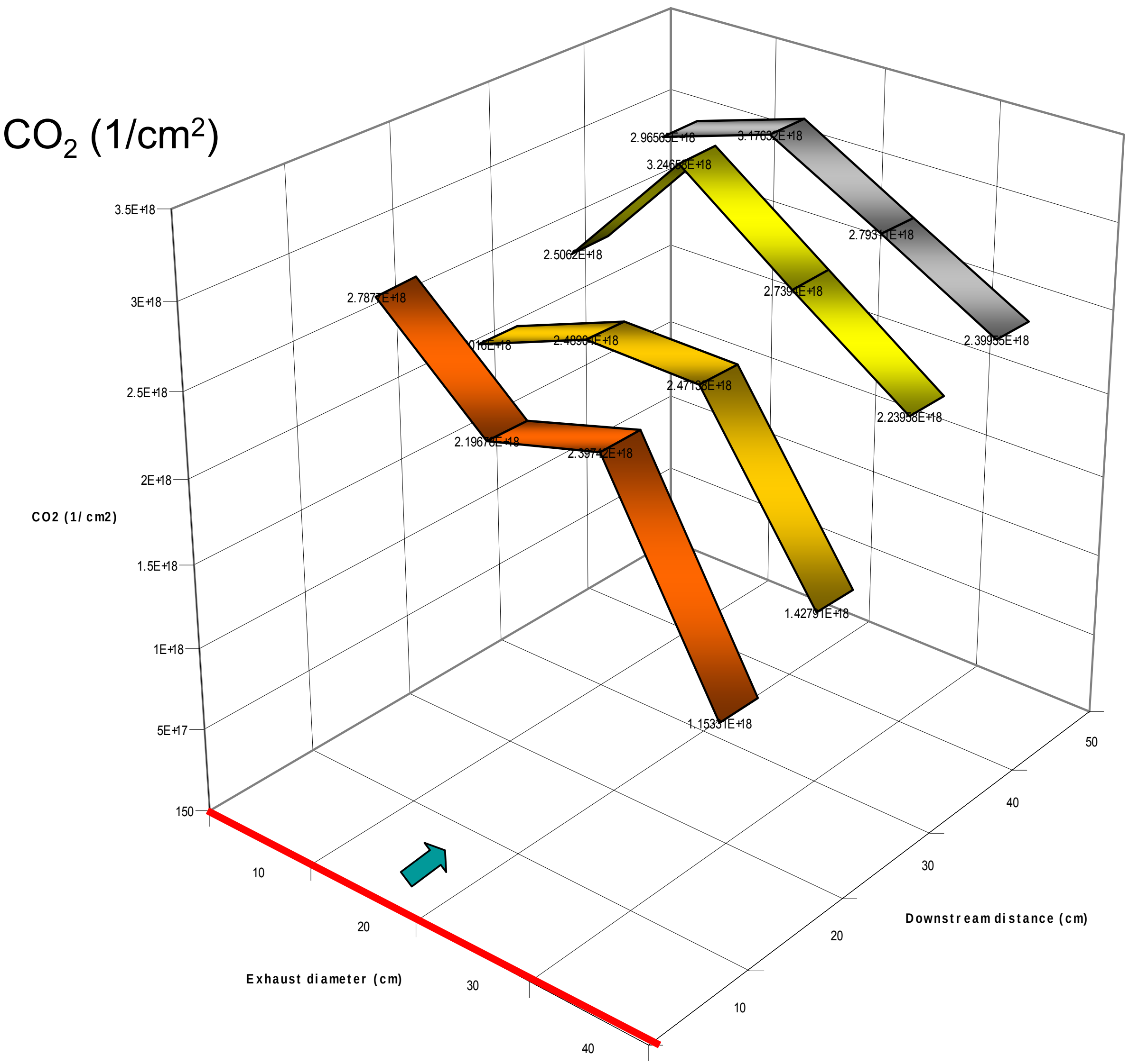


Burner experiments

McKenna burner

Hot gas cell

CO_2 (1/cm^2)

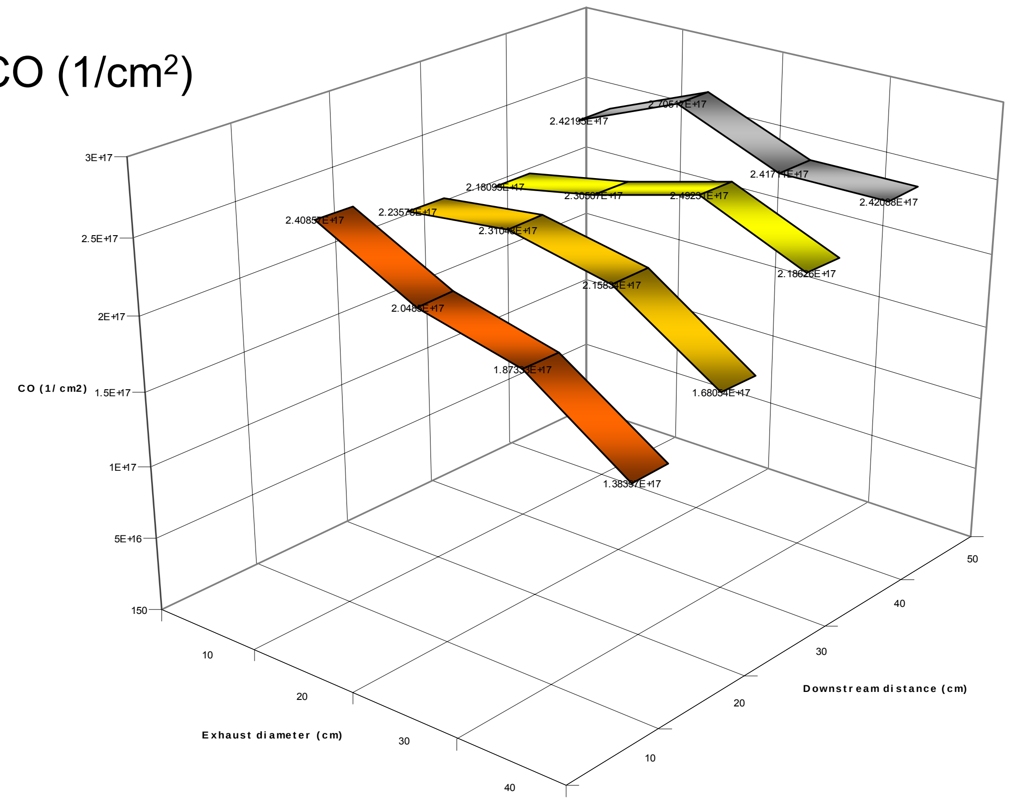


Burner experiments

McKenna burner

Hot gas cell

CO (1/cm^2)

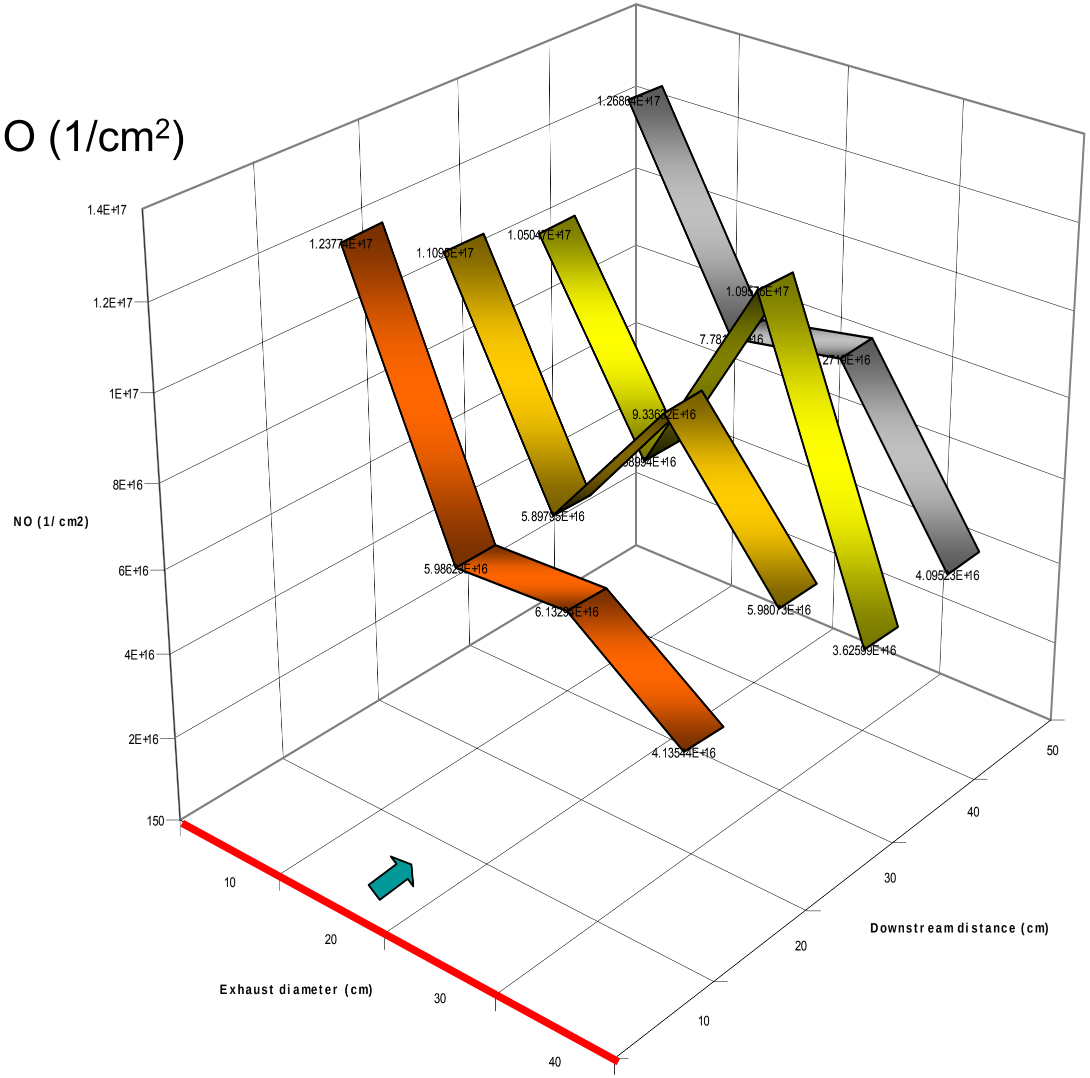


Burner experiments

McKenna burner

Hot gas cell

NO ($1/cm^2$)



Experiments with burner

CO and NO (pure calibration gases) were injected in the exhausts with different amounts as calibration gases to vary the concentration of these gases

Relevant chemical transformation of the injected CO and NO in the exhaust plume

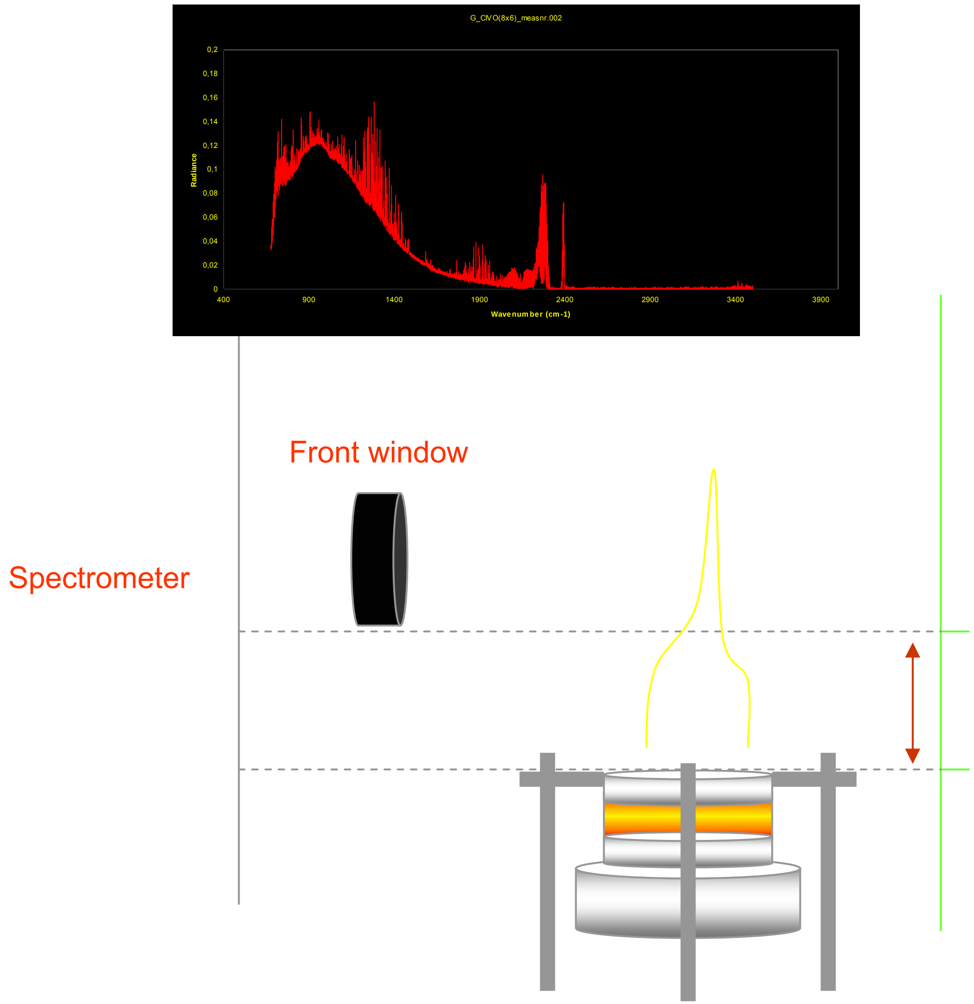
Problems with homogeneous mixing

Results show that this method is not accurate enough for operational use

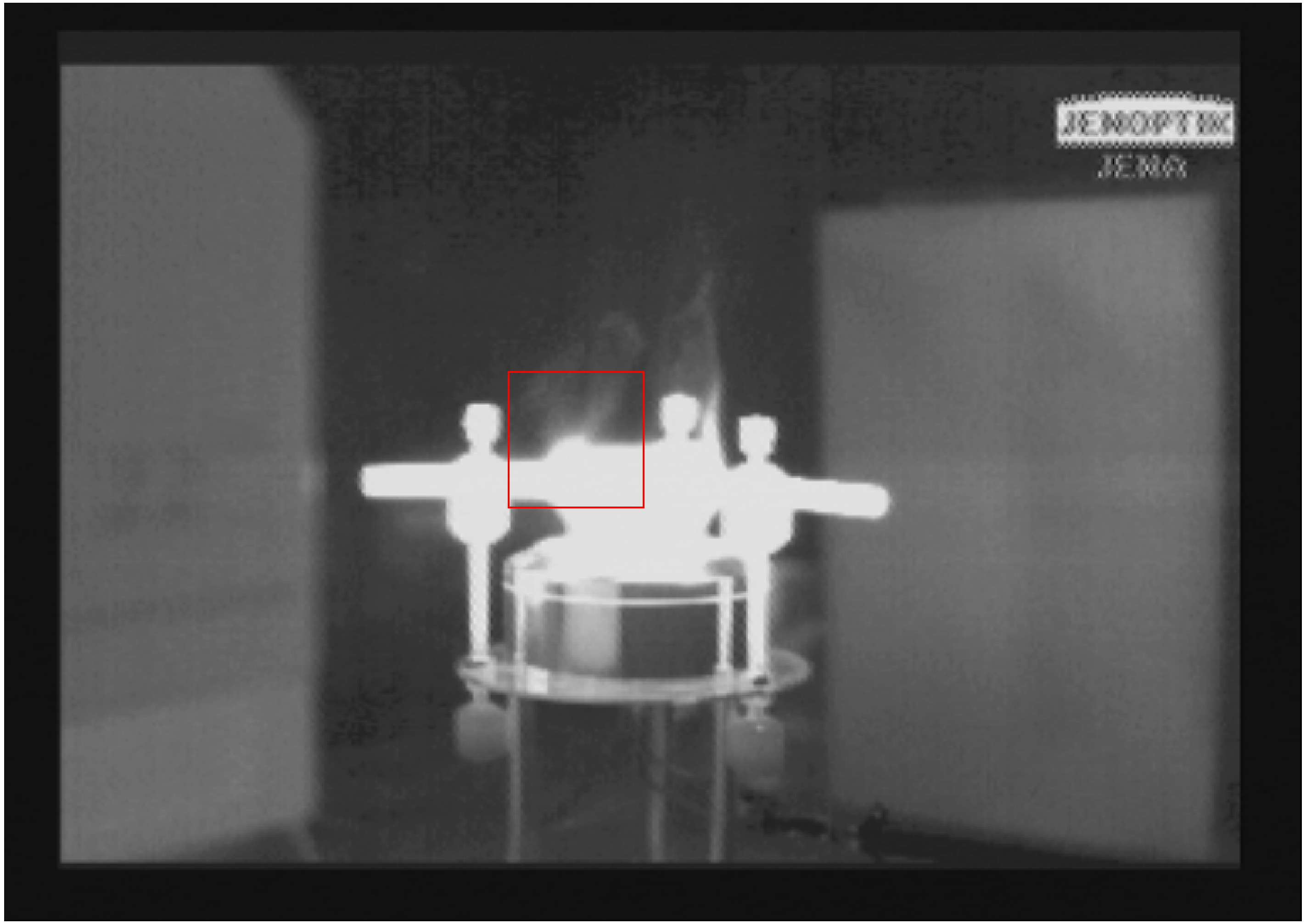
Burner experiments

McKenna burner

Hot gas cell



Distance and altitude of the flame were fixed
Time of measurements was about 5 minutes

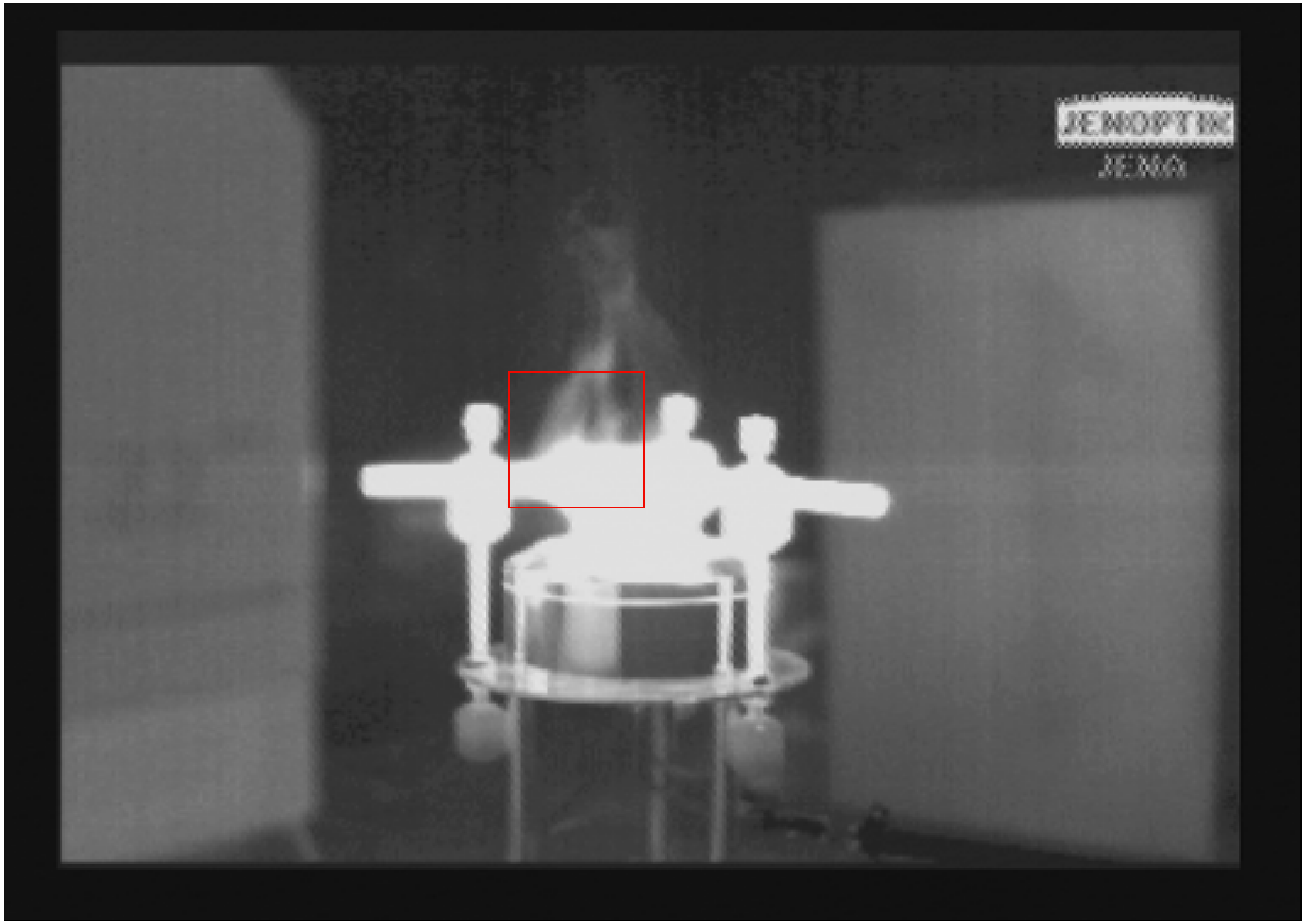


Thermo image from McKenna burner powered with 30 % of C_2H_4 and 30 % of air

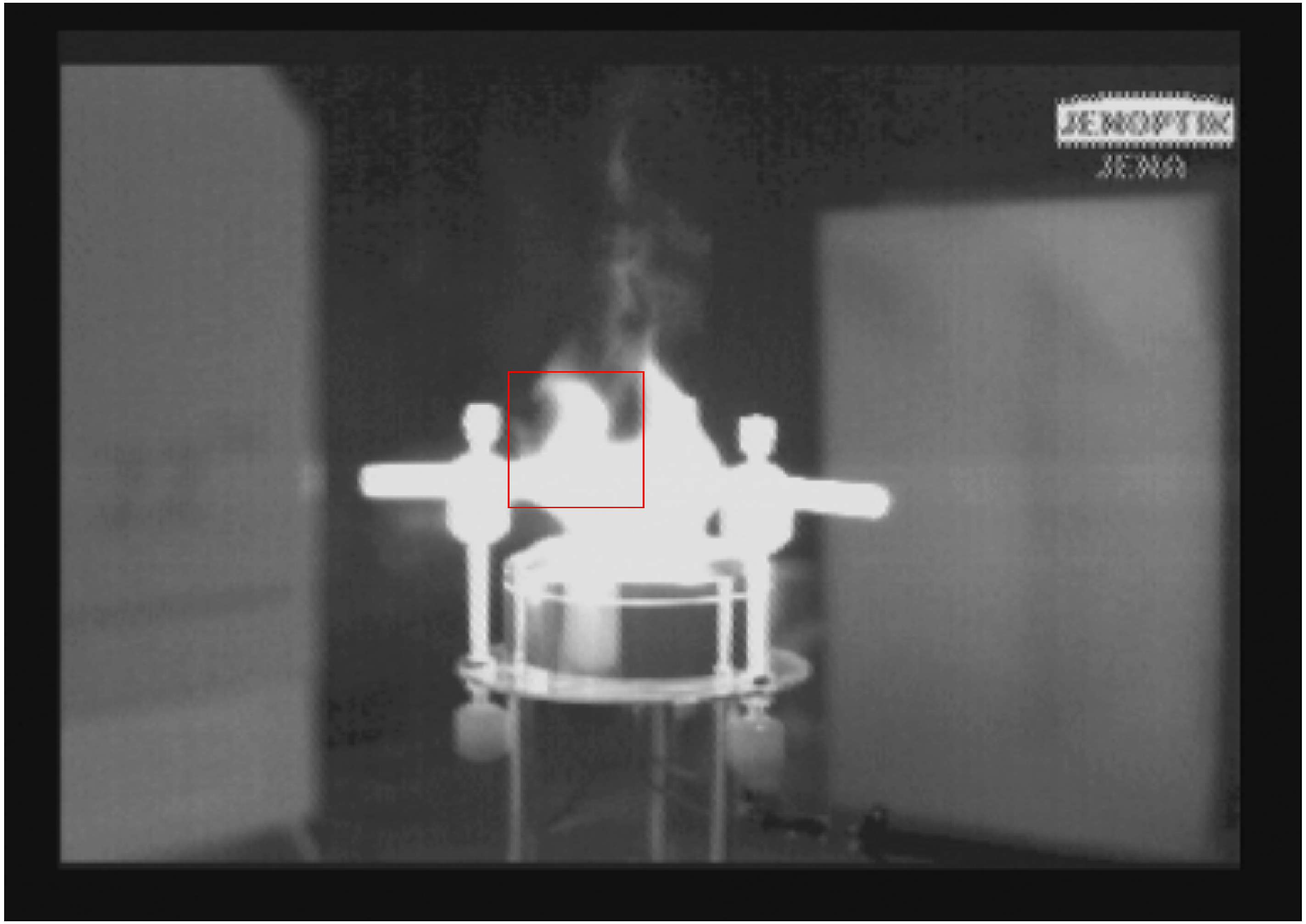
Burner experiments

McKenna burner

Hot gas cell



Thermo image from McKenna burner powered with 30 % of C_2H_4 and 30 % of air

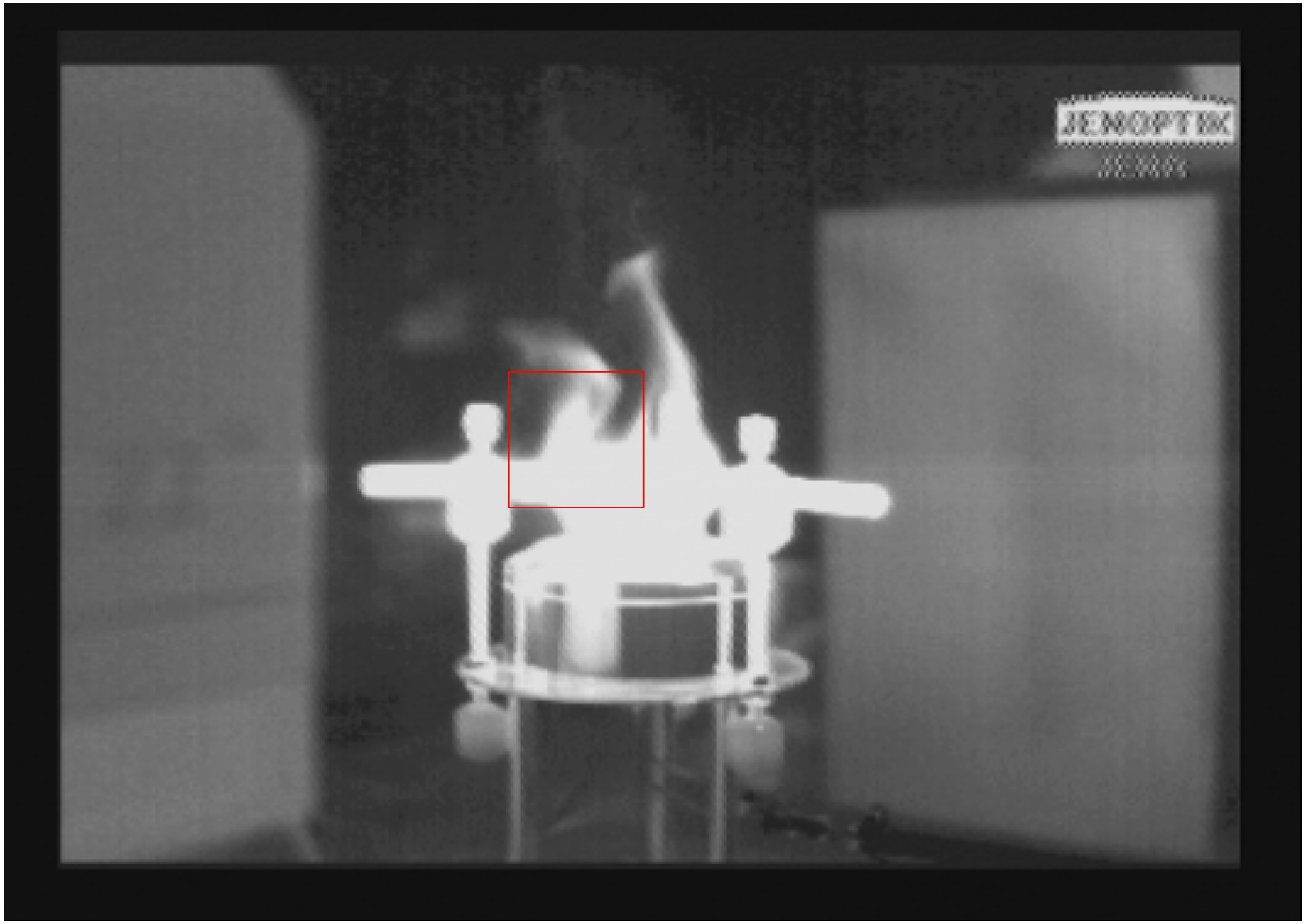


Thermo image from McKenna burner powered with 30 % of C_2H_4 and 30 % of air

Burner experiments

McKenna burner

Hot gas cell



Thermo image from McKenna burner powered with 30 % of C_2H_4 and 30 % of air

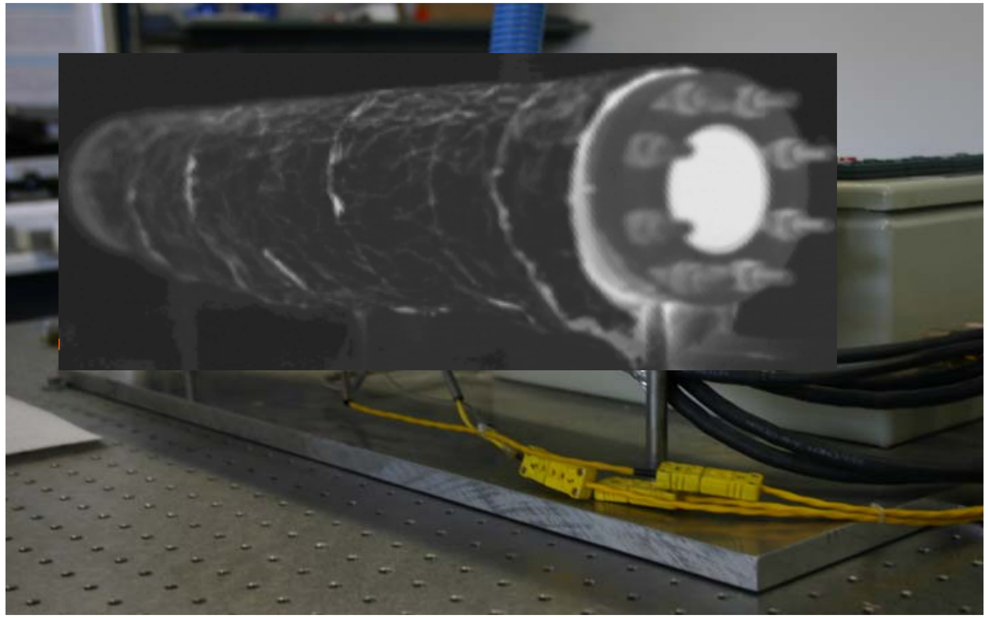
Experiments with calibration flame

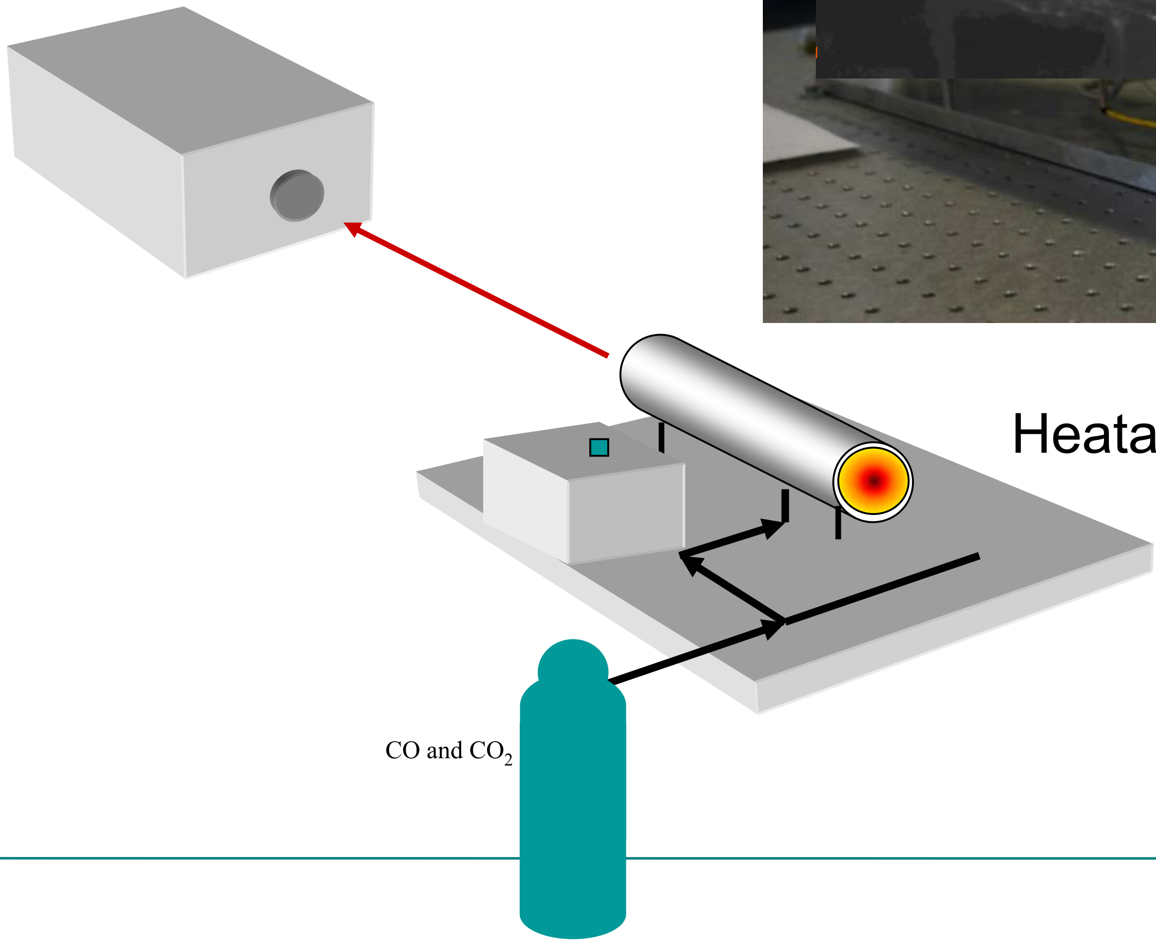
Measurements with a McKenna burner to determine CO and NO concentrations as well as temperature

Influences by any air streaming

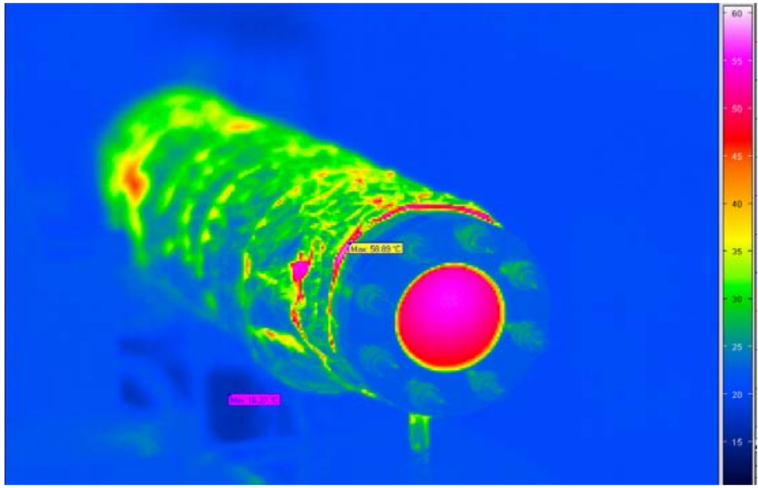
Repeatability of the experiment is not reliable

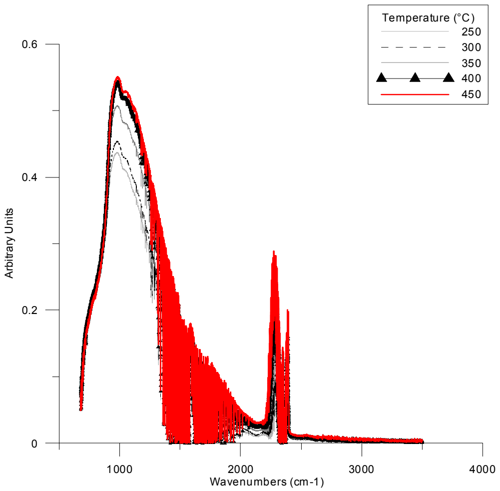
Calibration flames are much easier to handle than a burner but the same difficulties exist with added calibration gases

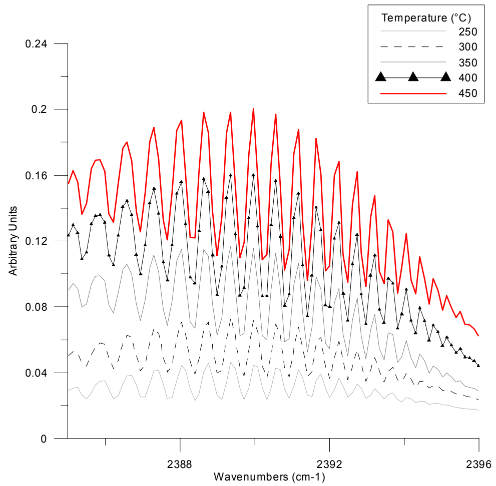


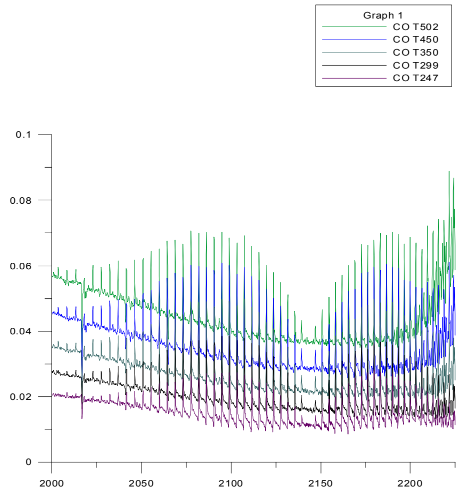

Spectrometer
Heatable Gas Cell
CO and CO_2

Absorption path length: 50 cm
Diameter: 5.5 cm
Window material: Calcium fluoride
Calibrated gas mixture:
CO_2 3.5%, CO 500ppmV and air
Temperature range: 300 - 750 K.









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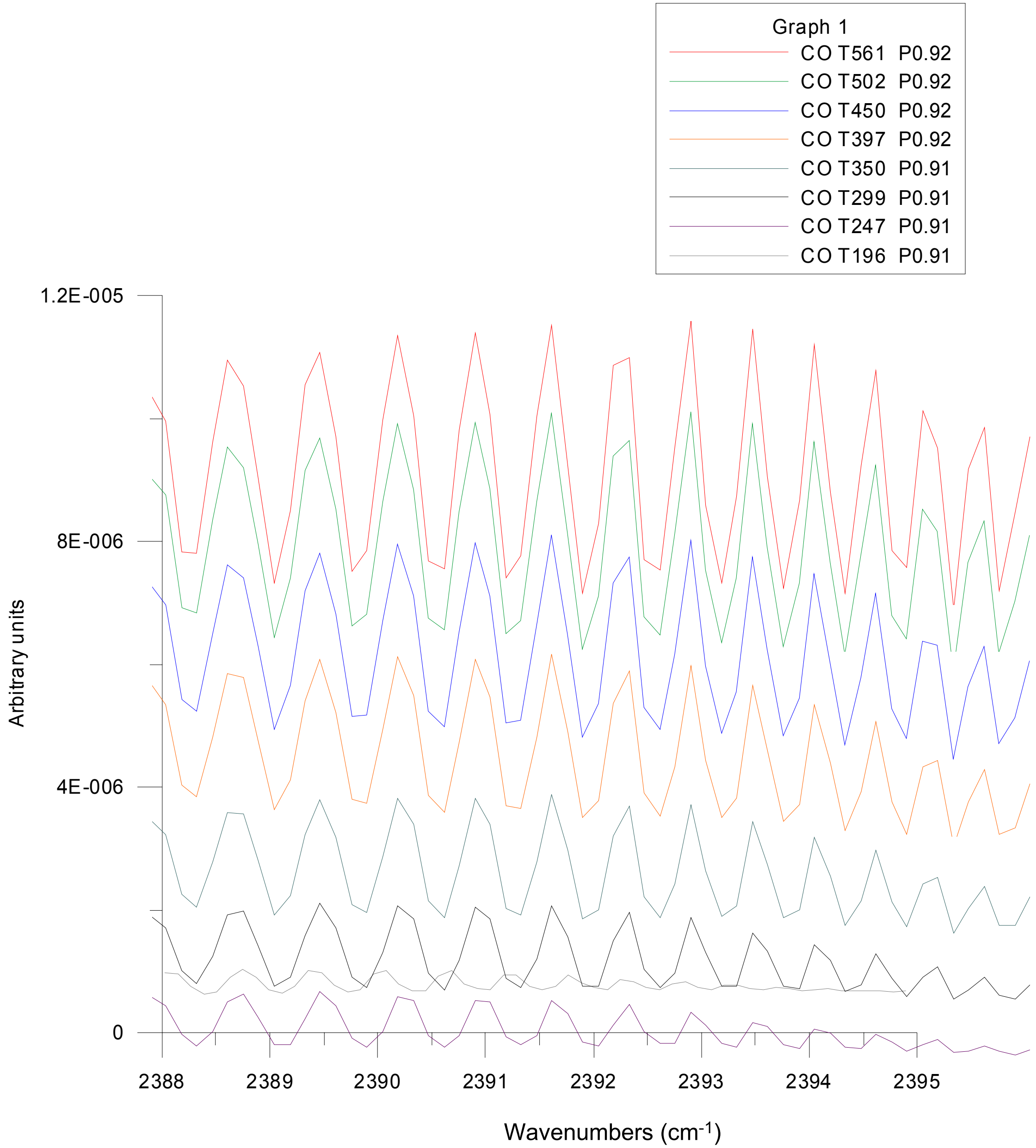
Burner experiments

McKenna burner

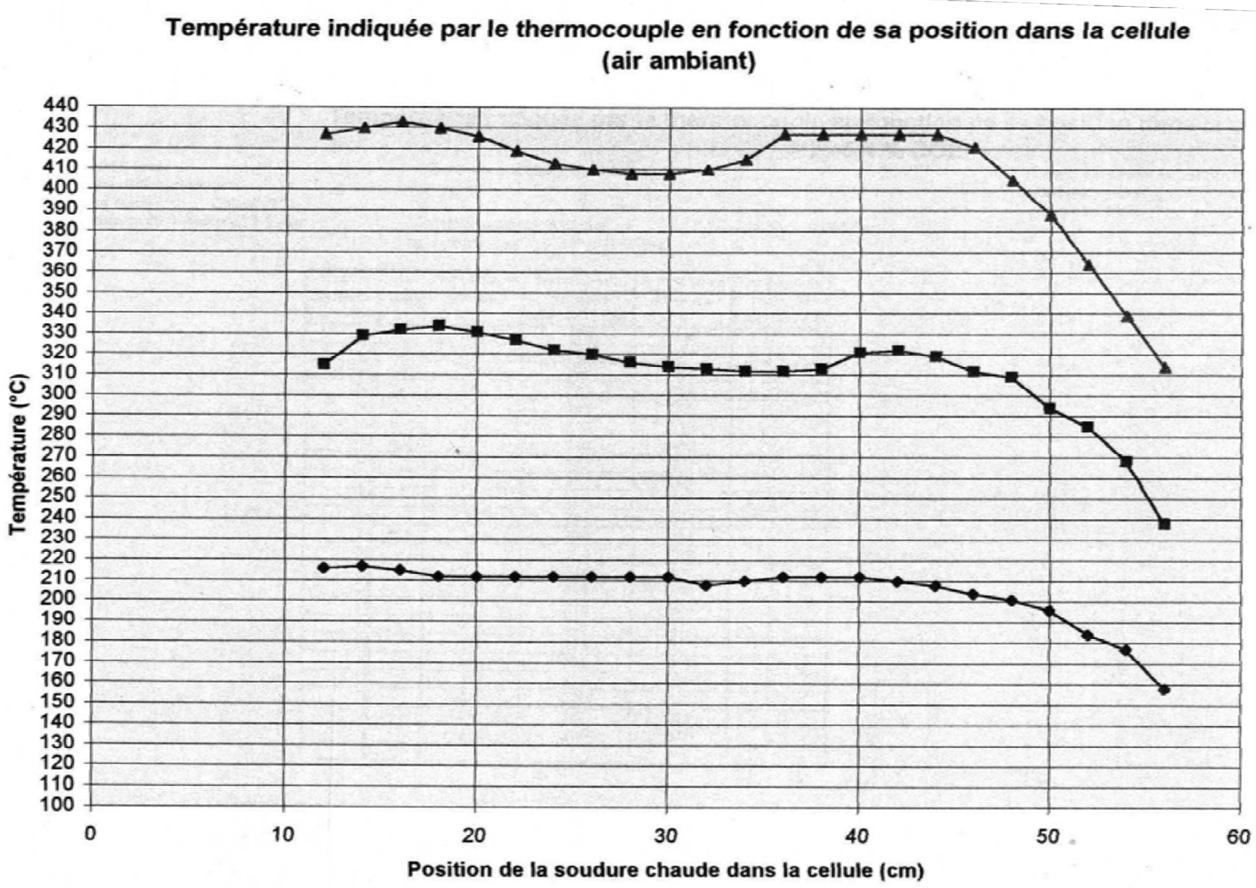
Hot gas cell



Burner experiments

McKenna burner

Hot gas cell



Experiments with heatable gas cell

Experiments with the hot cell includes a heatable cell, thermo-couples for temperature control, manometer and a regulation device

Cell was operated with a constant gas mixture (CO_2 and CO in synthetic air) in the cell during the measurement (no gas flow)

Materials for temperatures higher than 500°C are necessary

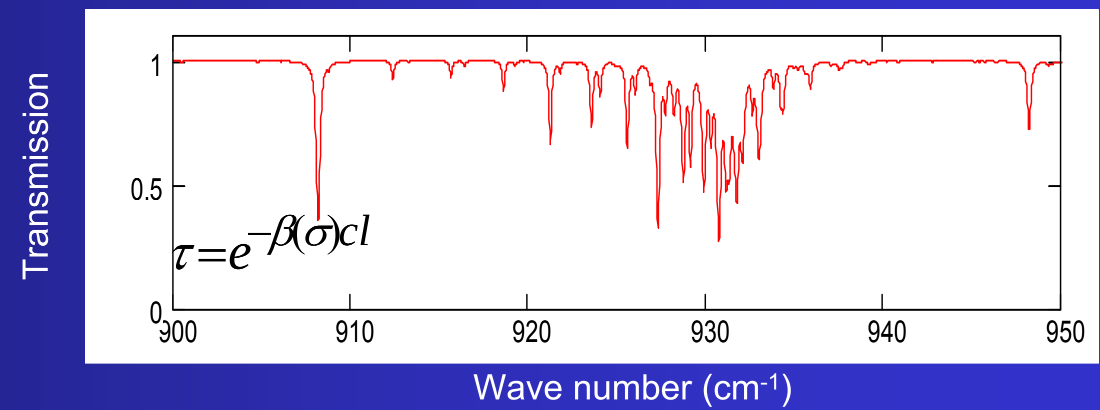
In-homogeneities of temperature and mixed gases inside the cell and influences by windows and walls of the cell

Calibration with determination of real ILS

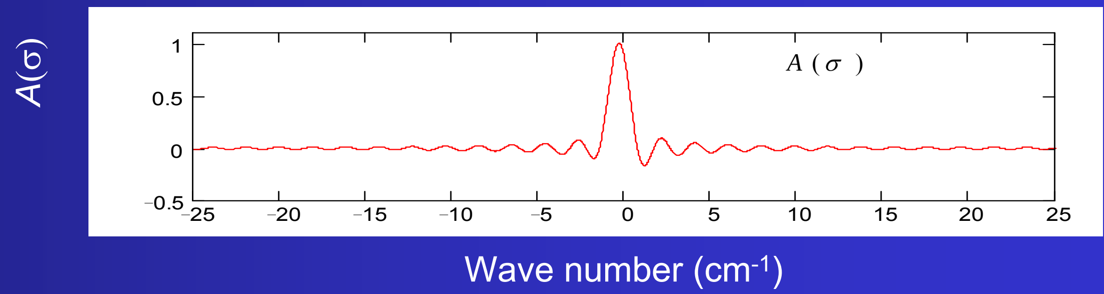
Non-linear Modelling Example: Spectrum of Ammonia

Example:

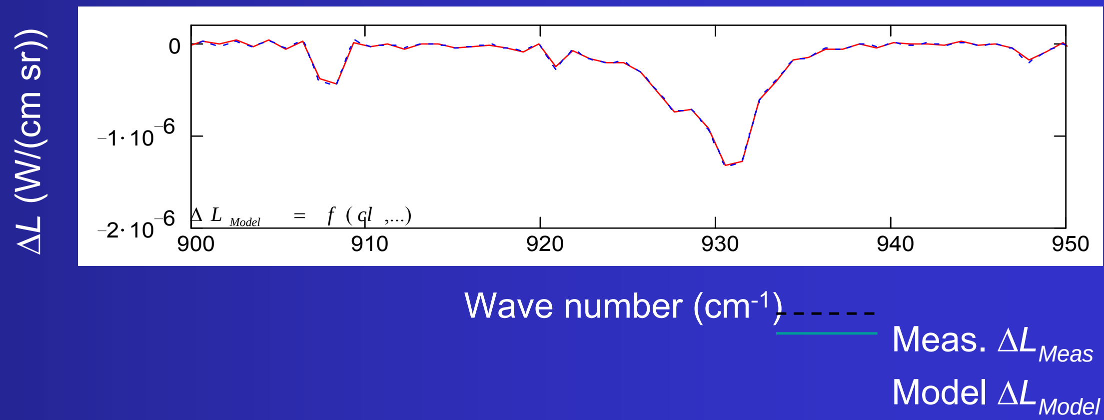
Radiative transfer model



Real ILS

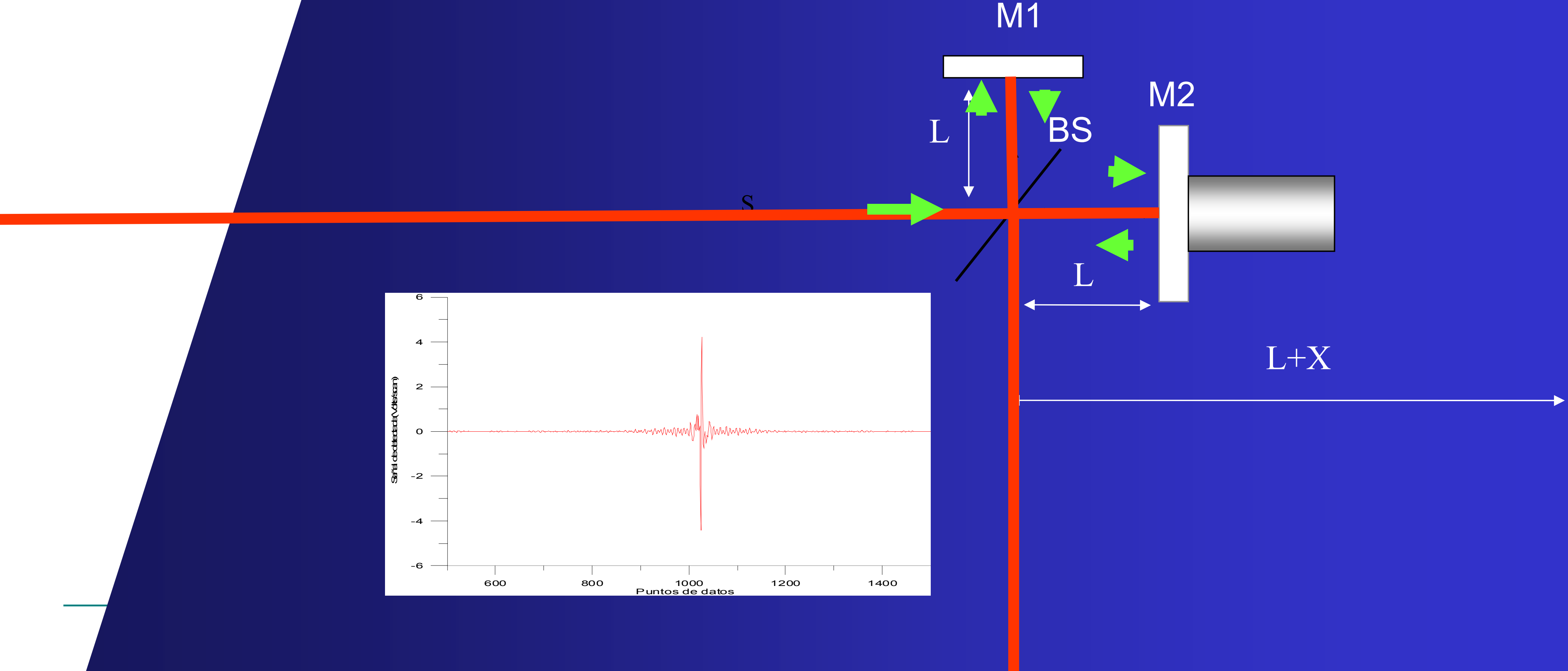


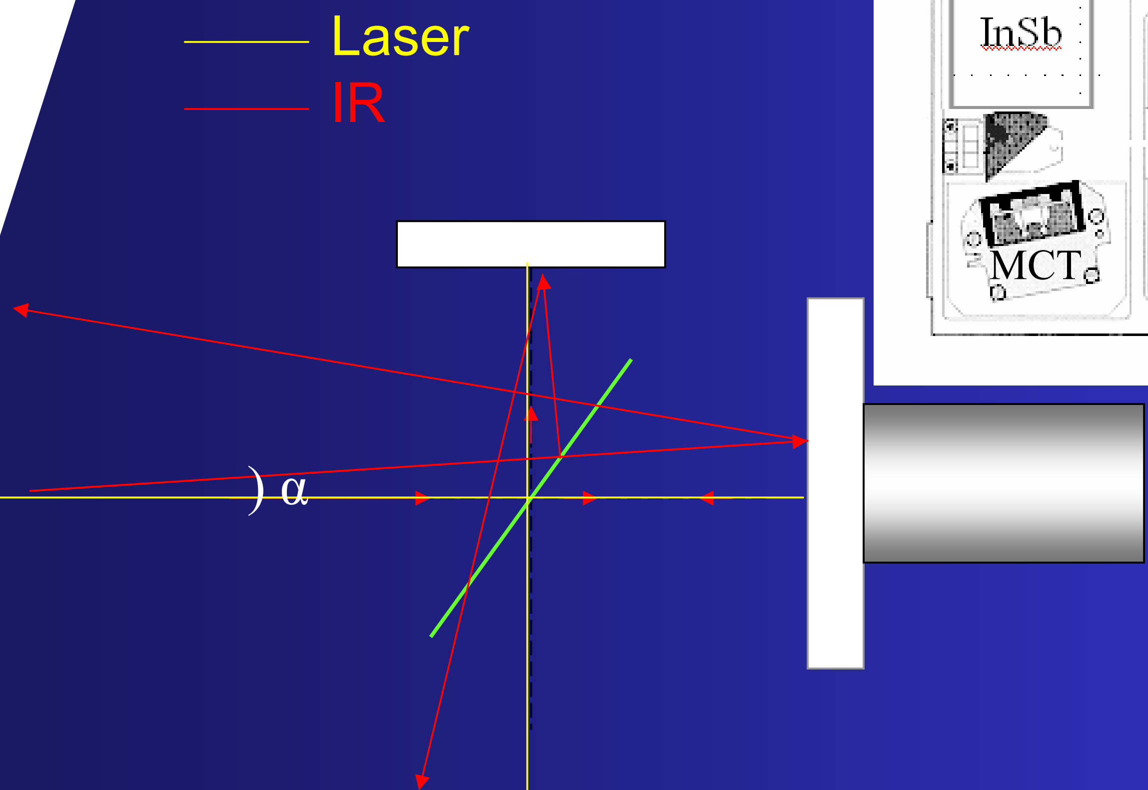
Calculated and measured radiance

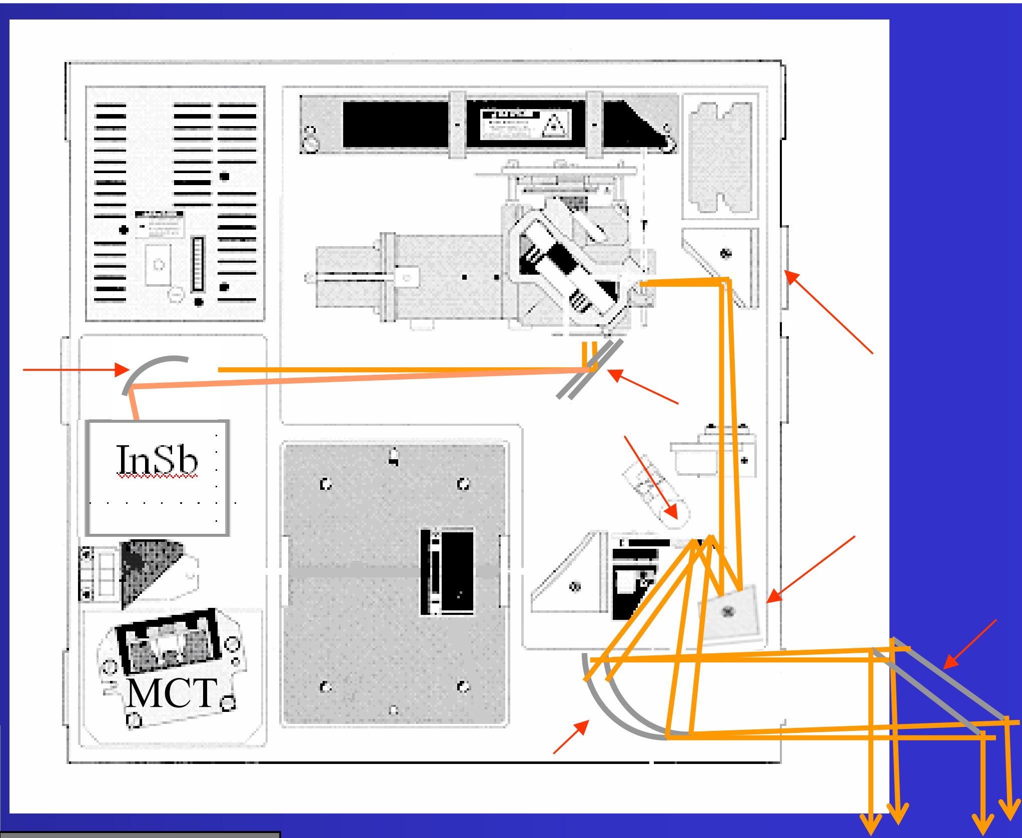


ILS

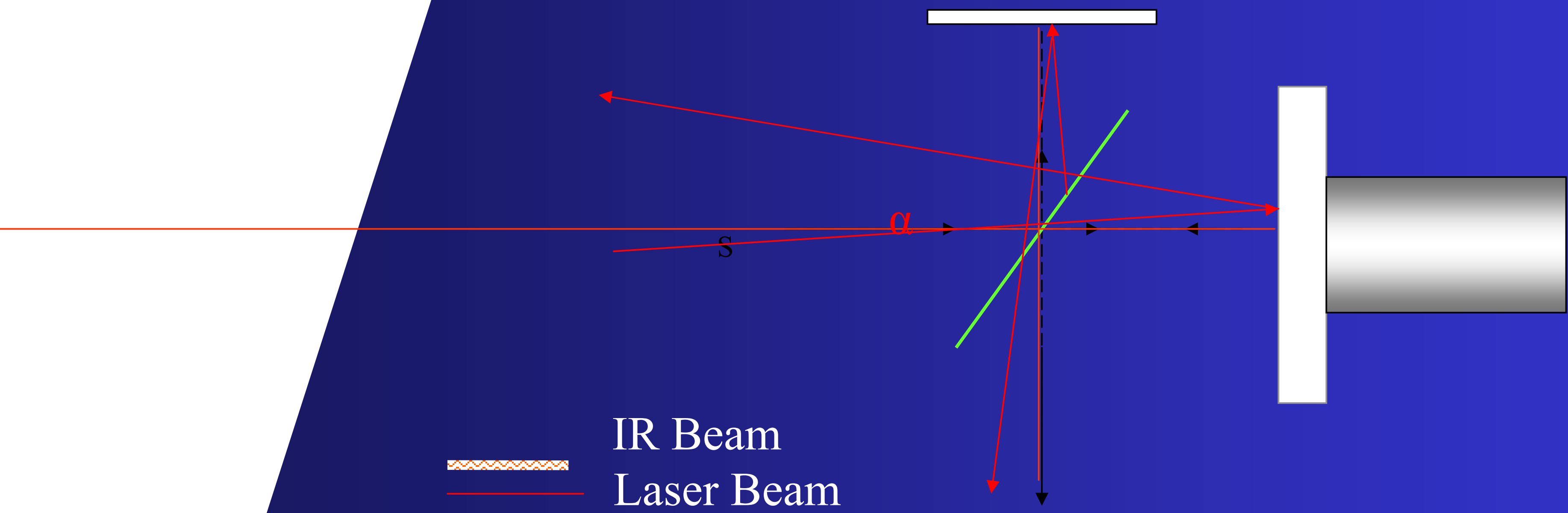
For an ideal interferometer operating with perfectly collimated radiation, the ideal instrumental line shape A_0 will be given by the Fourier transform of the function that will describe the finite movement of the mirror.

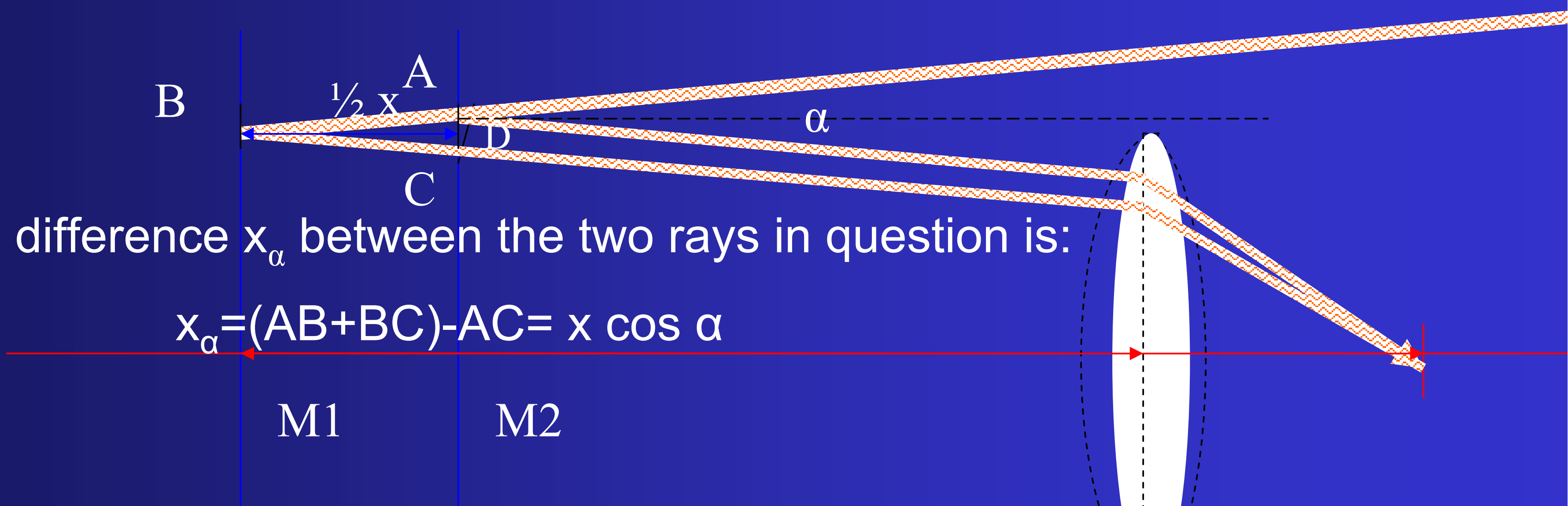



Laser
IR
α


InSb
MCT

Phase error- wrong sampling points





The path difference x_α between the two rays in question is:

$$x_\alpha=(AB+BC)-AC= x \cos \alpha$$

Determination of the real ILS

- Absorption experiment

  Gas with well separated lines and narrower than the resolution of the spectrometer: NH_3, CO

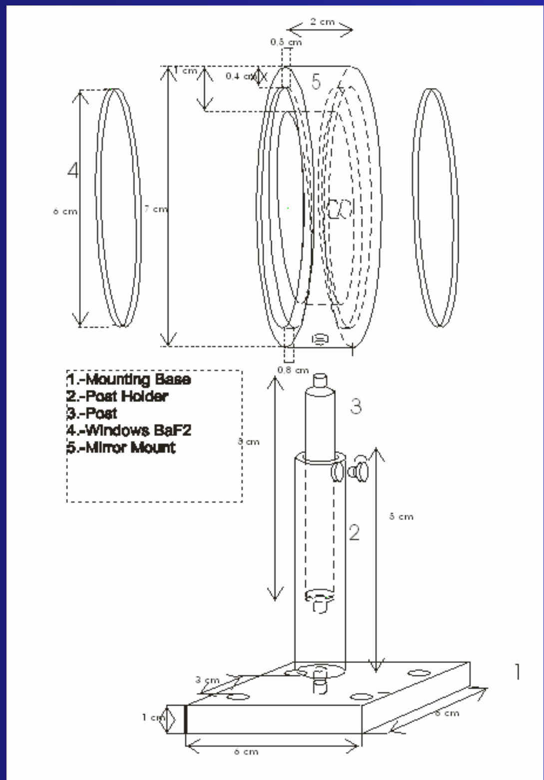
- Sub-models:

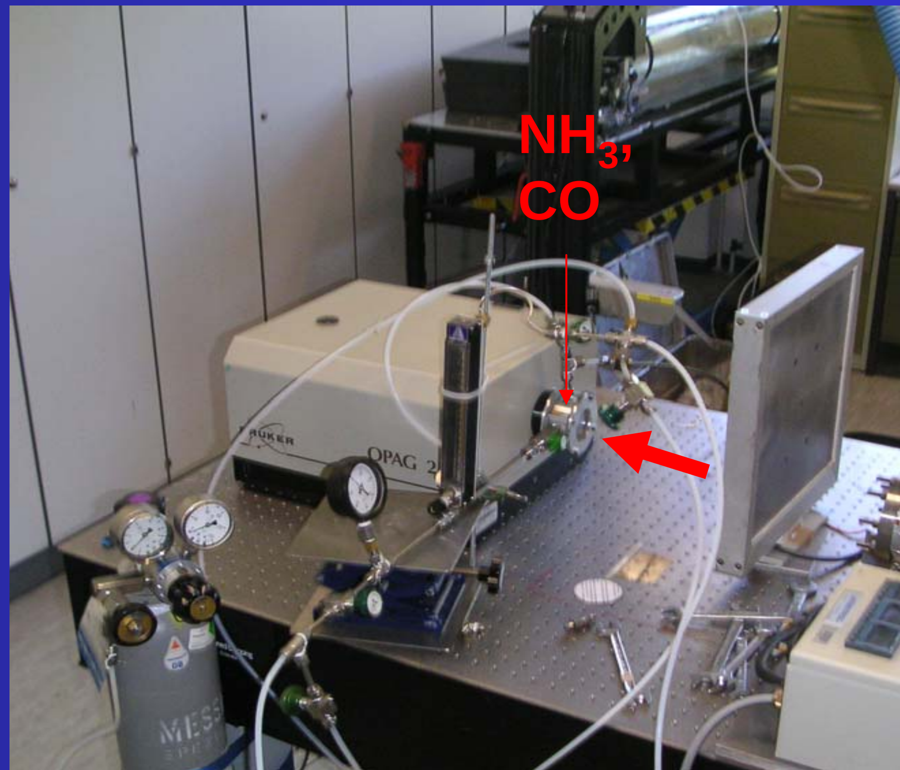
  Radiative transfer model

  Model of the ILS

Transmittance of a gas

Material: Stainless-steel
Optical depth: 1 cm
Field of view: 5 cm
Window material: BaF_2

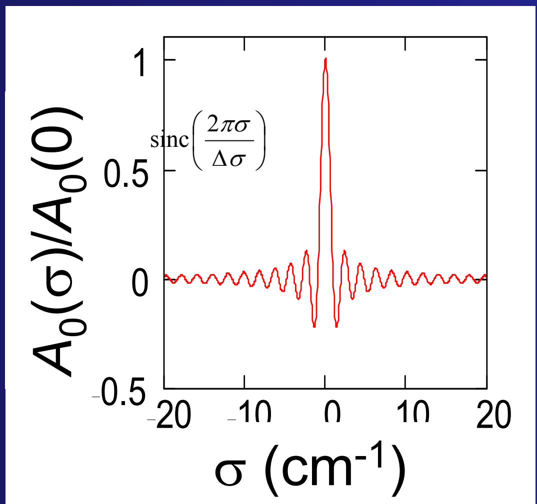


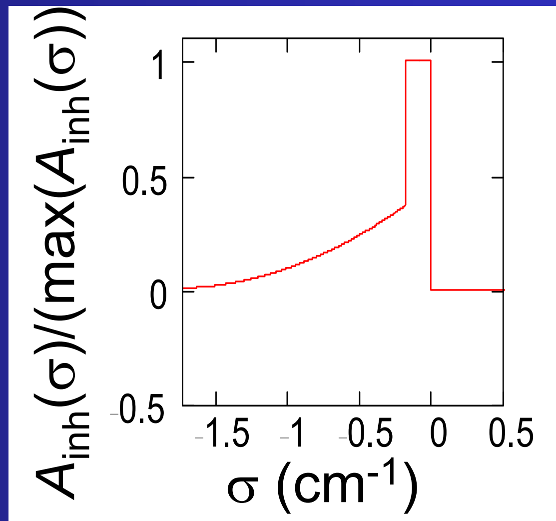


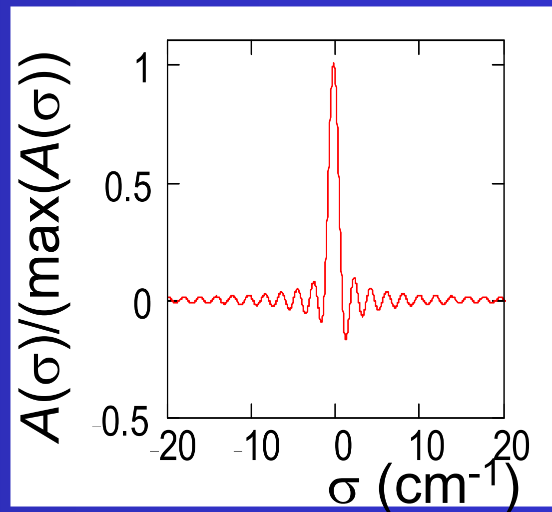
Real ILS calculation

Calculation of the Instrument Line Shape (ILS):
Model for Real Instrument

Ideal ILS:		Model for the inherent ILS:		Real ILS:
$A_0(\sigma, \Delta\sigma)$	*	$A_{inh}(\sigma, p_1..p_Q)$	=	$A(\sigma)$



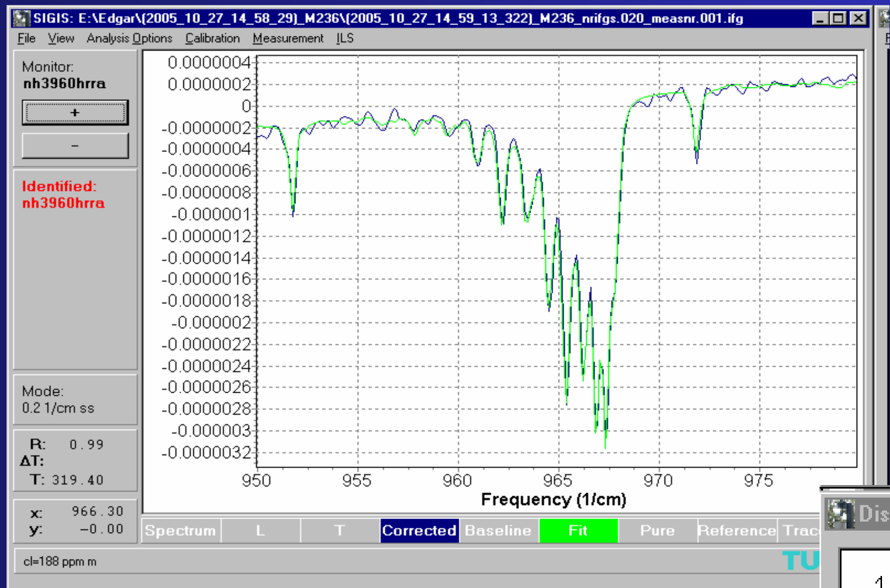


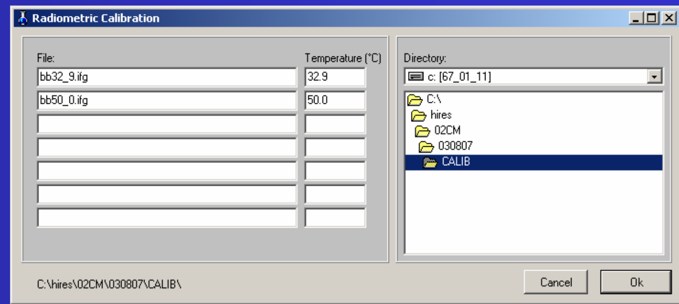


ILS determination

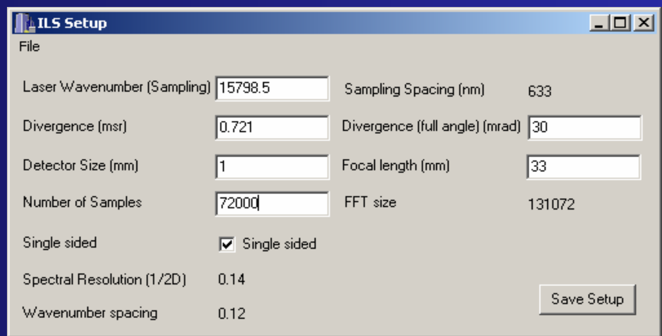
User Interface

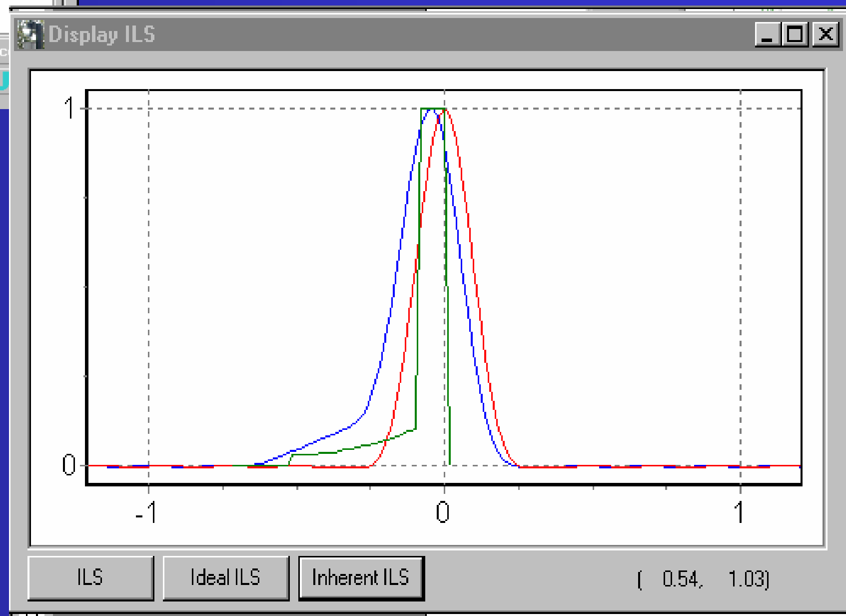
Calibration





ILS Visualization





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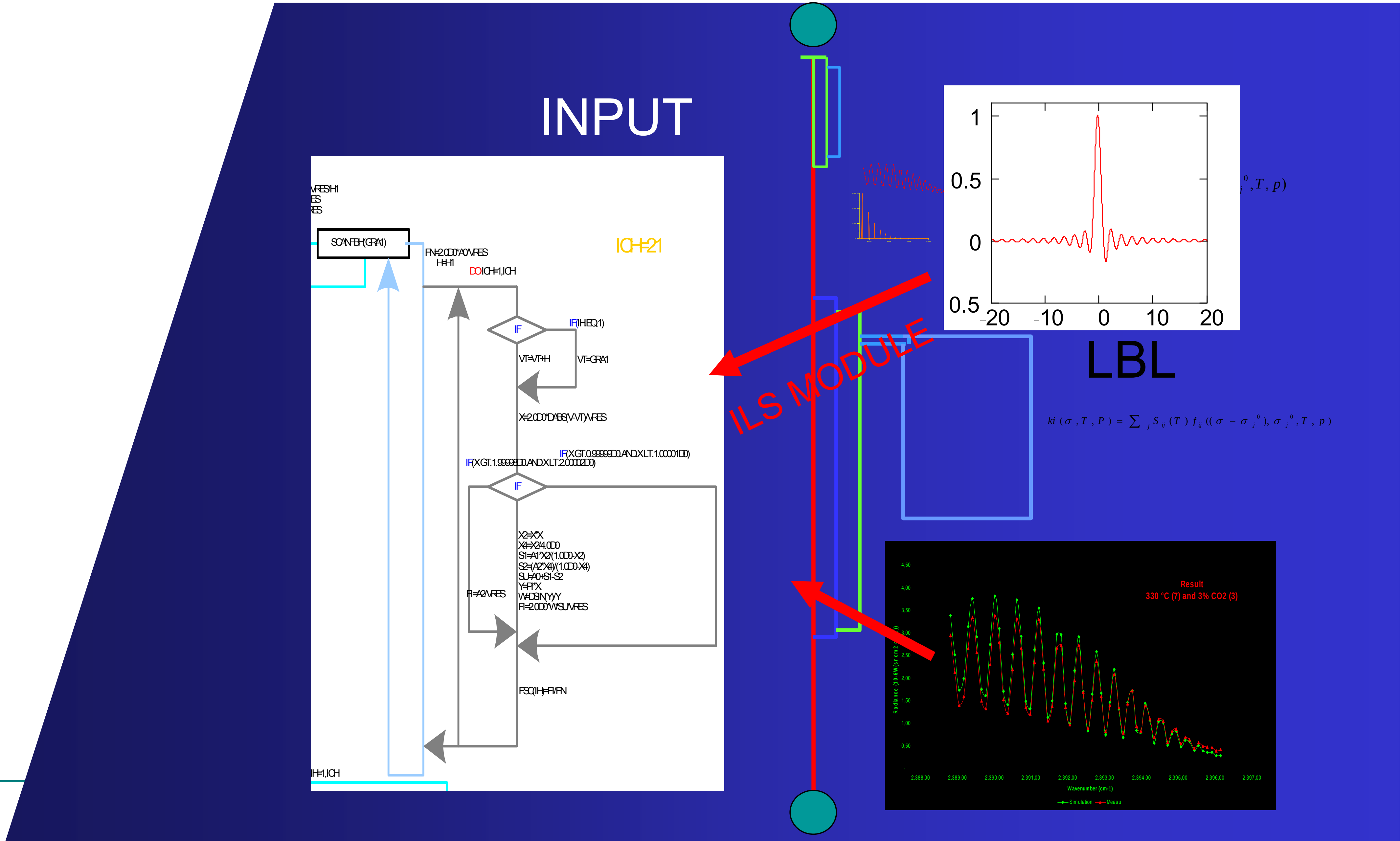
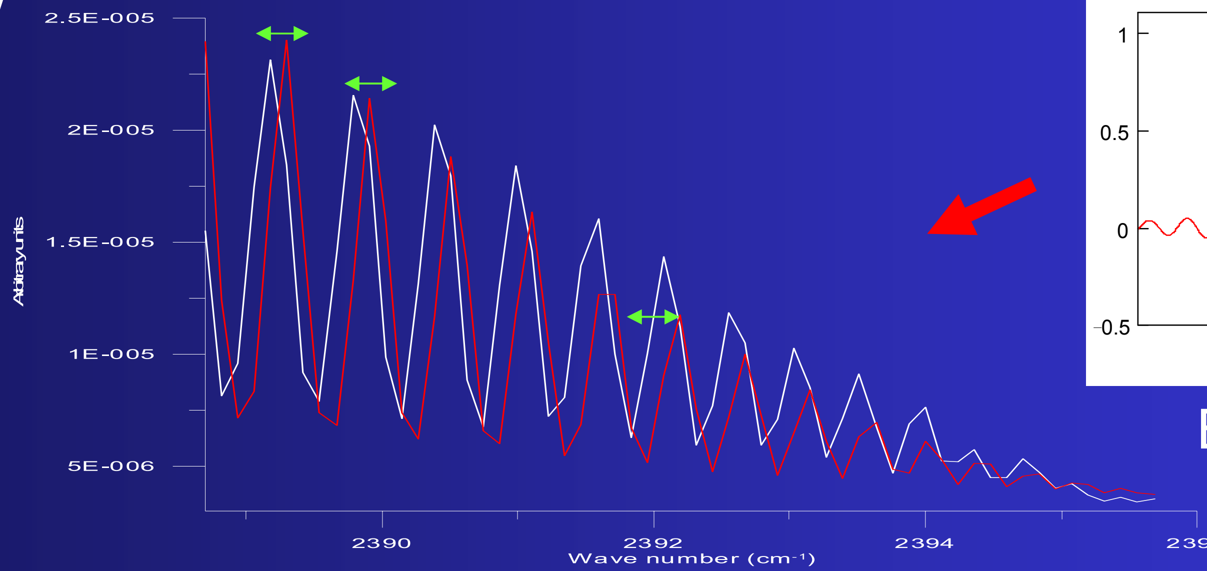
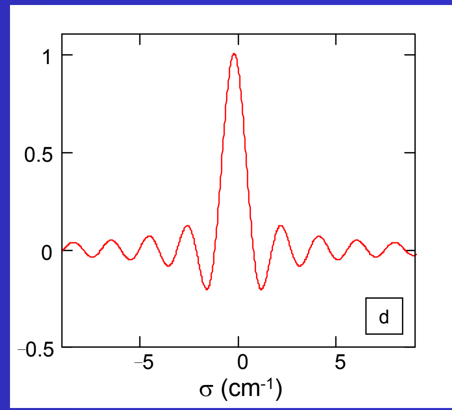
MAPS



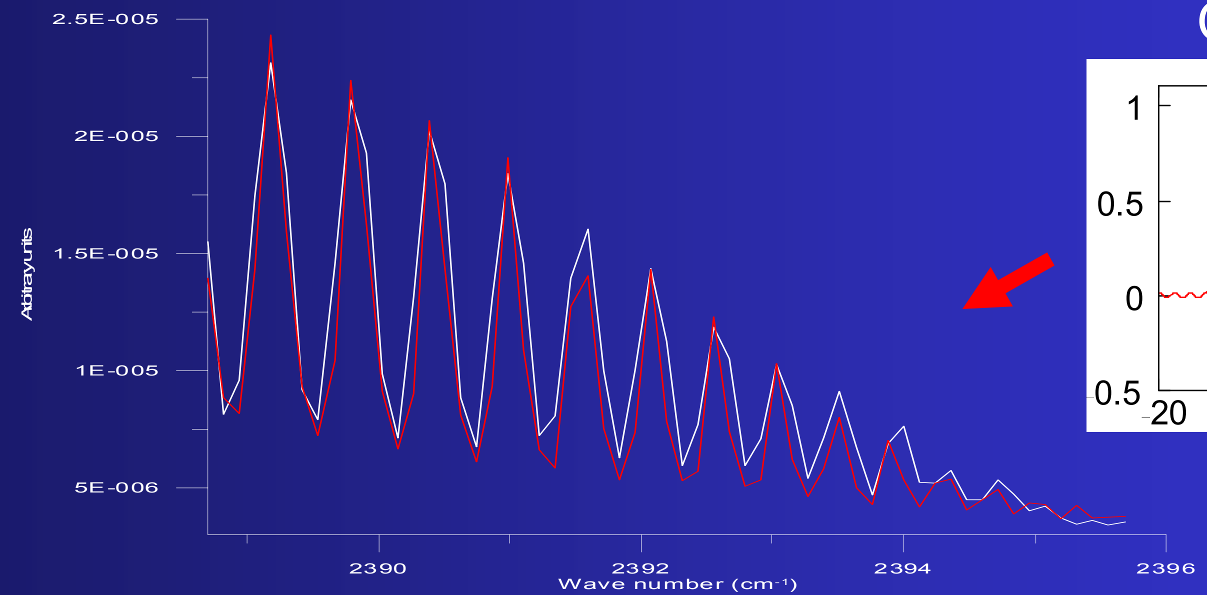
Implementation

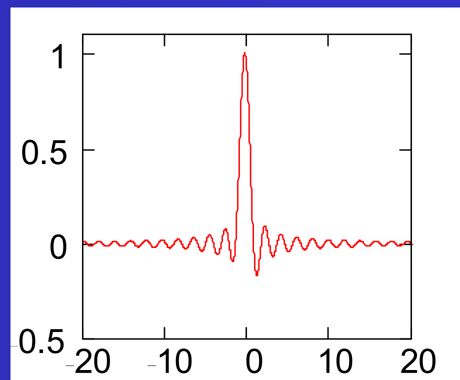




BH ILS

OPAG ILS





Acknowledgements

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Burner measurements were supported financially by ENI (Italy) also.