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Hyperspectral techniques for air pollutant detection and quantification

16ENV08 IMPRESS 2: Metrology for Air Pollutants Emissions

Presented by: Guillermo Guarnizo (UC3M)

11th January 2021

Stakeholder workshop via MS Teams

Outline

- Introduction to hyperspectral techniques
- Survey of the latest technologies related to hyperspectral detection of pollutant emissions
- Development of calibration methods and set-ups: Intercomparison of calibration methods
- Preparation of reference gas mixtures for validation activities
- Validation of hyperspectral methods for identification and quantification
- Conclusions

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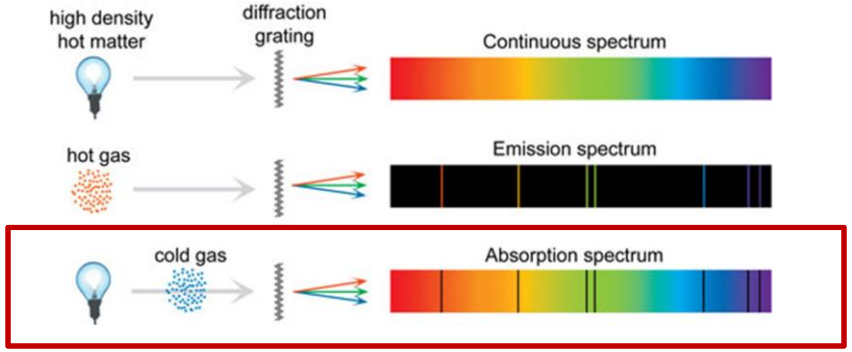
Hyperspectral techniques: Fundamentals

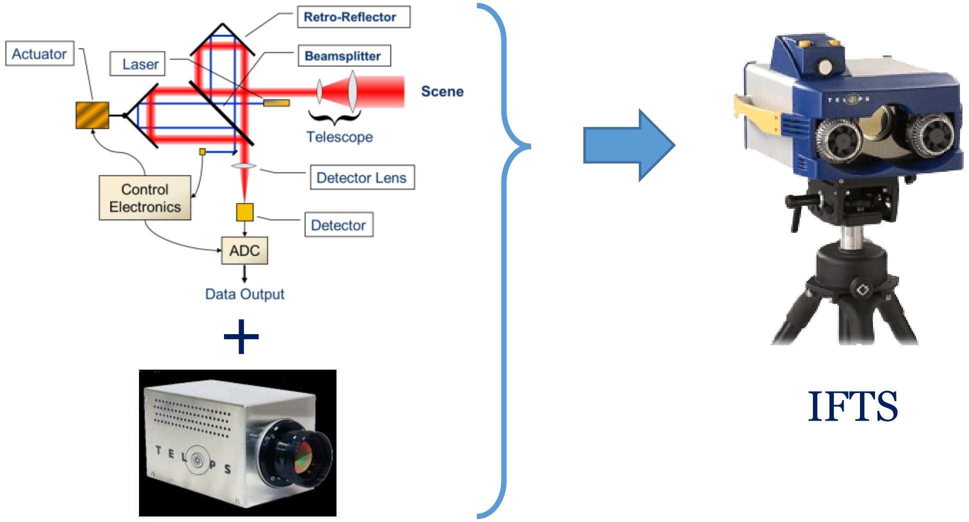
- Kirchhoff law (1860): Emissivity equals absorptance → $\alpha(\lambda) = \varepsilon(\lambda)$
- Absorption in gases: It can be measured by the radiance through the pollutant → $\varepsilon = \alpha = 1 - \tau$



- Lambert-Beer law: $\tau(\lambda) = e^{-a(\lambda)CL}$

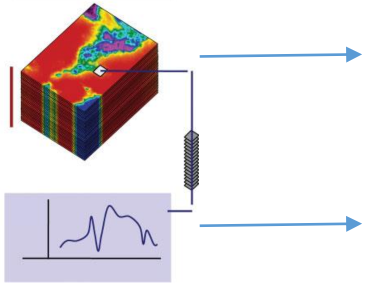
where
- a = Absorptivity (gas feature)
- C = Concentration
- L = Optical path
- CL = Column density (ppm.m)

- Dispersive or interferometer systems IFTS: FTIR based on Michelson interferometer + MIR InSb Camera



IFTS

- Detection of continuous spectra



Three-dimensional data-cube

IR spectra for one pixel

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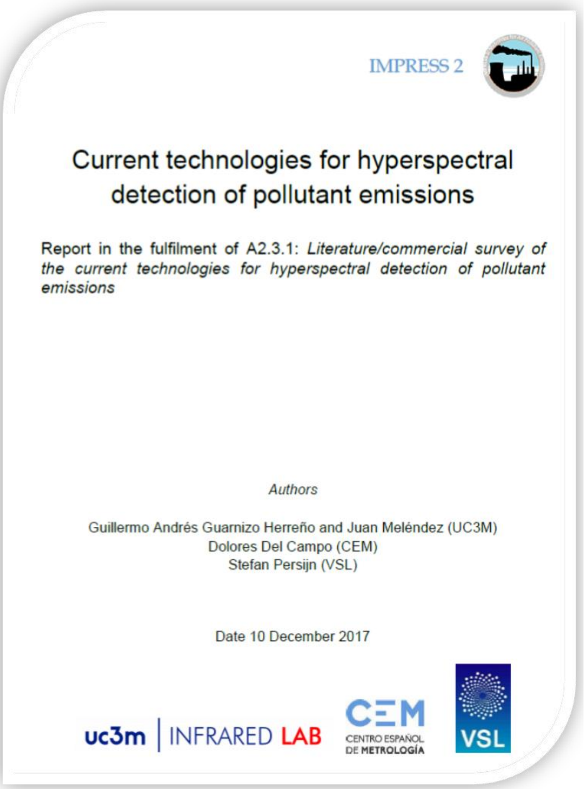
Survey of the latest technologies related to hyperspectral detection of pollutant emissions

- Most pollutant gases are very selective absorbers and emitters of infrared (IR) radiation
- Their concentration in air can be quantified → High spectral resolution IR data (e.g. HITRAN or PNNL IR database)
- Overview of recent literature:
  - Books focused on principles of hyperspectral detection
  - Review and peer-reviewed papers
- Research groups working on hyperspectral techniques
- Available commercial systems


IMPRESS 2

Current technologies for hyperspectral detection of pollutant emissions

Report in the fulfilment of A2.3.1: *Literature/commercial survey of the current technologies for hyperspectral detection of pollutant emissions*

Authors

Guillermo Andrés Guarnizo Herreño and Juan Meléndez (UC3M)
Dolores Del Campo (CEM)
Stefan Persijn (VSL)

Date 10 December 2017

uc3m | INFRARED LAB
CEM CENTRO ESPAÑOL DE METROLOGÍA
VSL

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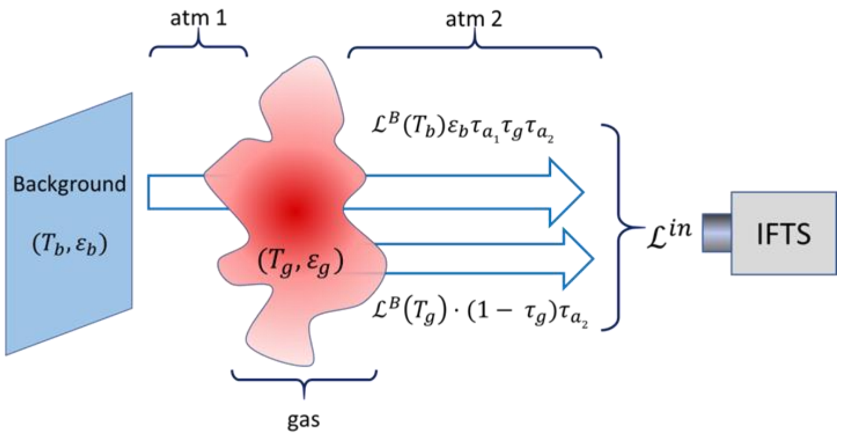
Calibration methods for hyperspectral systems

Procedure for passive systems (UC3M)

Radiometric model



Measurement: $\mathcal{L}^{in} = \mathcal{L}_m = \mathcal{L}^{\mathcal{B}}(T_b)\cdot\varepsilon_b\cdot\tau_{a_1}\tau_g\tau_{a_2} + \mathcal{L}^{\mathcal{B}}(T_g)\cdot(1-\tau_g)\tau_{a_2}$

Reference: $\mathcal{L}^{in} = \mathcal{L}_r = \mathcal{L}^{B}(T_b)\cdot\varepsilon_b\cdot\tau_{a_1}\tau_{g_0}\tau_{a_2}$

$$\tau_{nom} \equiv \frac{\mathcal{L}_m}{\mathcal{L}_r} = \tau_g + \frac{\mathcal{L}^{\mathcal{B}}(T_g)}{\mathcal{L}^{\mathcal{B}}(T_b)}\cdot(1-\tau_g)\cdot\frac{1}{\varepsilon_b\tau_{a_1}} \equiv \tau_g + \tau'$$

$\Rightarrow \tau(\lambda) = e^{-a(\lambda)CL}$ → Lambert-Beer law provides CL = column density

Uncertainty estimation in gas column density due to:

- Measurement noise
- In absorption mode: Error due to gas emission

  Better for cold air pollutants
- In emission mode: Error due to radiometric calibration of IFTS →

  Better for hot air pollutants

CEM Calibration facilities

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Preparation of reference gas mixtures

Mixtures preparation

- ✓ Following CEM gravimetric method
- ✓ ISO 6142-1 – Preparation of calibration gas mixtures
- ✓ Analytical check – ISO 6143, to ensure prepared concentrations

Compounds	UC3M	NPL & VSL
CH_4	(602,4 ± 1,4) µmol/mol	(200,0 ± 1,5) µmol/mol
C_3H_8	(499,9 ± 1,2) µmol/mol	(200,0 ± 1,0) µmol/mol
N_2O	(250,4 ± 2,5) µmol/mol	(200,5 ± 2,0) µmol/mol

Matrix: synthetic air ($20\%\ O_2$, $80\%\ N_2$)

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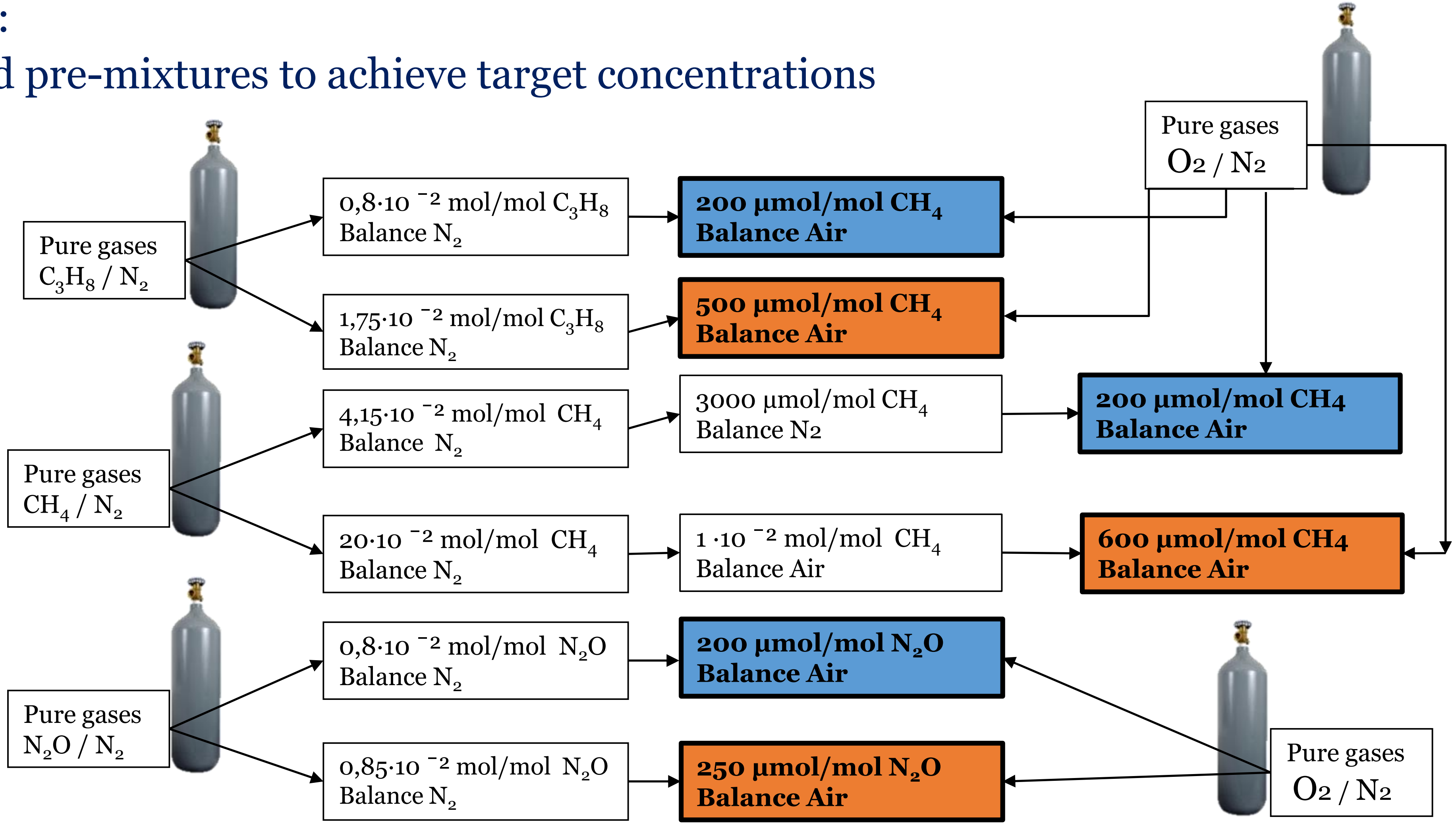
Preparation of reference gas mixtures

Dilutions:

CEM used pre-mixtures to achieve target concentrations



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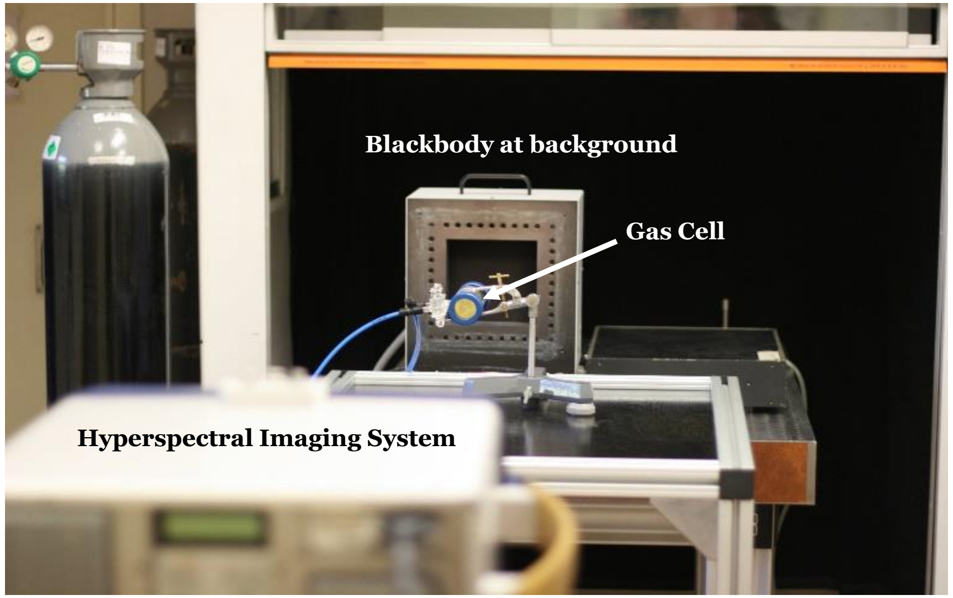
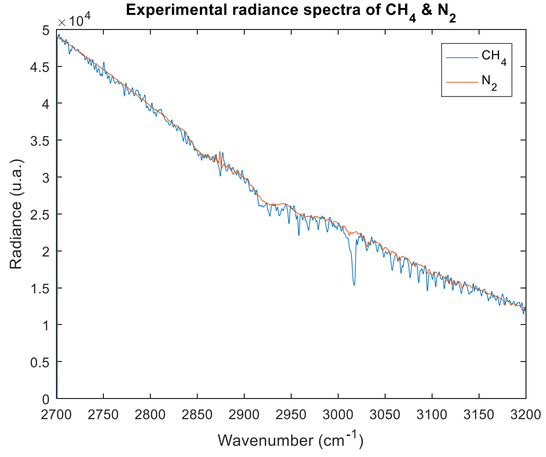
Identification and quantification of air pollutants: UC3M

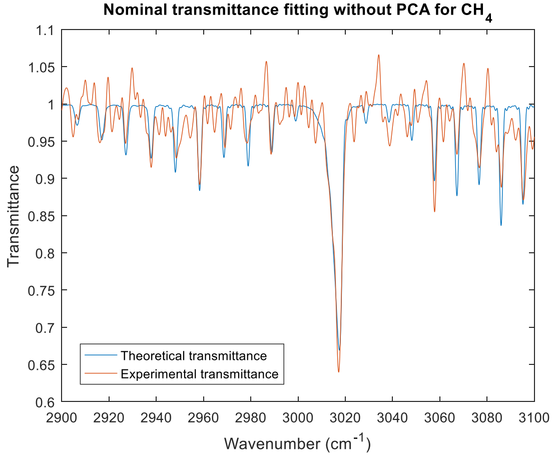


Air pollutant stand-off measurements

- MIR region: 1,5 µm to 5,5 µm
- Spectral resolution: 1 cm^{-1}
- 2 set of acquired data: air pollutant and reference gas
- 3 gases studied: Methane (CH_4), Nitrous Oxide (N_2O) and Propane (C_3H_8)



Spectra of pollutant (blue) and reference (red)



Transmittance spectra: experimental (red) and fitted (blue)

Features of hyperspectral method:

- ✓ A spectrum for each pixel of the image
- ✓ Transversal uniformity in gas cell verified
- ✓ Robust fitting algorithm to retrieve physical variables: Column density and temperature
- ✓ Possibility to establish a minimal concentration value for quantification

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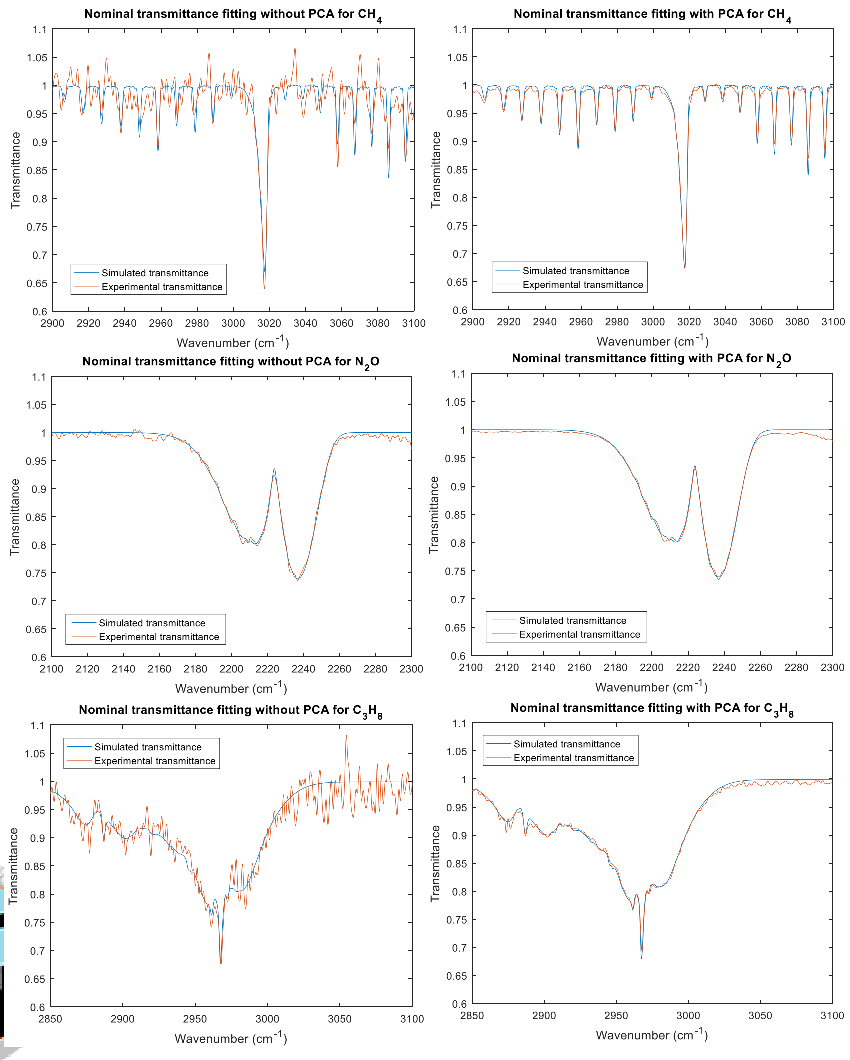
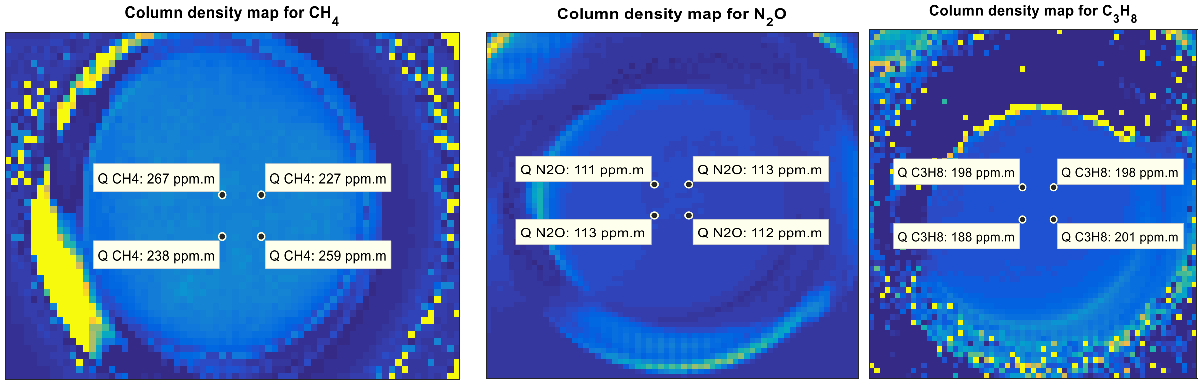
Identification and quantification of air pollutants: UC3M

PCA processing for noise reduction & enhanced fitting for one pixel



Column density maps (ppm.m) for the three air pollutants agreed by the partners



Pollutant Gas	Concentration (ppm)	Column density (ppm.m)*	Retrieved column density (ppm.m)**
Methane (CH_4)	600	258	250 ± 9,8
Nitrous oxide (N_2O)	250	107,5	112,3 ± 1,4
Propane (C_3H_8)	500	215	199,7 ± 3,8

* Calculated values based on the gas cell of 43 cm used on measurements.
** Retrieved values from a 7 x 7 pixels central area of the hyperspectral image.

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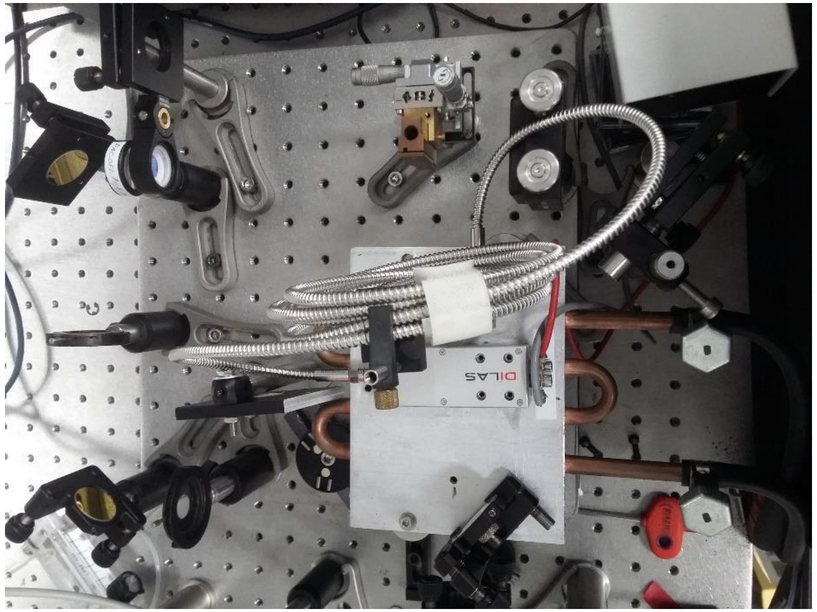
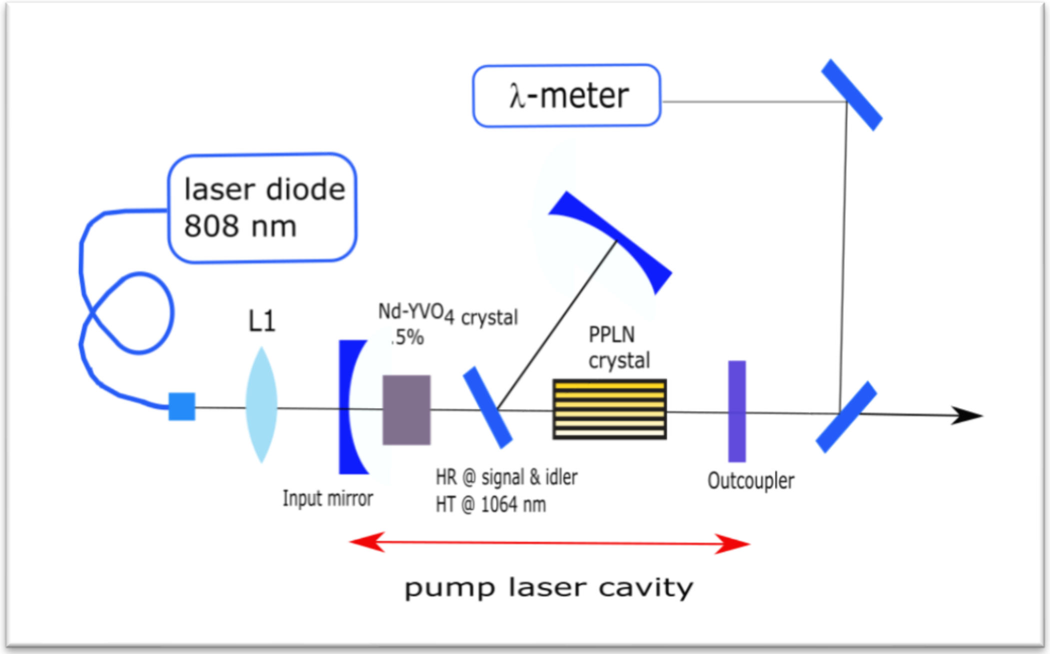
Identification and quantification of air pollutants: VSL

- VSL designed compact OPO (tuneable IR source)
- Parts have been ordered and system assembled. Unfortunately system not working properly (Nd-YVO4 laser unstable)





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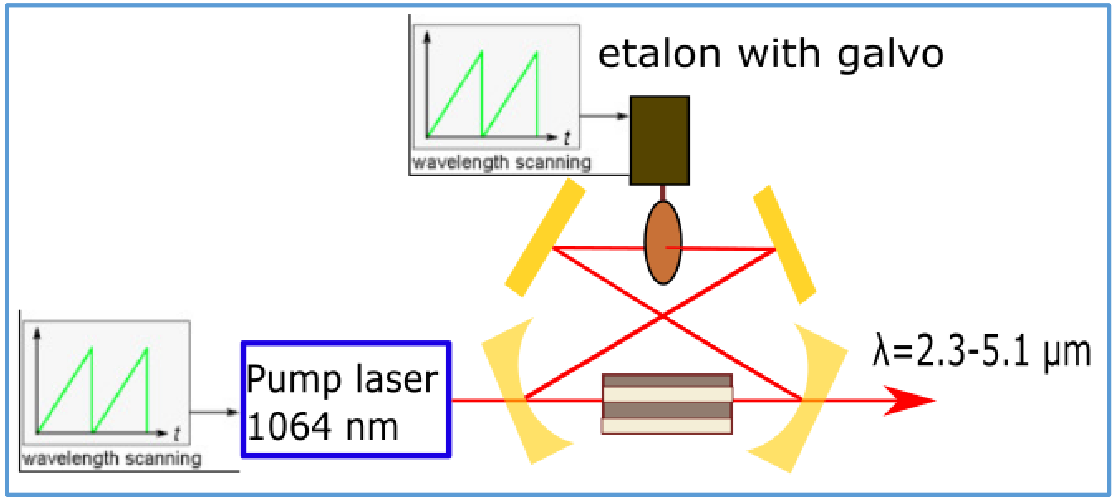
Identification and quantification of air pollutants: VSL

- As designed OPO did not work, a different route was chosen using a Nd-YAG pumped OPO



Features OPO system

- Wavelength range 2.3-5.1 μm
- Output power up to 2.5 Watt
- Continuous wave operation
- Rapid tuning via etalon (up to 10's of Hz) or pump laser (up to 1 kHz)

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Identification and quantification of air pollutants: VSL

- OPO can enhance the thermal contrast in measurements using hyperspectral imagers and so improve quantification of gas concentrations

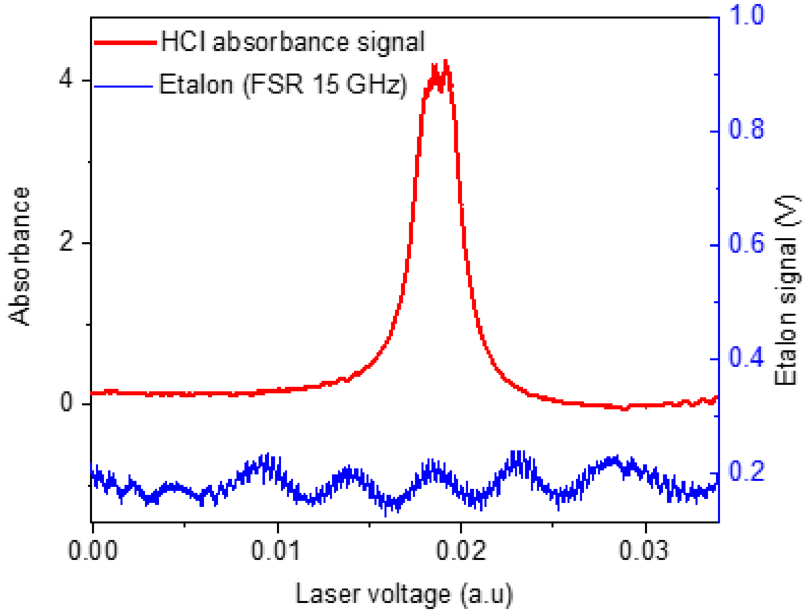

Figure 2 Direct absorption measurement of the HCl line centred at 2963.29 cm[-1]. The OPO was tuned at a rate of 20 Hz over the absorption line.

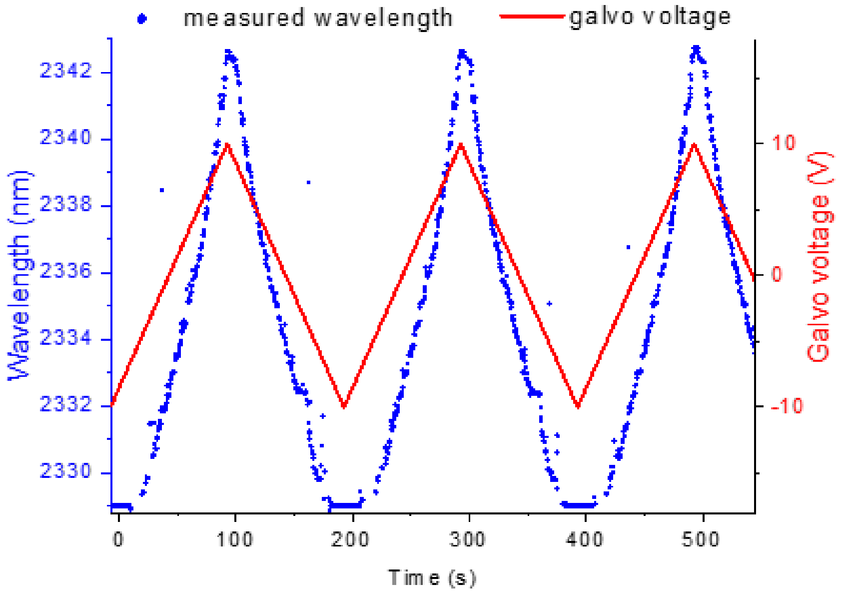

Figure 3 Tuning of the OPO using only etalon tuning.

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Conclusions

- A rigorous survey on novel hyperspectral techniques has been drafted. Books, papers and commercial systems are included in the final document
- Traceable calibration methods for hyperspectral imagers have been established for passive systems
- A defined group of air pollutants for validation measurements has been prepared and certified by CEM
- Excellent results in quantification of pollutants have been achieved by UC3M with an improved hyperspectral method
- The OPO-based method proposed by VSL are good enough in spite of the problems they had with Nd-YVO4 laser unstable

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Thanks for your attention

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