WORKSHOP ZERO GASES

Measurement methods for zero gases

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LNE

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Context

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- Specifications for purity of zero gas given by european standards for the measurements of NOx (EN14211) and SO_2 (EN14212) in air
  - Relevant impurities in zero gas : NO / NO_2 / SO_2 / NH_3 / H_2O / H_2S /CO_2 / O_3

Species	Limit Value (nmol/mol)	Specification zero gas
NO	-	≤ 1 nmol/mol
NO_2	21 (calendar year)	≤ 1 nmol/mol
SO_2	47 (one day)	≤ 1 nmol/mol
NH_3	-	≤ 1 nmol/mol
H_2O	-	≤ 150 µmol/mol
H_2S	-	≤ 0.1 µmol/mol
CO_2	-	≤ 4 µmol/mol
O_3	60 (8 hours)	≤ 2 nmol/mol

- To meet the requirements of european standards for zero gas

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Objectives

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- Measurement of impurities in zero gas
  - To develop a measurement approach with existing and novel optical techniques
  - To measure low concentrations by optical techniques and by classical detection techniques combined with the standard addition method
- Improvement of the measurement capabilities for impurities in zero gas
  - Reduction of the uncertainty of the measurement for chemical pollutants in air
- Application of the developed measurement approaches
  - Testing of cleaning systems

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Available techniques for NO/NO_2

Principle	Typical detection limit (nmol/mol)	Price indication	Known issues
Chemiluminescence	1 (NO/ NO_2)	10 k€	- Cross-sensitivity to other nitrogen oxides - Cross-sensitivity to VOCs
UV photometer	1000 (NO_2)		
FTIR	4 (NO) 2 (NO_2)	40 k€	- Volume - Path of the cell
QC-Spectrometer	0.1 (NO/NO_2)	50 k€	- Limited life time lasers
BB-CEAS	0.1 (NO_2)	6 k€	

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Activities in MACPoll for NO/NO_2

Develop and/or test conventional methods:

- Trace detection of NO_2 with chemiluminescence and zero gas measurement by standard addition (NPL, SMU, VSL)

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Standard addition -1

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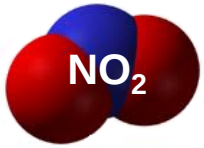
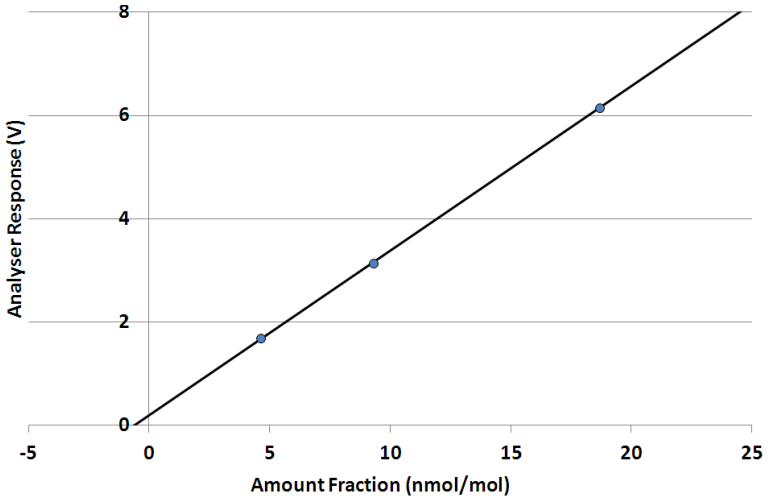
- Novel method for quantification of NO and NO_2 in zero gas
- NPL Adjustable Gas Standard (AGS)
- Portable dilutor
- Calibrated with NPL PRGMs





- Reference standards from 0.5 nmol/mol – 20 nmol/mol
- Quantification by standard addition using chemiluminescence

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Standard addition -2

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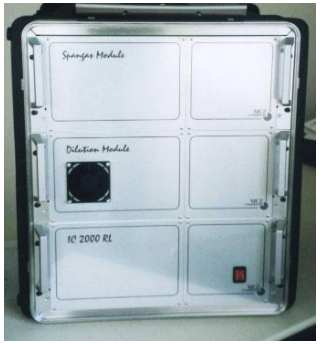
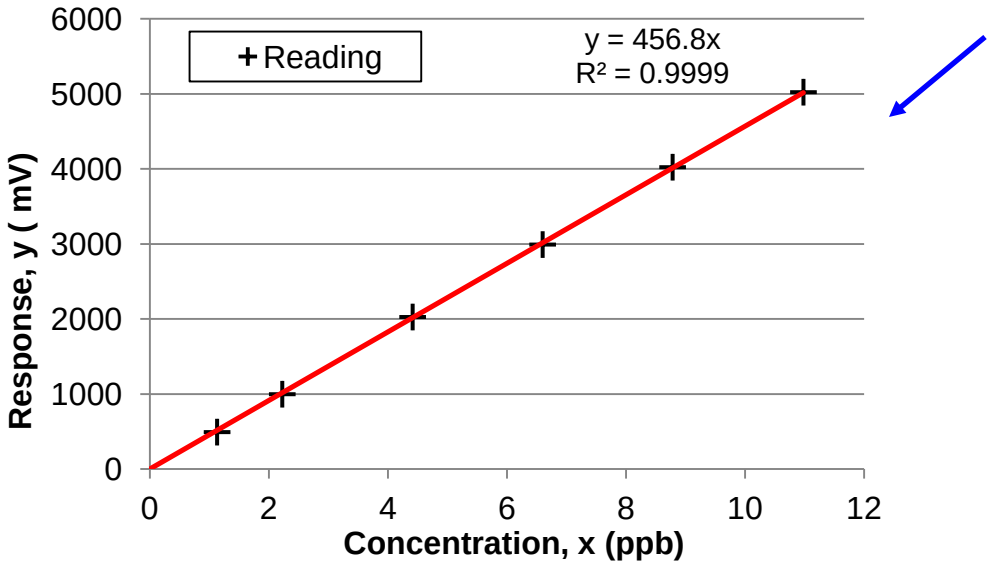
VSL : Thermo 42i TL
SMU : Thermo 42C

VSL : Molbloc/molbox system with MFCs at 200 and 5000 sccm (Fluke)

SMU : CGM2000 MCZ system



Dilution of reference standards



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Activities in MACPoll for NO/NO_2

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Develop and/or test conventional methods:

- Trace detection of NO_2 with chemiluminescence and zero gas measurement by standard addition (NPL, SMU, VSL)

Develop and/or test novel 'absolute' optical methods:

- Home-built LED-based CEA-spectrometer (VSL)
- Commercial cavity ring down spectrometer (NPL)
- Commercial QCL-based absorption spectroscopy (LNE)

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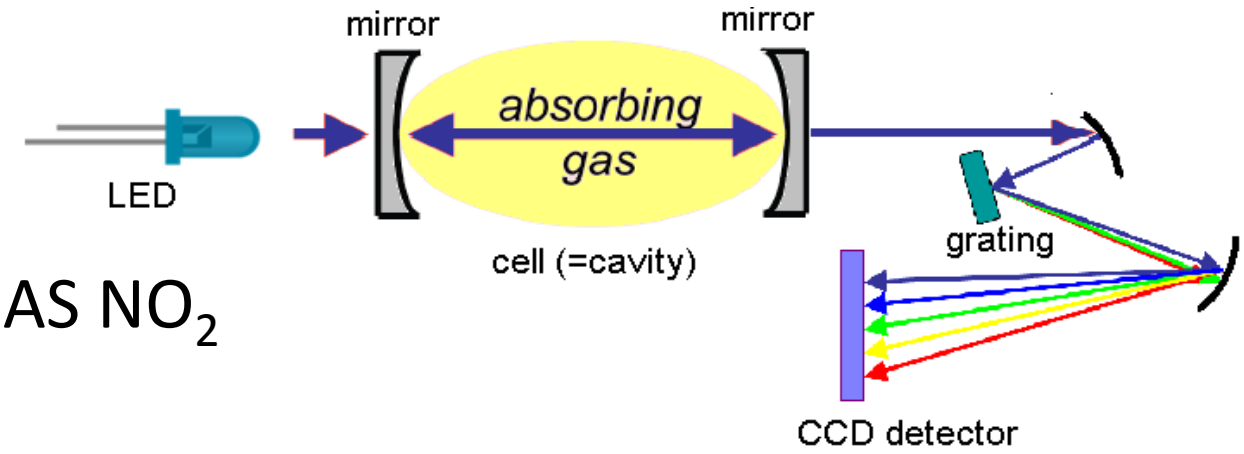
Absolute optical methods -1

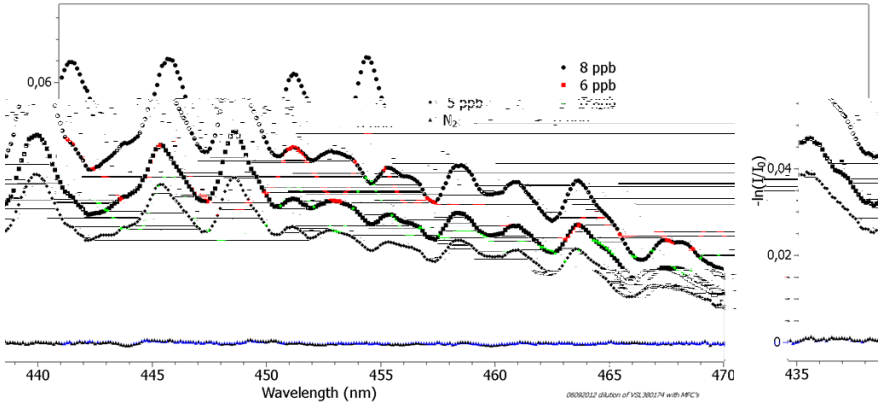


Broadband CEAS NO_2

- Trap light within the optical cavity formed by 2 highly reflective mirrors
- Measure intensity transmitted through the cavity
- Effective absorption pathlength of many kilometers

⇒ Relatively inexpensive

⇒ Detection limit
about 0.1 nmol/mol



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Absolute optical methods -2

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NO_2 facility based on CRDS

- Used to validate reference standards from 100 – 1000 nmol/mol generated by dynamic dilution (Molbox/Molbloc)
- Used to measure NO_2 trace levels in zero gas
- Selective technique for the analysis of NO_2
- Direct measurement with lower uncertainty

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Absolute optical methods -3

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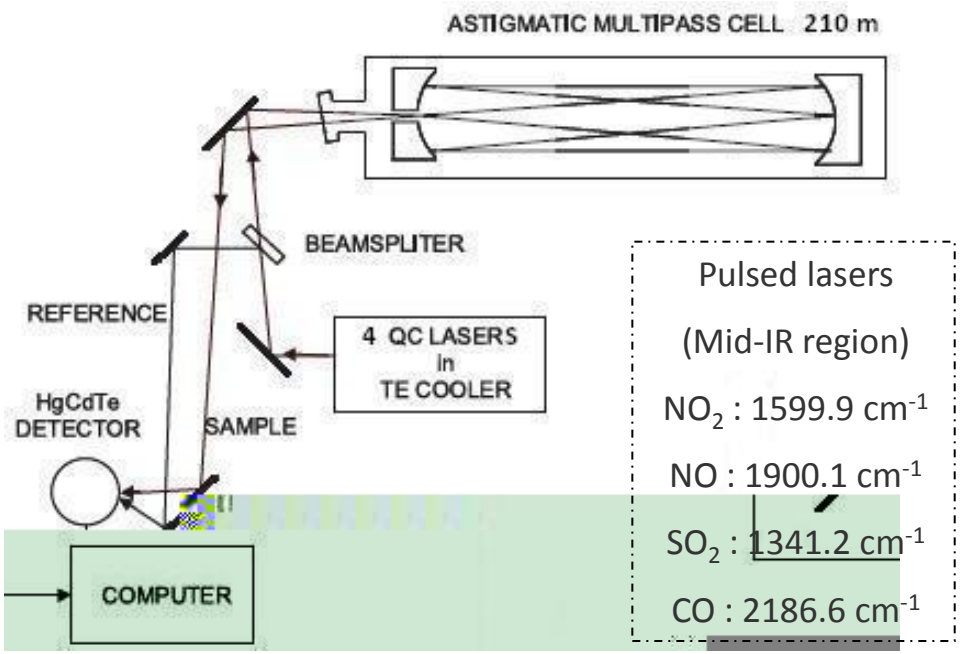


Pulsed lasers

(Mid-IR region)

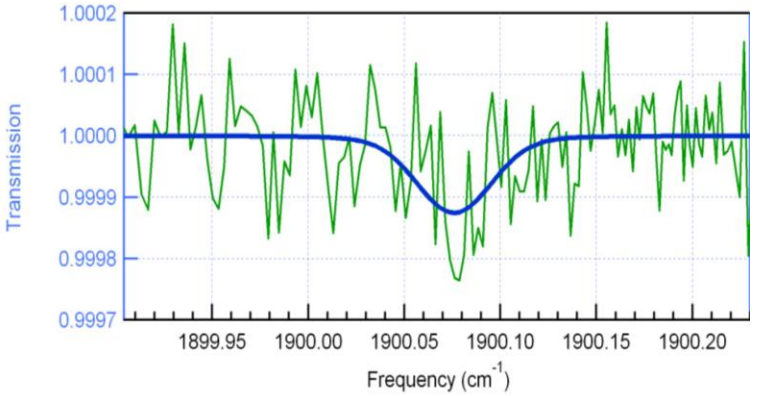
NO_2 : 1599.9 cm^{-1}

NO : 1900.1 cm^{-1}

SO_2 : 1341.2 cm^{-1}

CO : 2186.6 cm^{-1}

QC-TILDAS (Mid-IR)



[NO] = 1.5 ± 0.5 nmol/mol

- Detection limit ~ 0.5 nmol/mol
- Main uncertainties : line strengths (Hitran database) & fitting

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Available techniques for SO_2

Principle	Typical detection limit (nmol/mol)	Price indication	Known issues
UV fluorescence	1	15 k€	- Cross sensitivity: NO, NO_2, HC, H_2S, H_2O, hydrocarbons - Quenching effect: O_2
Ionic chromatography	40		- Liquid matrix
FTIR	2	40 k€	- Path of the cell
QC-Spectrometer	0.1	50 k€	- Limited life time lasers

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Activities in MACPoll for SO_2

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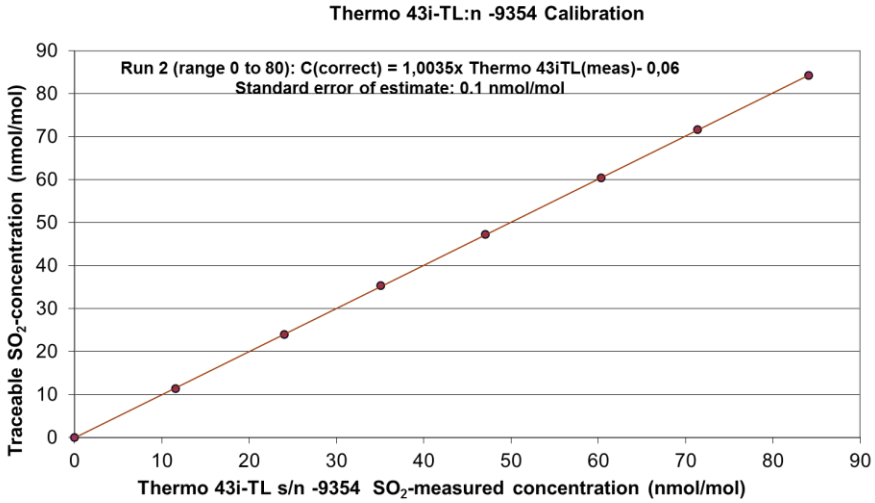
Develop and/or test conventional methods:

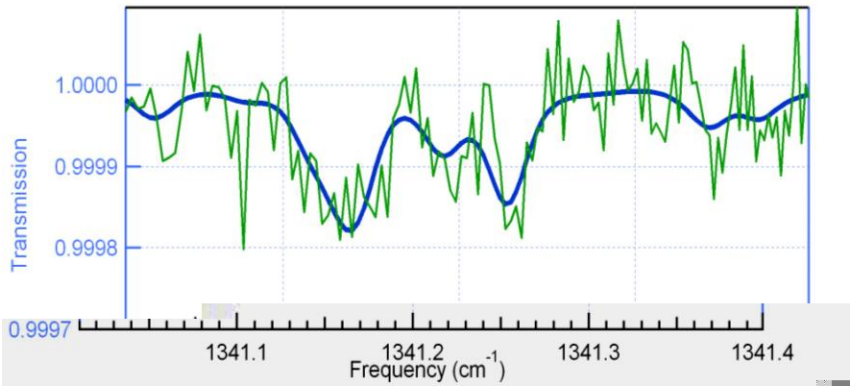
Trace detection of SO_2 with UV fluorescence and zero gas measurement by standard addition (FMI, SMU)



Develop and/or test novel 'absolute' optical methods:

Commercial QCL-based absorption spectroscopy (LNE)

$[SO_2]$ = 2.2 ± 0.3 nmol/mol



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Available techniques for NH_3

Principle	Typical detection limit (nmol/mol)	Price indication	Known issues
FTIR	1	40 k€	- Path of the cell
QCL-based CEAS	3	20 k€	- Difficult alignment
NIR-laser based CRDS	1	15 k€	- Vulnerable to mirror contamination

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Activities in MACPoll for NH_3

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Set-up of a system for the measurement of trace levels of NH_3 based on cavity ring-down spectroscopy in two different spectral regions

- Near-IR (University of Helsinski)
- Mid-IR (VSL)

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Absolute optical methods -1

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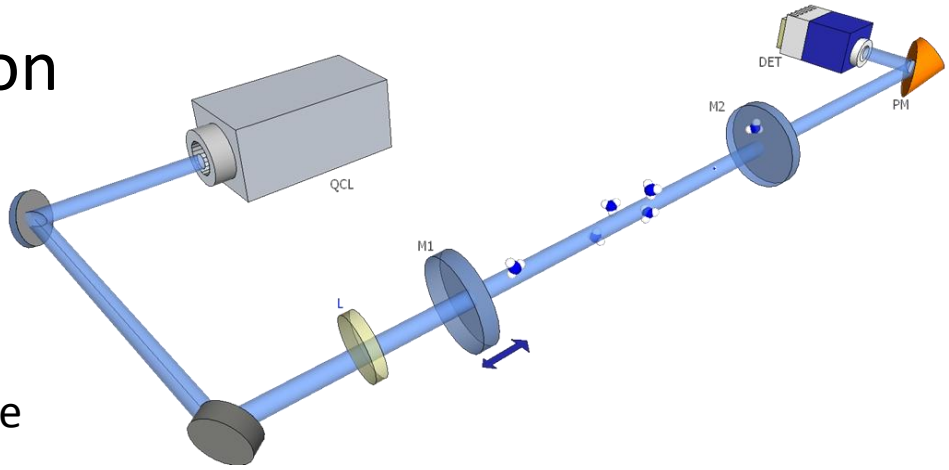
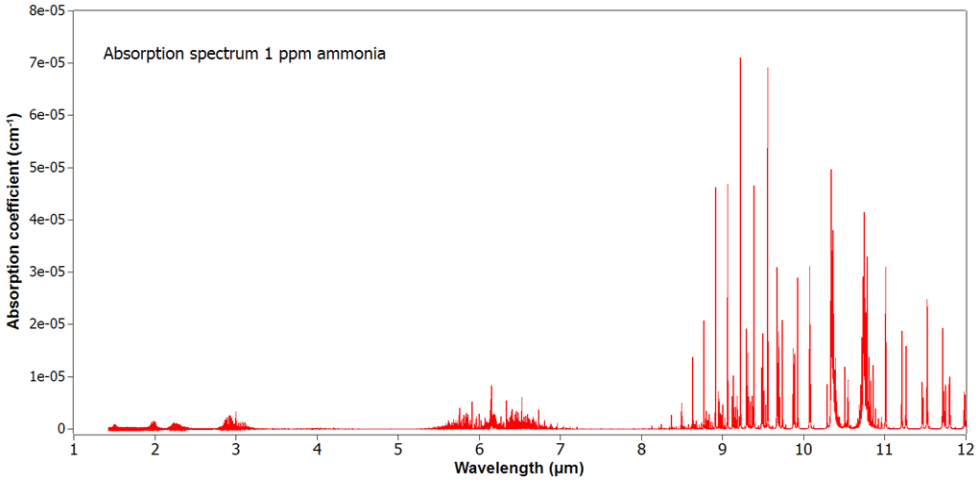
Cavity-enhanced absorption spectroscopy (Mid-IR)



- Laser scans at a few kHz over the absorption line
- Data are averaged over 1 second or more
- $\lambda_{detection}$=9.5 µm



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Absolute optical methods -2

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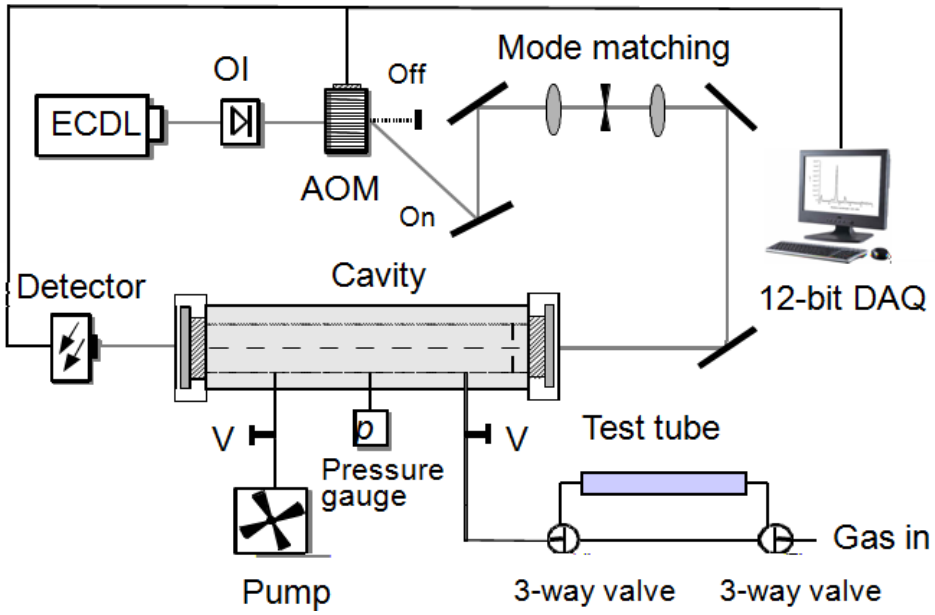
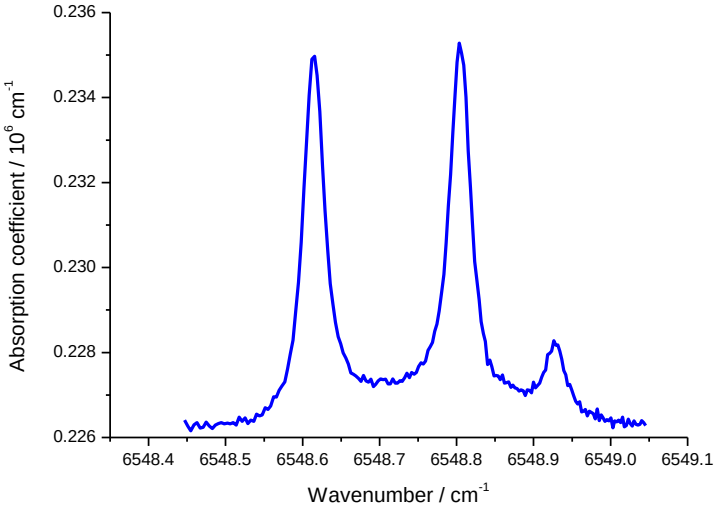
Cavity ring down spectrometer (Near-IR)





$[NH_3]$ = 91 nmol/mol

Line strength (6548.79 cm^{-1}, 296 K) = 1.67×10^{-21} cm / molecule

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Available techniques for H_2S, CO_2 and H_2O

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Principle	Typical detection limit (nmol/mol)	Price indication	Known issues
FTIR	2 (CO_2) 100 (H_2O) 400 (H_2S)	40 k€	- Path of the cell
CRDS	1000 (H_2S) 10 000 (H_2O) 1 000 (CO_2)	50 k€	- Spectral interference - Limited life time lasers
Dew point mirror	40 (H_2O)	5-10 k€	- Measuring only water vapour

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Multiplexing optical system

PTB

Laser driver

Diode laser

Detector

DAQ

PC

„TDLAS“: **T**unable **D**iode **L**aser **A**bsorption **S**pectroscopy

H_2O and CO_2

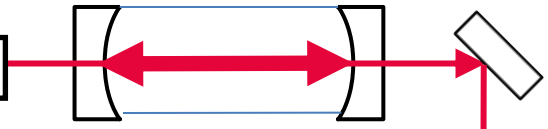
- Light source: 2.7 µm diode laser
- Gas cell: Herriott-cell with 76m optical pathlength

MIKES

Laser driver

Diode laser

„CRDS“: **C**avity **R**ingd**o**wn **S**pectroscopy



H_2S

Detector

DAQ

- Light source: 1.5 µm diode laser
- Gas cell: High finesse optical cavity (~ 10 km effective pathlength)

The two systems are combined through a common gas handling and data evaluation

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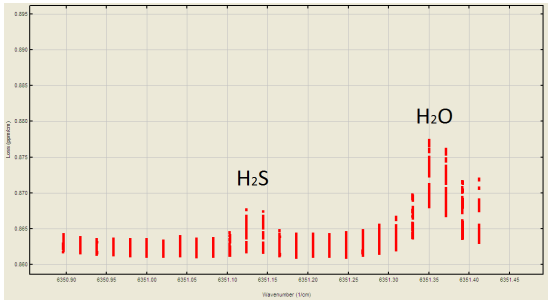
Absolute optical method (H_2S)

Collaboration with Picarro

- CRDS instrument (Picarro G2204) operating at 1574.5 nm with detection limit <2 nmol/mol (1σ, 5 s)
- Simultaneous measurement of H_2O and CO_2 (cross-interference)

- Modification of the instrument for traceable measurements in progress (e.g. T & P of the gas sample)
  - Main uncertainty : H_2S line strength (will be measured using a H_2S permeation source)



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Absolute optical method (H_2O, CO_2)

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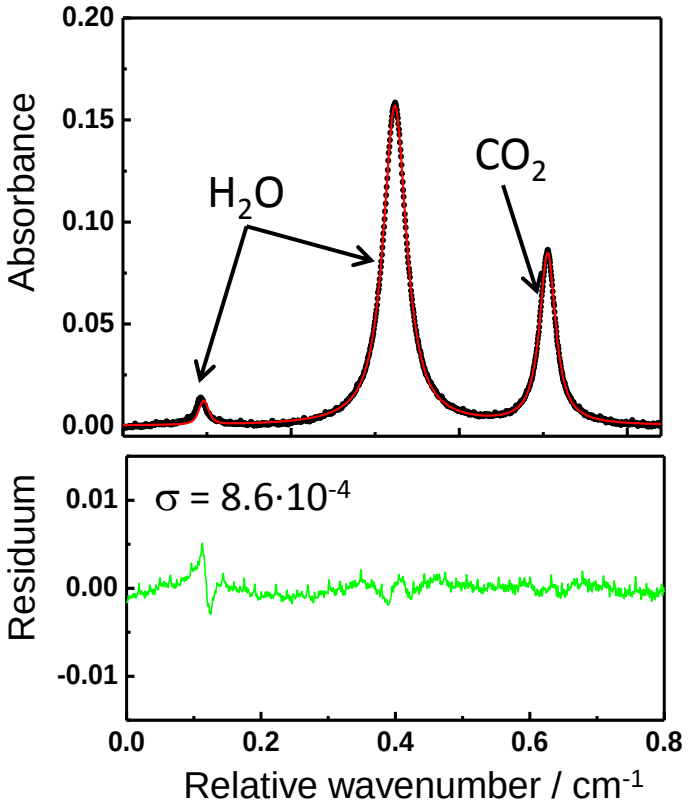
Simultaneous measurement of H_2O and CO_2
200 mbar pressure, 293-295 K

Determined amount fractions:
4-5 µmol/mol CO_2, 60-90 µmol/mol H_2O

Minimum detectable concentration:
H_2O: 1.1 µmol/mol
(limit in zero gas: 150 µmol/mol)
CO_2: 0.16 µmol/mol
(limit in zero gas: 4 µmol/mol)

Typical measured spectra



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Conclusion / Outlook

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- Comparison between classical techniques (standard addition) and optical techniques
  - Classical techniques
    - Low detection limits (<0.5 nmol/mol)
    - Traceable measurements
  - Optical techniques enabled :
    - Simultaneous detection of several gases
    - Absolute and traceable measurements

- Testings of filter, zero air generator and zero gas cylinder in progress
  - Pollutants of interest : NO, NO_2, SO_2
  - Laboratories involved : NPL, VSL, LNE

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Thank you very much for your attention

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