20IND06 PROMETH2O

WP1: Improved trace water measurement methods and techniques

M1 to M18 Report

M18-M27 Planning

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

WP1: Key Information

❖ ***To develop new and improved optical methods and techniques for trace water measurements***

Target: H_2O traces in Ar, N_2, H_2 [from 5 ppm (-65 °C) to 5 ppb (-105 °C) @ 0.1 MPa]. Relative uncertainty for the measurements: 3 % (5ppm) and 8 % (5 ppb)

4x systems:

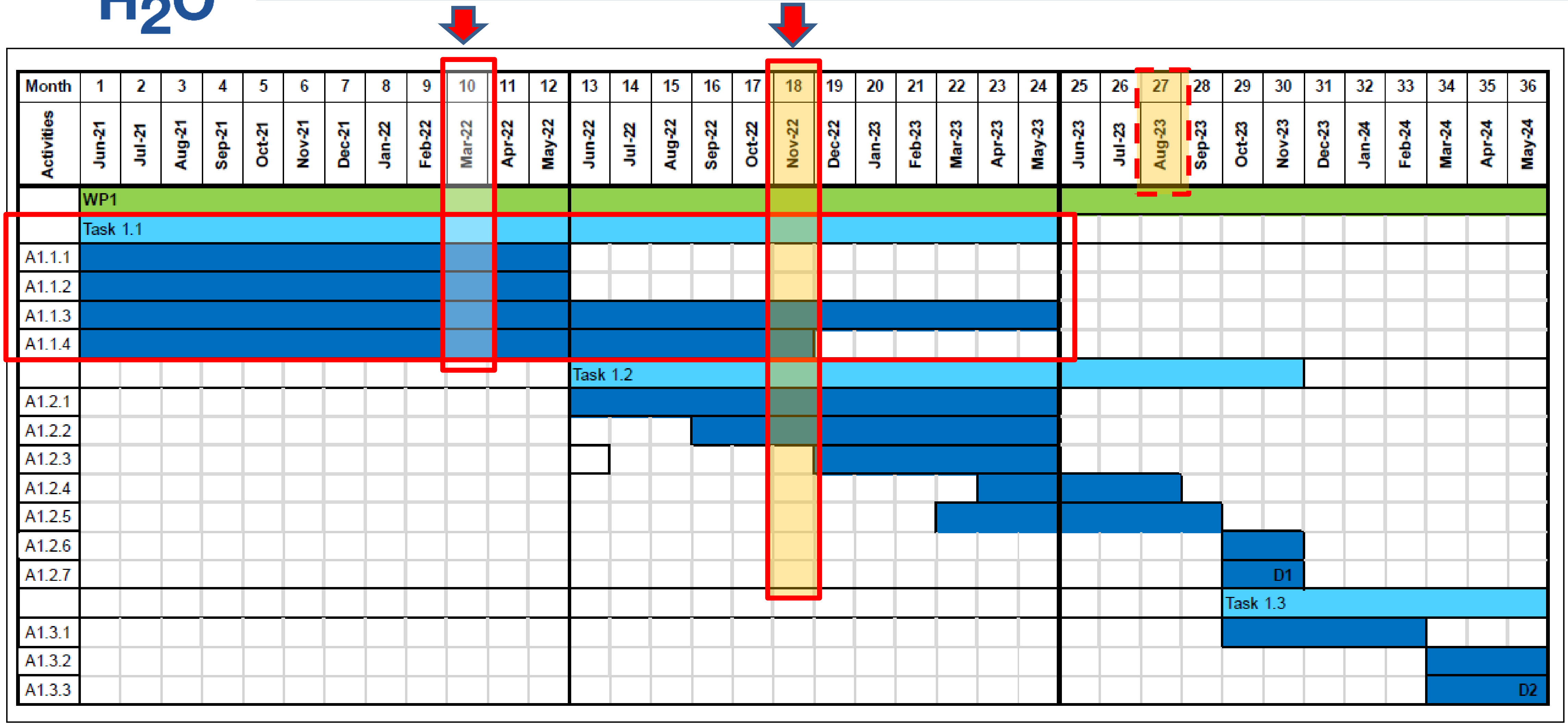
- ❑ Enhancements in NIR comb-calibrated frequency-stabilized cavity ring down spectrometer (CC-FS-CRDS) **(SUN)**;
- ❑ NIR cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer development **(QROMETRIC);**
- ❑ Far-UV absorption spectroscopy system development **(DTU)**;
- ❑ Upgrade of existing high-resolution FTIR system **(TUBITAK)**.

Task 1.1: Development and improvement of optical analyzers

Task 1.1

M9 (web) meeting

M18 meeting at VSL



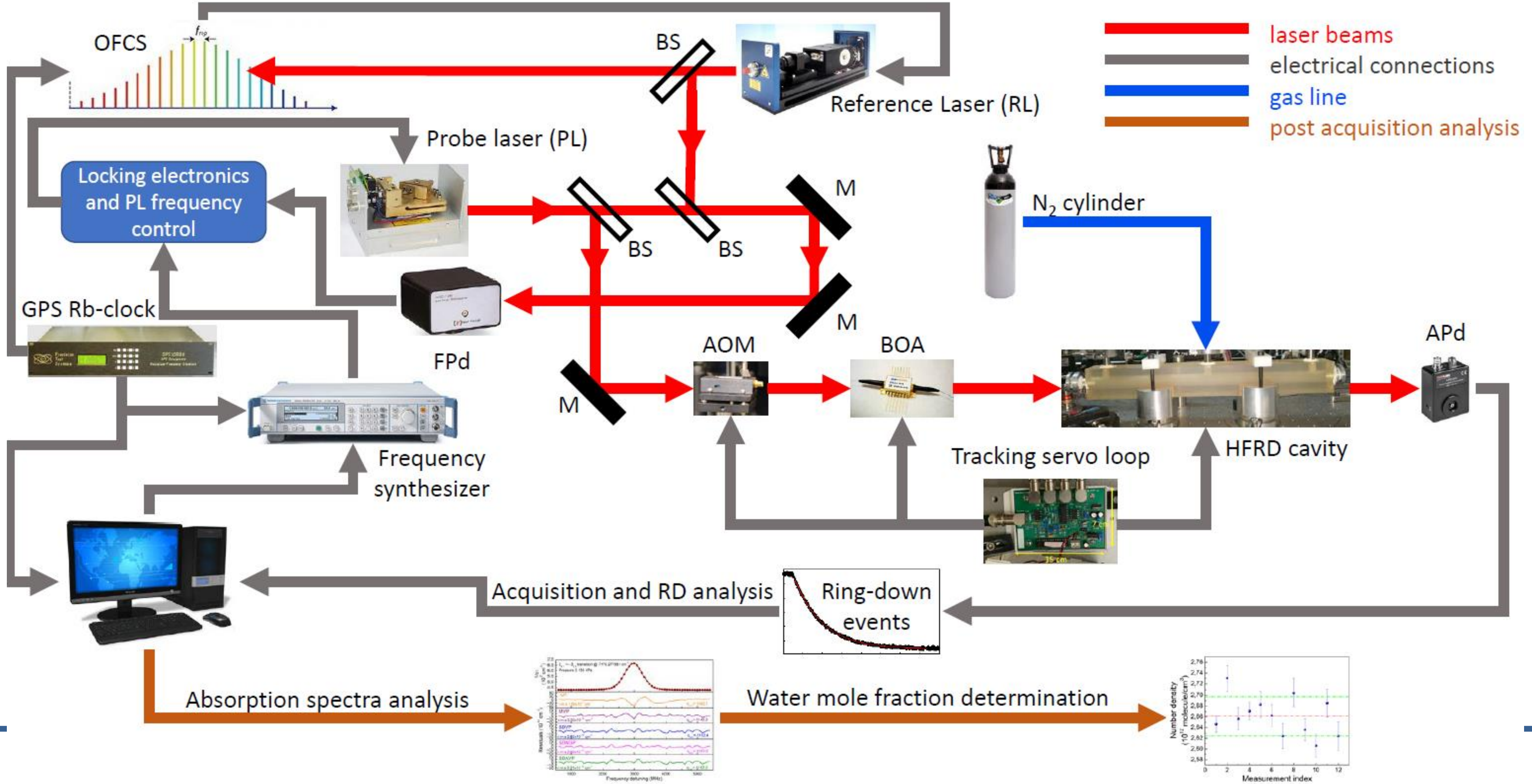
A1.1.1

CC-FS-CRDS for ultra-sensitive traceable measurements of water vapor in UHP gases

With an input from Antonio Castrillo

A1.1.1 M12	SUN will develop a compact NIR CC-FS-CRDS spectrometer to increase the sensitivity, thus lowering the limit of detection, referenced to an optical frequency comb, for traceable measurements of water vapour in H_2 and N_2 from 5 ppm down to 50 ppb with standard relative uncertainty between 3 % and 8 % and operation pressure as low as 10 kPa.	**SUN**

A.1.1.1 CC-FS-CRDS: Experimental setup



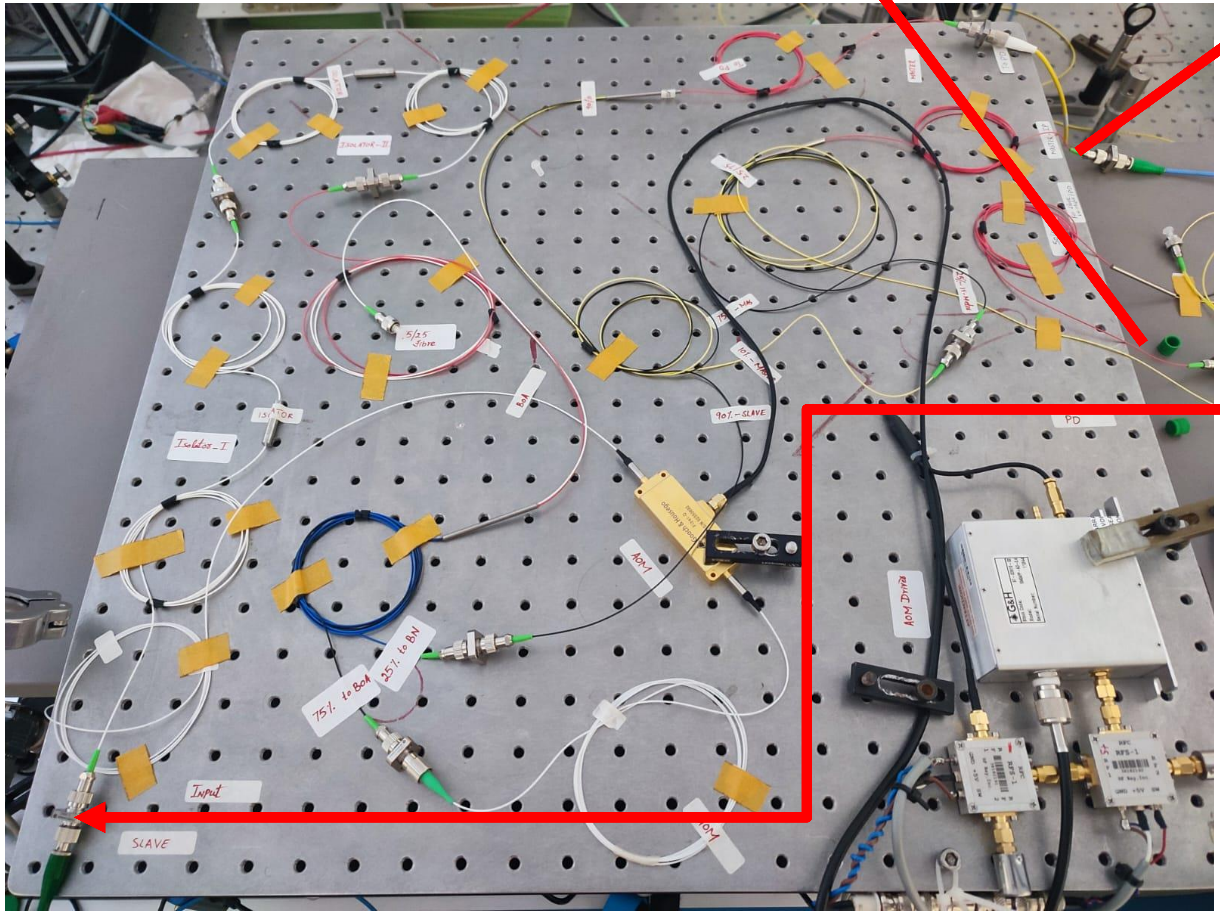
PROMET H2O

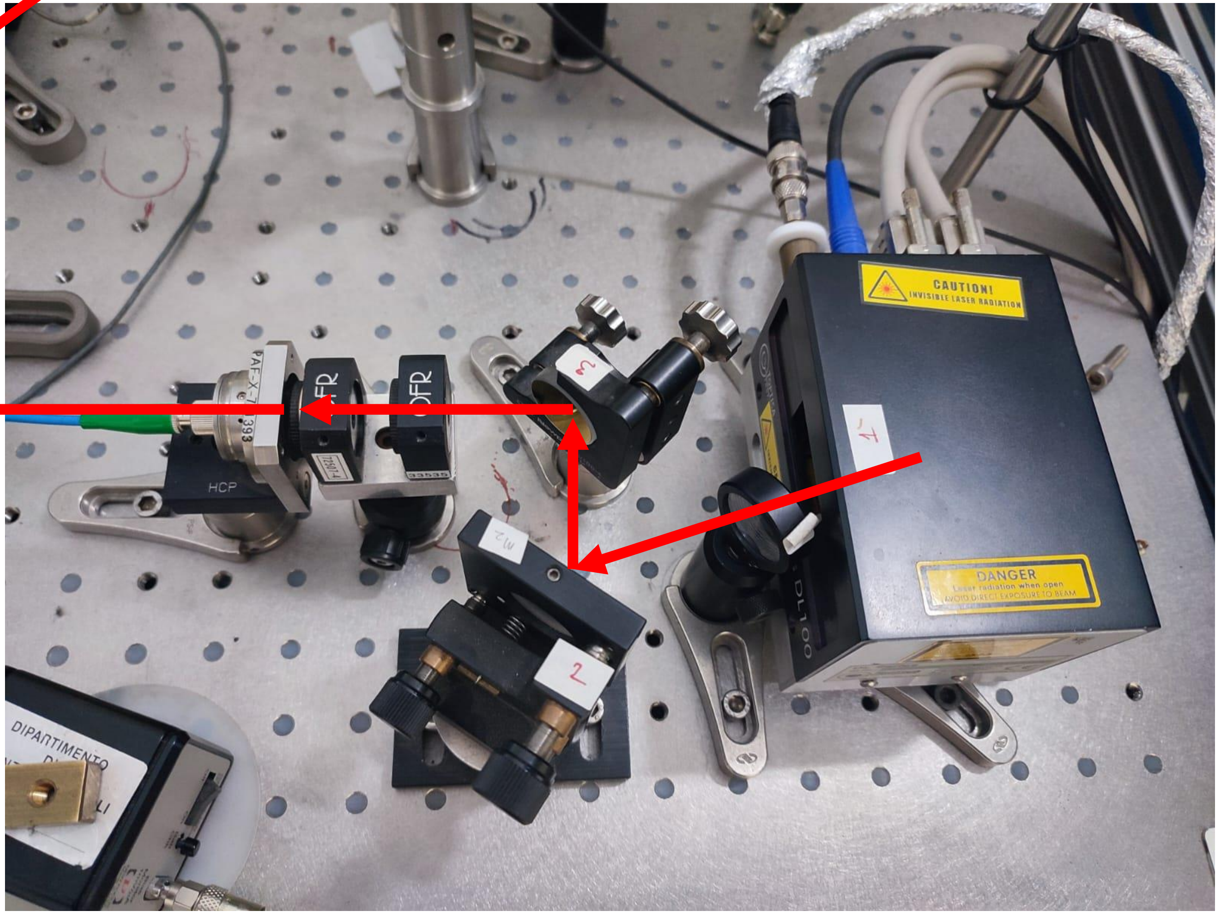
Università degli Studi della Campania *Luigi Vanvitelli*

A1.1.1 CC-FS-CRDS: Experimental setup

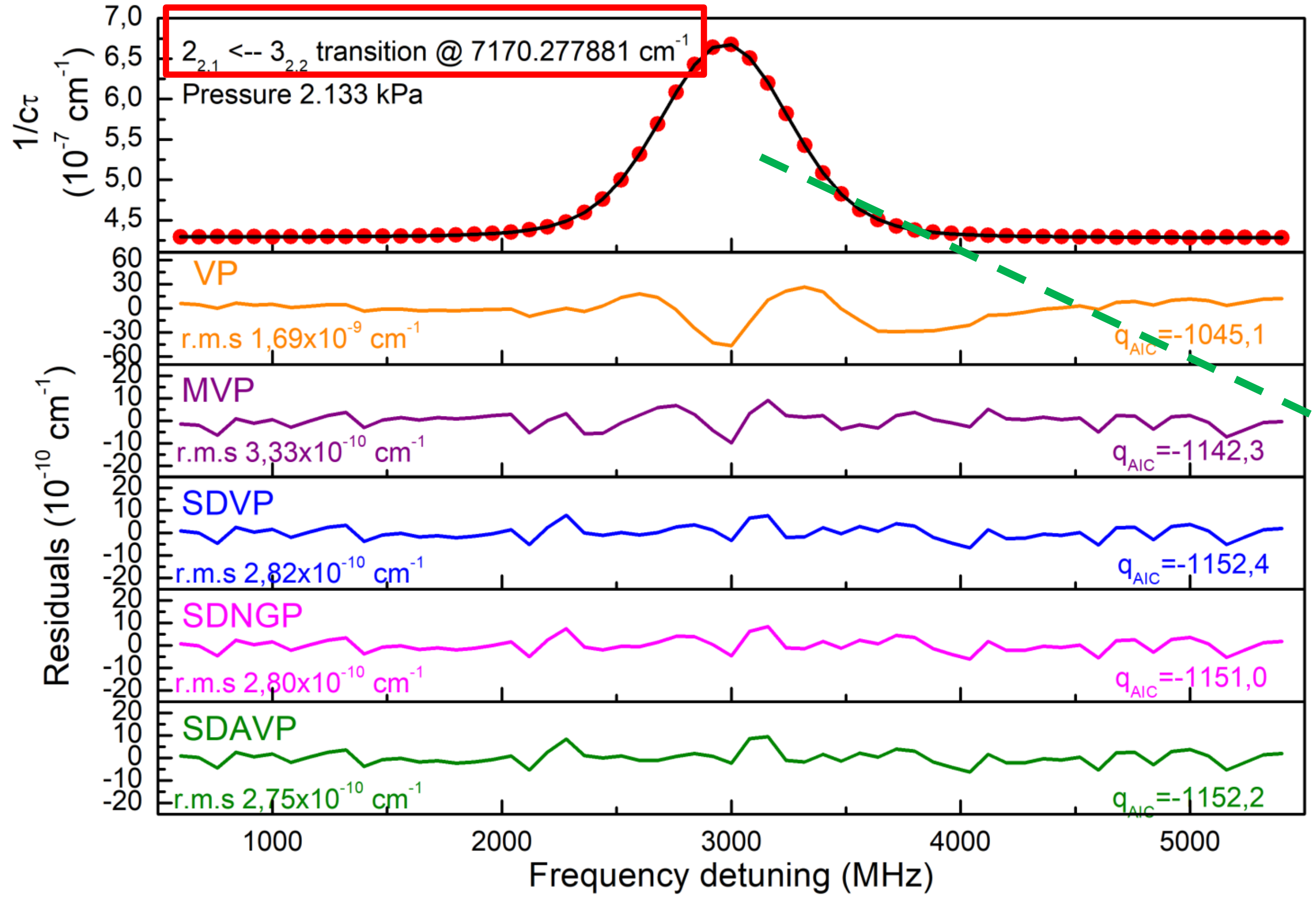
To CRDS

To frequency reference





A.1.1.1 Lineshape evaluation & choice



$$q_{AIC} = N[ln2 + ln\sigma^2 + 1] + 2(p + 1)$$

Akaike Information Criterion (q_{AIC}) & r.m.s.:

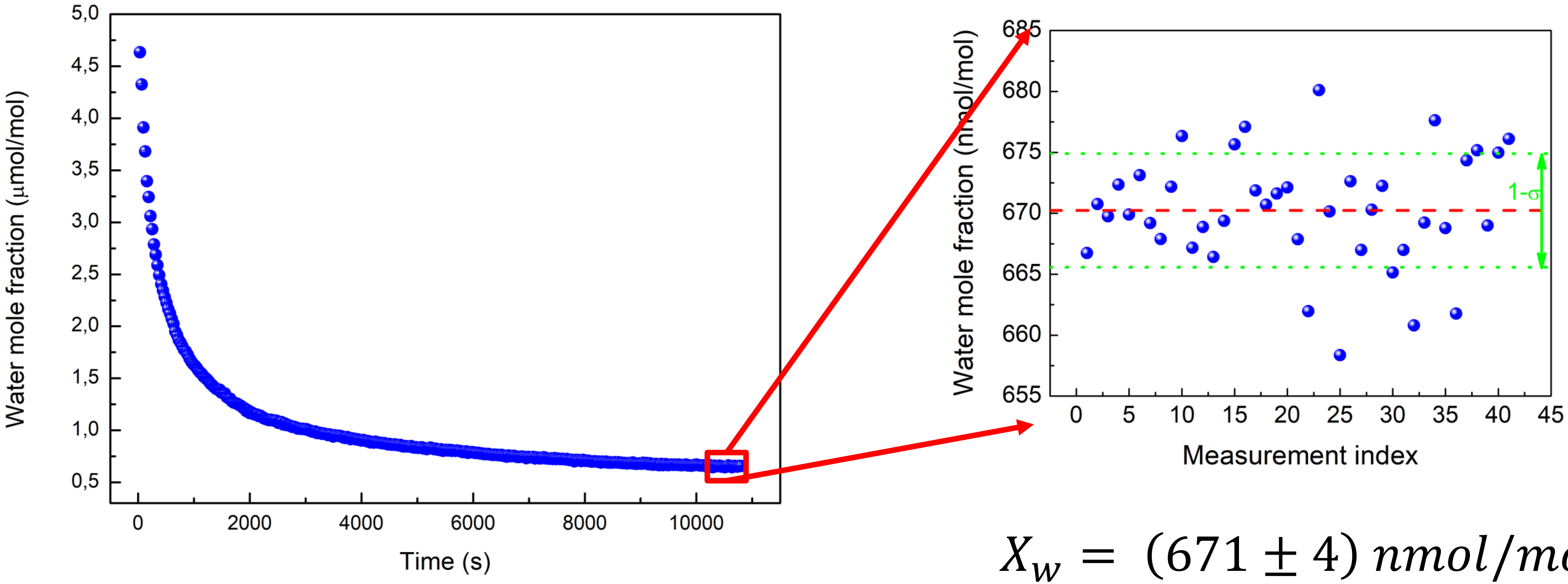
SDVP & SDNGP almost equivalent

$$X_w = \frac{\boxed{\alpha_{TOT}} k_B T}{S(T)P}$$

Line intensity (S) from PRA **79**, 052507 (2009) Measured @ NIST by J. Hodges *et al.* using a CRDS spectrometer and a primary standard humidity generator.

A1.1.1 CC-FS-CRDS: Continuous H_2O measurements & reproducibility

N_2 gas flow from a cylinder with a 99.9999% nominal purity; Pressure 13 kPa; 2 l/min flux



$$X_w = (671 \pm 4)\ nmol/mol$$

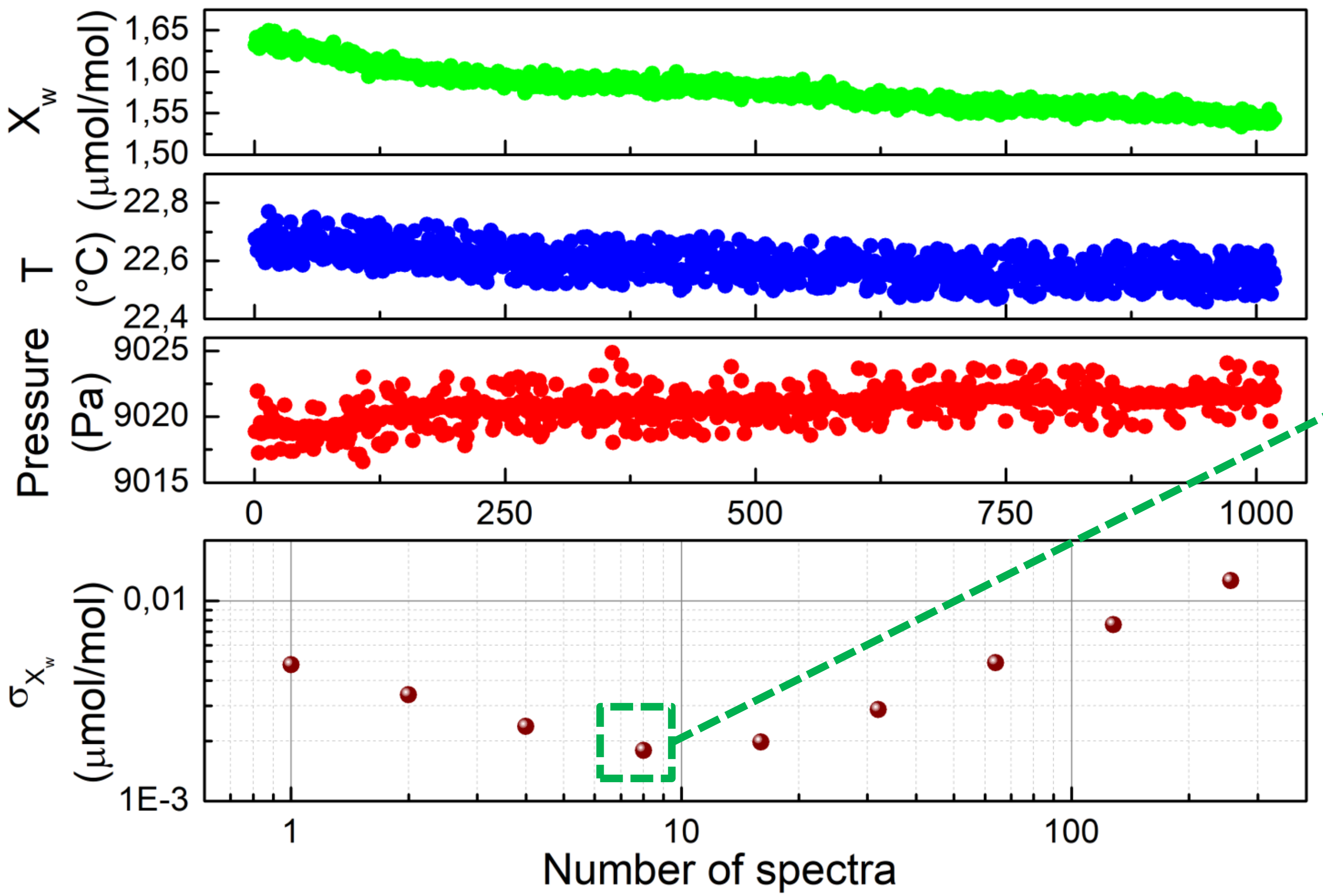
A1.1.1 CC-FS-CRDS: Revised uncertainty budget on X_W

Contribution	Type A	Type B
(k=1)	(%)	
Statistical	0.5	
Line strength		0.3
Frequency scale		Negligible
		0.1
RD per point & frequency step		< 0.2
Laser scan width		< 0.2
Gas temperature		0.05
Partition function		0.04
Pressure		0.05
Overall combined uncertainty 0.7		

Well within the request of A1.1.1

New contributions

A1.1.1 CC-FS-CRDS: Sensitivity assessment: minimum detectable X_W



$$X_{W_{min}} = 1.8\ nmol/mol$$

One order of magnitude below the target level requested in A1.1.1

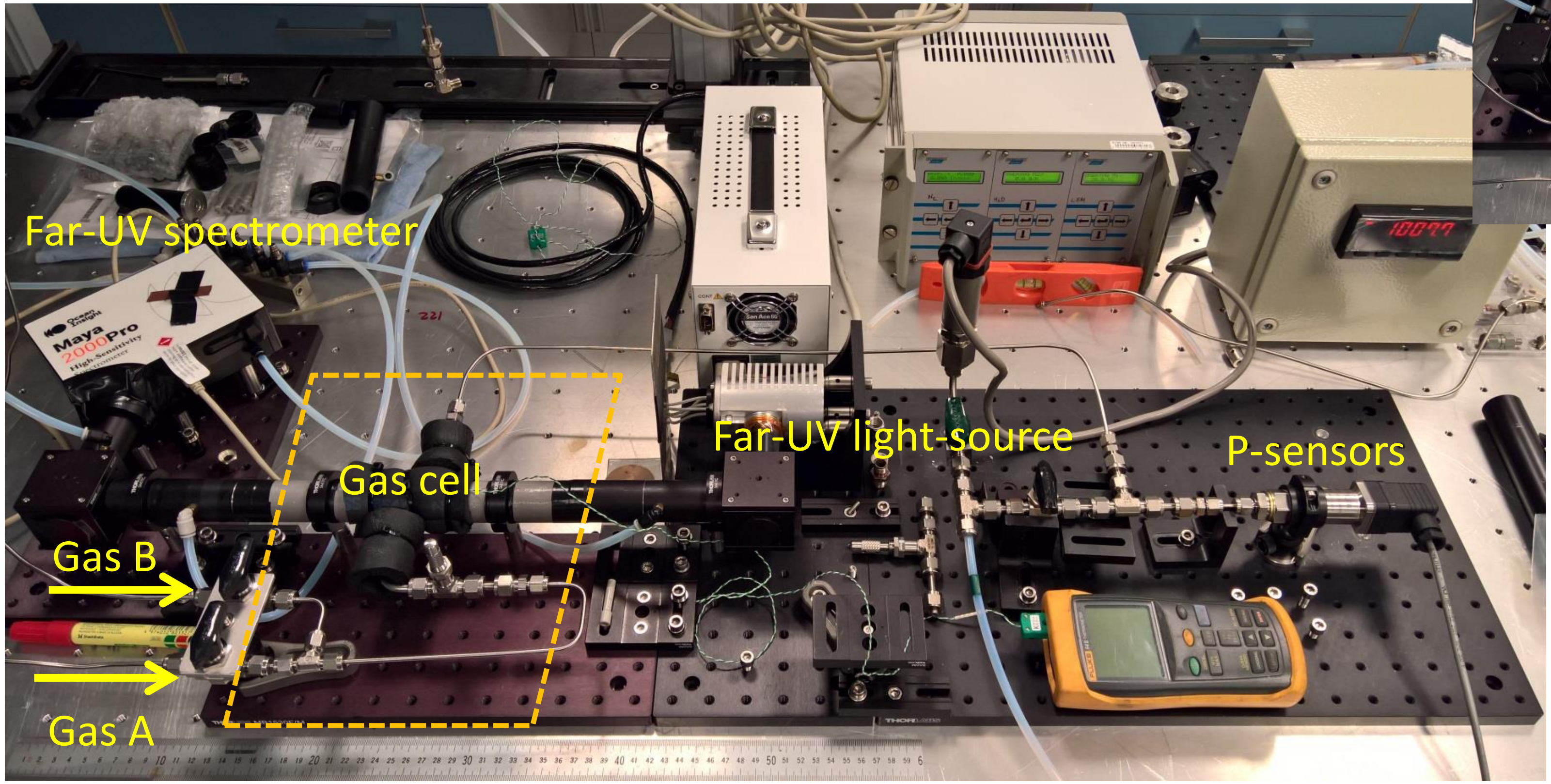
A1.1.2

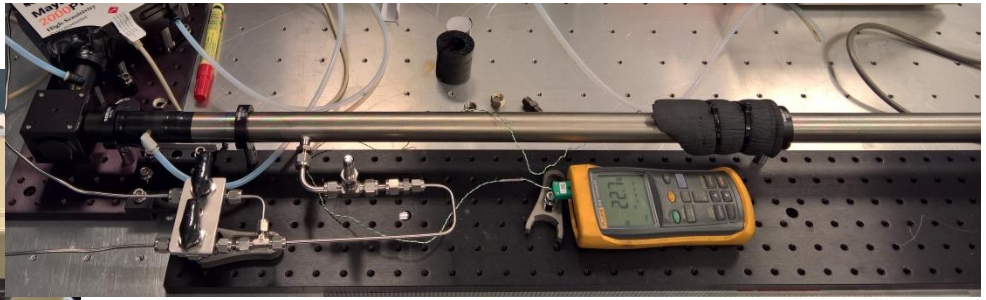
Development of a compact and transportable **far-UV** system

With an input from Alexander Fateev

A1.1.2 M12	DTU will develop a compact and transportable far-UV system for trace water vapours measurements in Ar, N_2 and H_2 from 5 ppm to 5 ppb with standard relative uncertainty between 3 % and 8 % and operation pressure up to 1 MPa.	**DTU**

A1.1.2 Water evaporation system

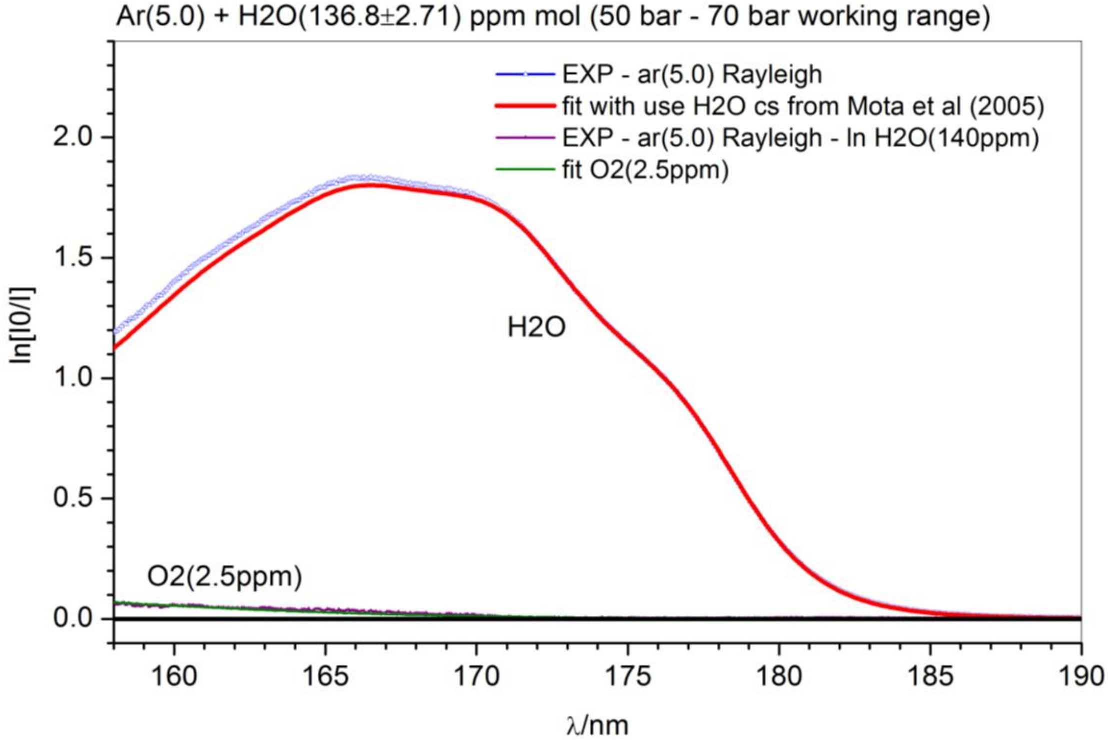


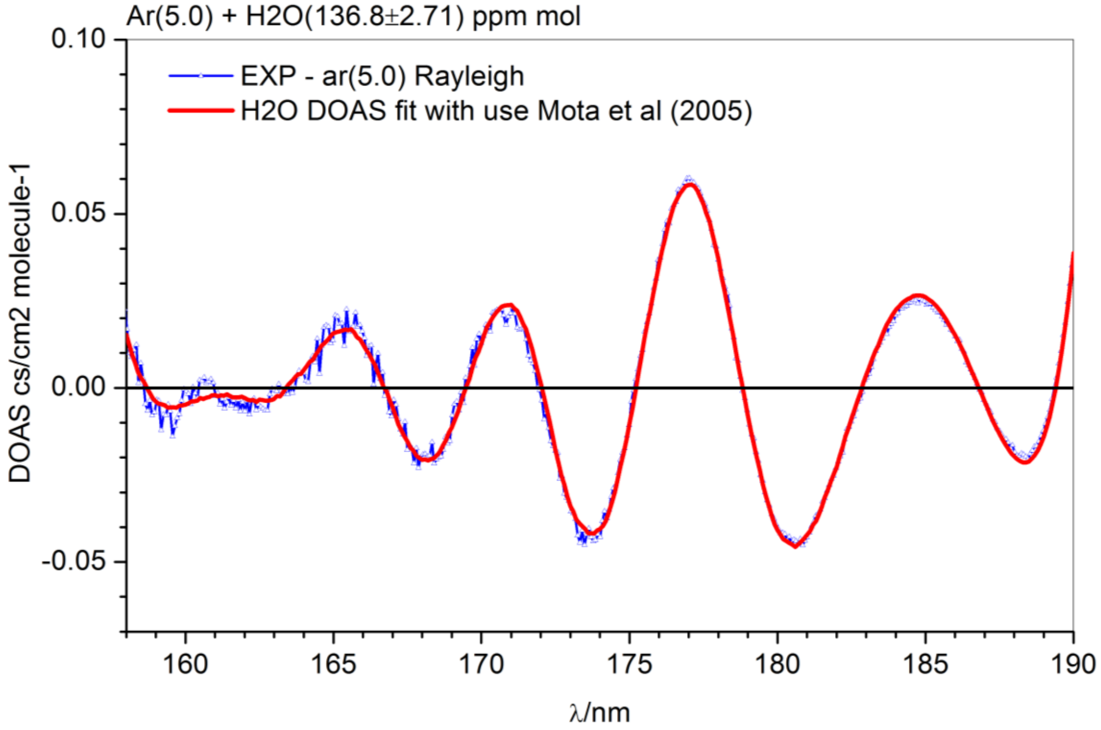


Far-UV system:

- highly-modular;
- various gas cells (from ca. 0.5 mm to ca. 100 cm);
- <u>flow</u> or <u>static</u> measurement conditions <u>from “0” bar to 100 bar</u>;
- 100 cm cell with DURSAN coatings;
- can be heated;

A1.1.2 Validation with 100 cm cell (DURSAN)

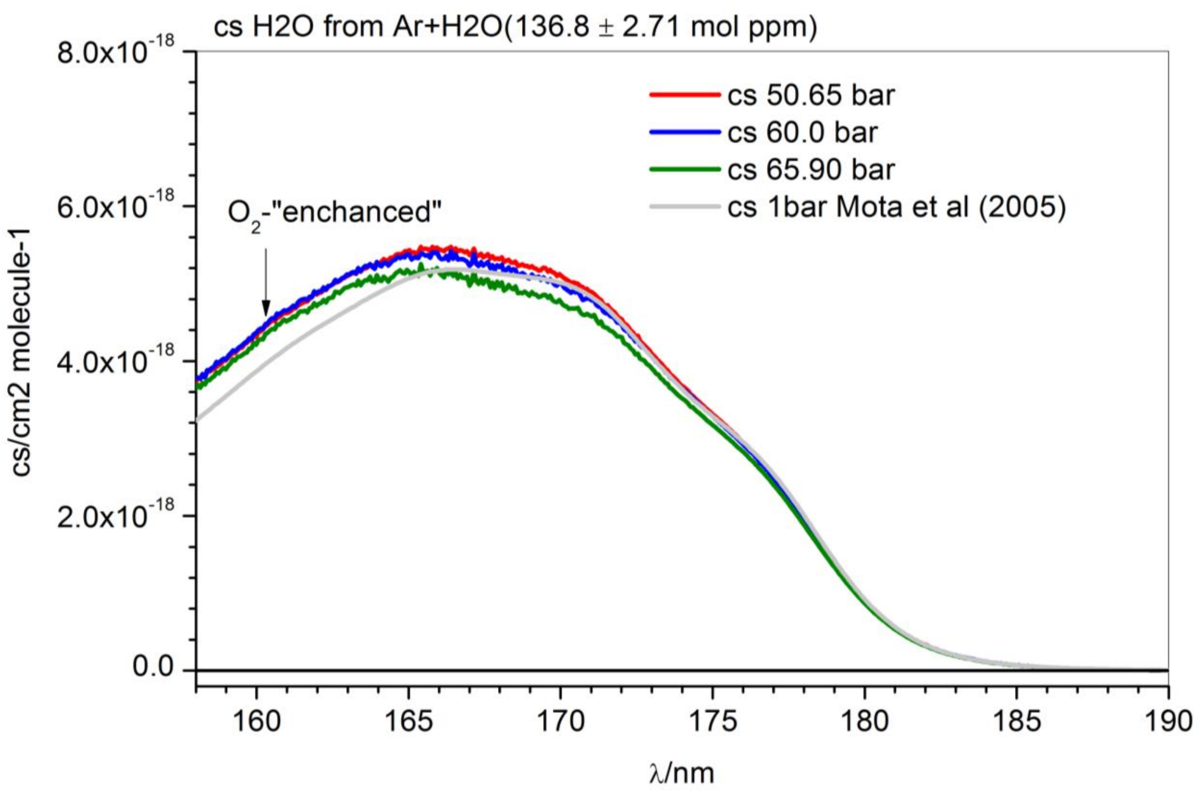


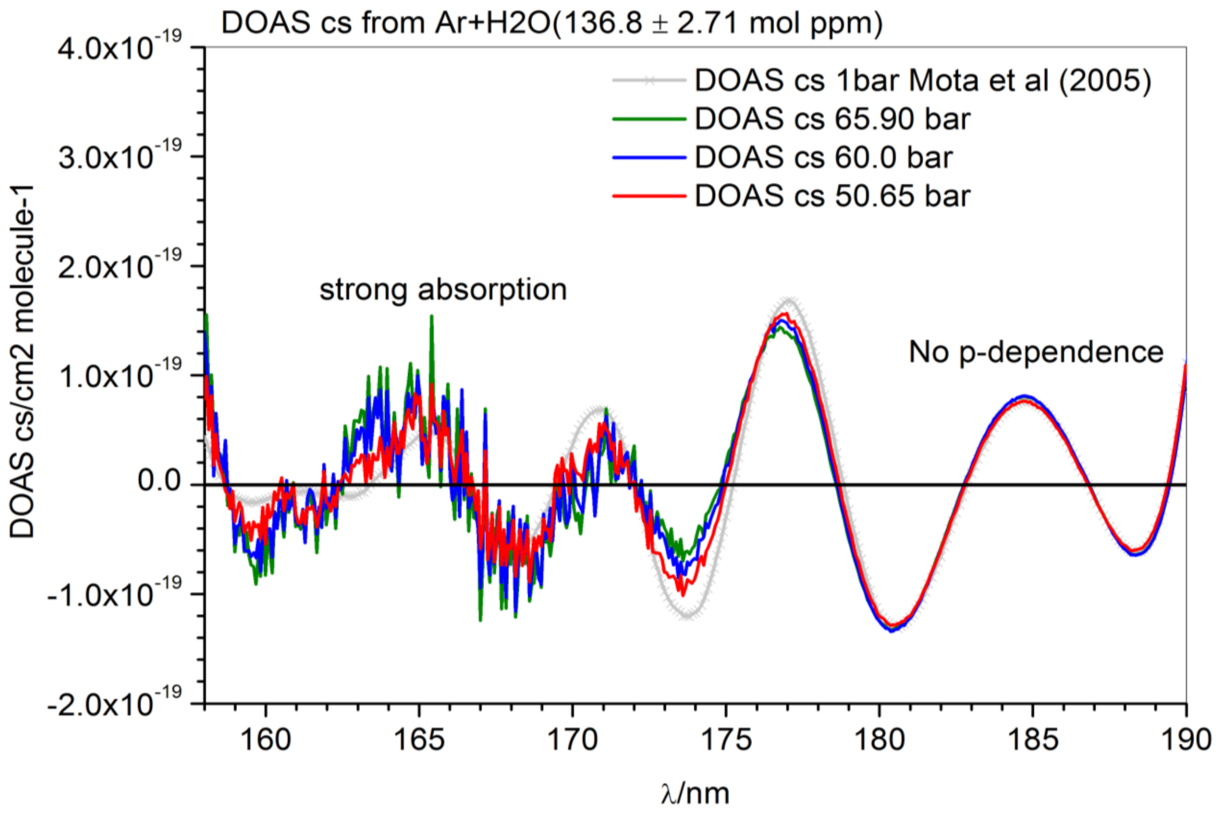


- ❑ Two ways spectra analysis: “whole” and “DOAS”-based
- ❑ Ar(99.999%)+H_2O(136.8ppm) premixed gas (Air Liquide), 50 bar–70 bar working pressure range

- ❑ Fit with use H_2O cs from Mota et al (2005)
- ❑ DOAS fit does not depend on O_2
- ❑ O_2 traces (stated Ar(99.999%) purity for $O_2 \leq$ 2 ppm)

A1.1.2 H_2O at high pressures

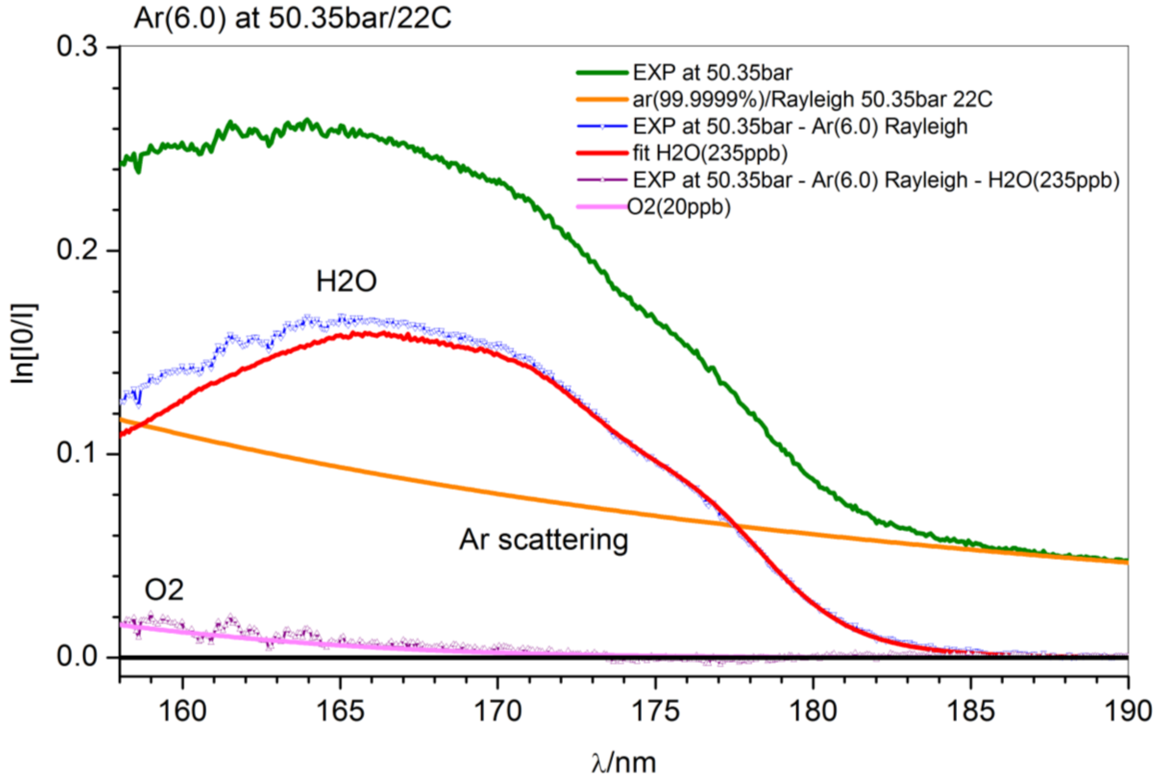


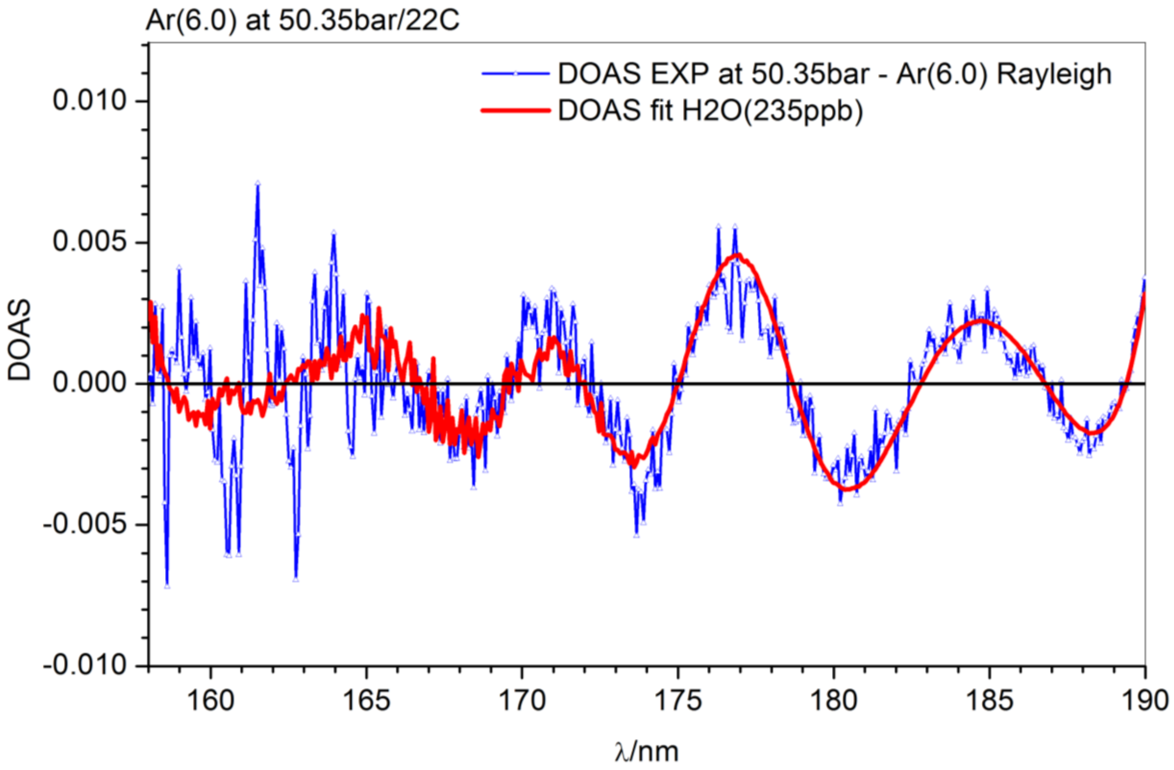


- ❑ O_2-related H_2O cs spectra "lift" < 170 nm
- ❑ "noisy" band tops because strong absorption: can be removed with use a shorter cell or lower H_2O concentration

- ❑ O_2 features can be eliminated in DOAS spectra
- ❑ No p-dependence in 180-190 nm
- ❑ Minor p-dependence in 158-180 nm

A1.1.2 Ar(6.0)=99.9999% case

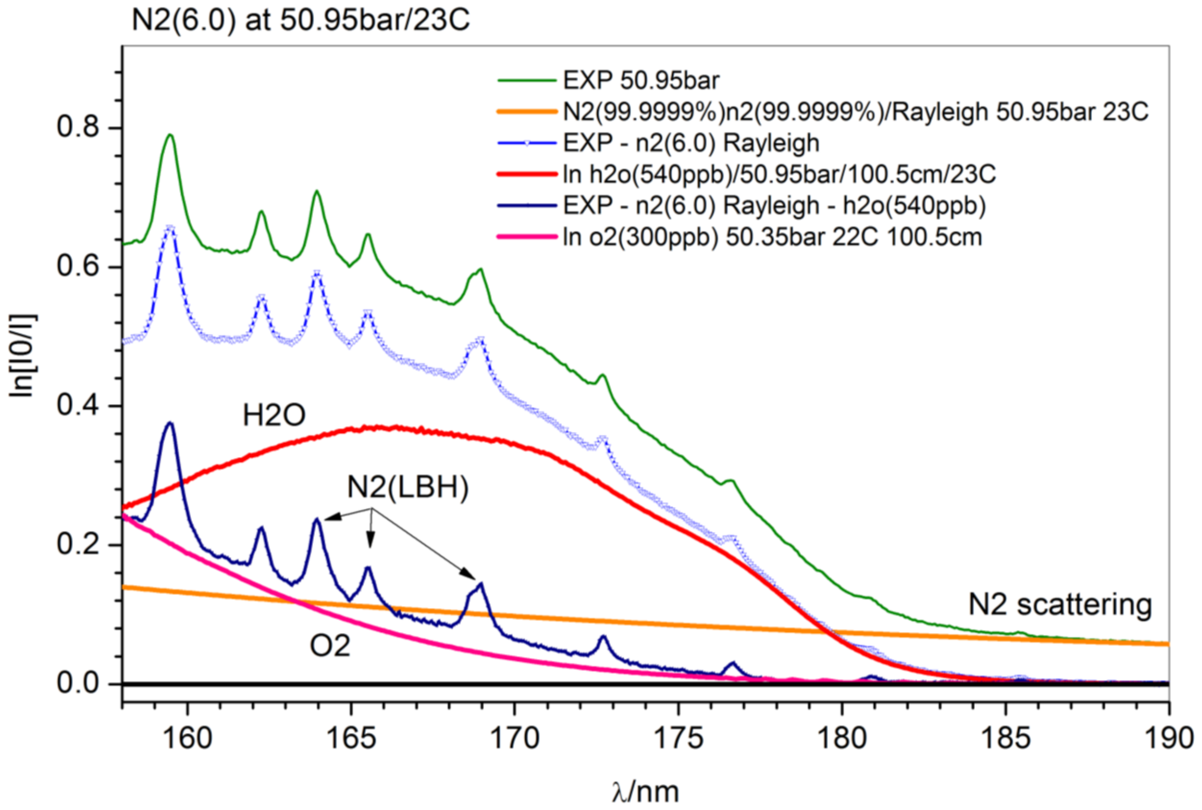


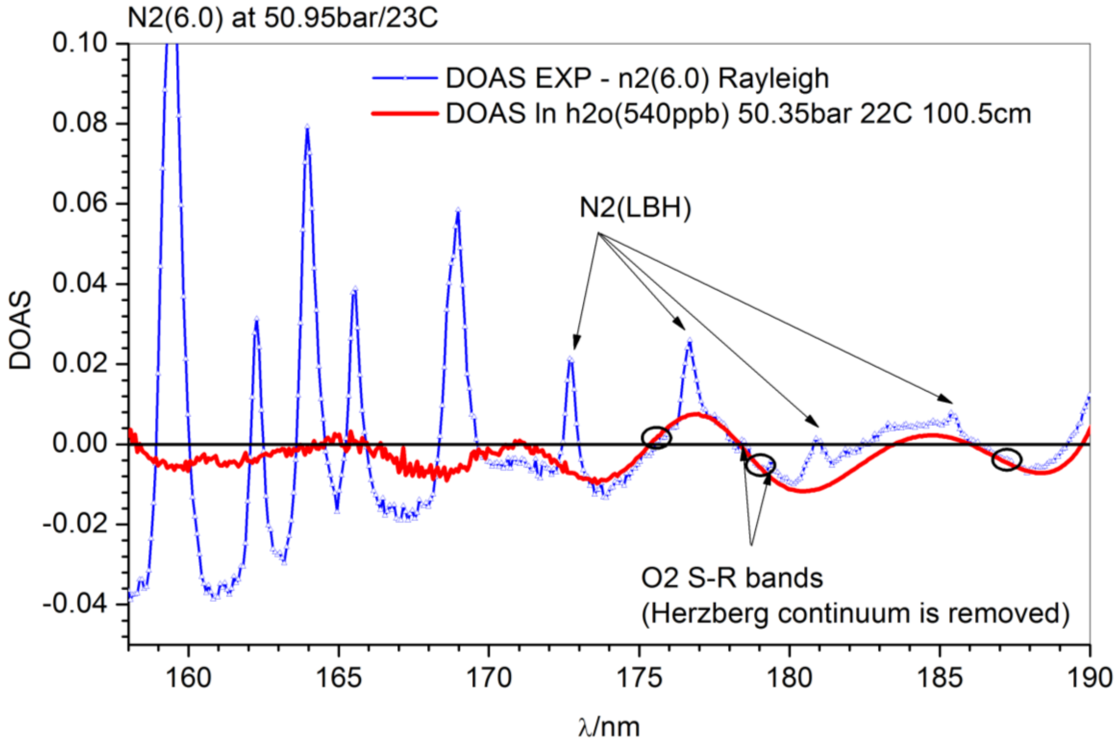


- Extinction spectra: absorption + scattering
- In flow measurements
- Fit with use H_2O cs at 50.65 bar (H_2O=235ppb)
- O_2 traces (20ppb)

- No effect from O_2 on DOAS spectra
- 12 s spectrum acquisition time
- Cross-spectra fit: “whole” and “DOAS”

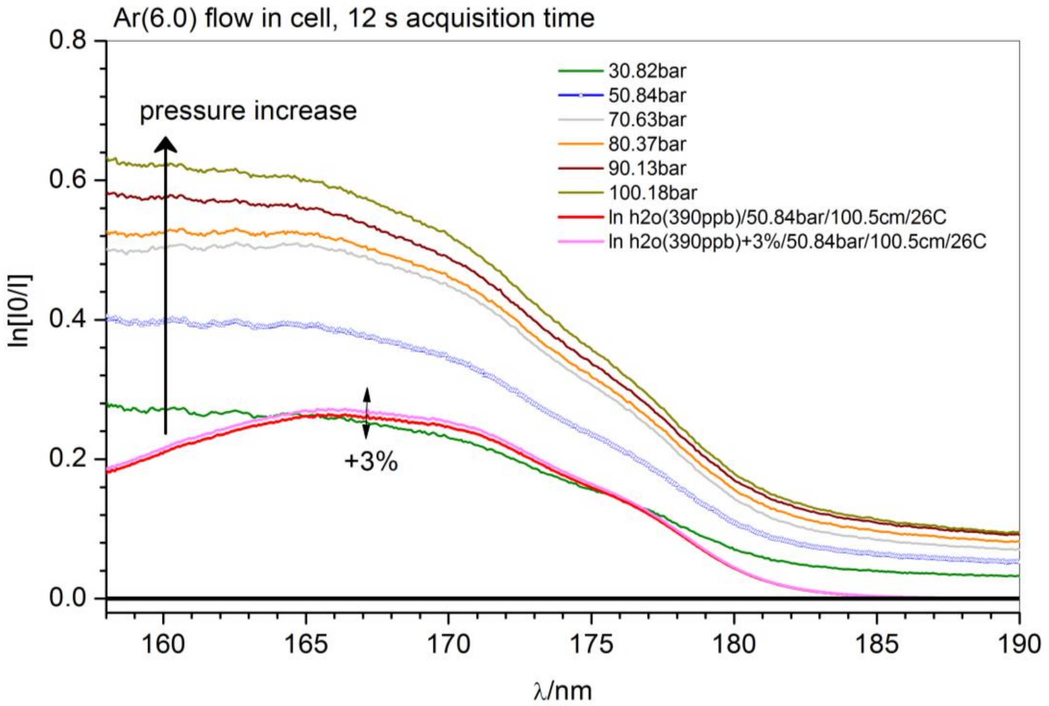
A1.1.2 N_2(6.0)=99.9999% case

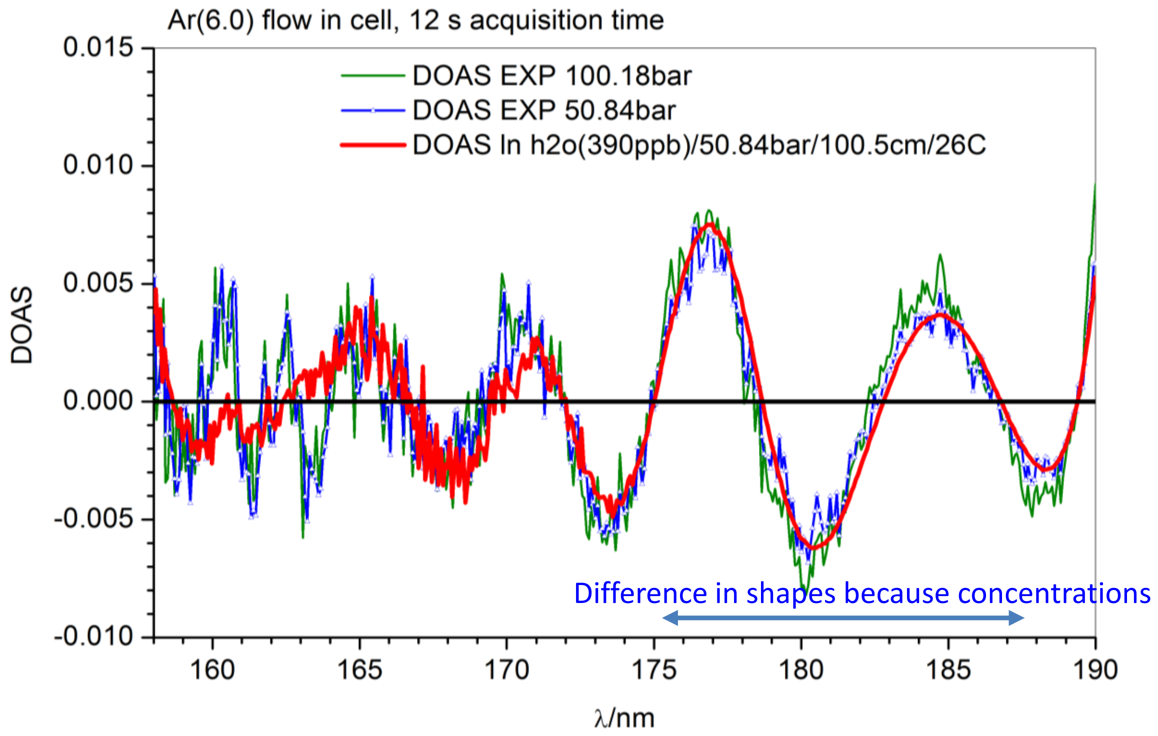




- ❑ More complex spectra however the ABS spectral shape is H_2O-dominated
- ❑ Appearance of N_2(LBH) system at 158 nm < (collisional-induced absorption)
- ❑ Cross-spectra fit: “whole” and “DOAS”

A1.1.2 Limits & Uncertainties





- ❑ ABS increase dominates over H_2O decrease (enhancement factors)
- ❑ ABS-values are high
- ❑ 3% difference in H_2O visually seen
- ❑ S/N (ΔABS) can be increased (12 s <)

ABS ~ cs x X_{H2O} x p x T^{-1} x L; ABS as an integral or ABS(λ)
cs = cross sections (do not depend on ILS of spectrometer)
p = gas pressure in cell (KISTLER 100 bar abs)
T = temperature (TC, ΔT); L = gas cell length (ΔL)
ΔX_{H2O} to be calculated after P/TC calibrations

A1.1.3

Improvements in the existing **FTIR-based** trace water measurements in N_2 and Ar

With an input from Seda OĞUZ AYTEKİN

A1.1.3 M24	TUBITAK will improve the existing FTIR-based trace water measurements in N_2 and Ar from 5 ppm to 50 ppb with standard relative uncertainty between 3 % and 8 % and operation pressure up to 1 MPa. The existing high-resolution FTIR system will be upgraded with a new pump system and a new multi-pass gas cell to enable water vapor measurements down to 50 ppb and operating pressure in the cell up to 1 MPa.	**TUBITAK**

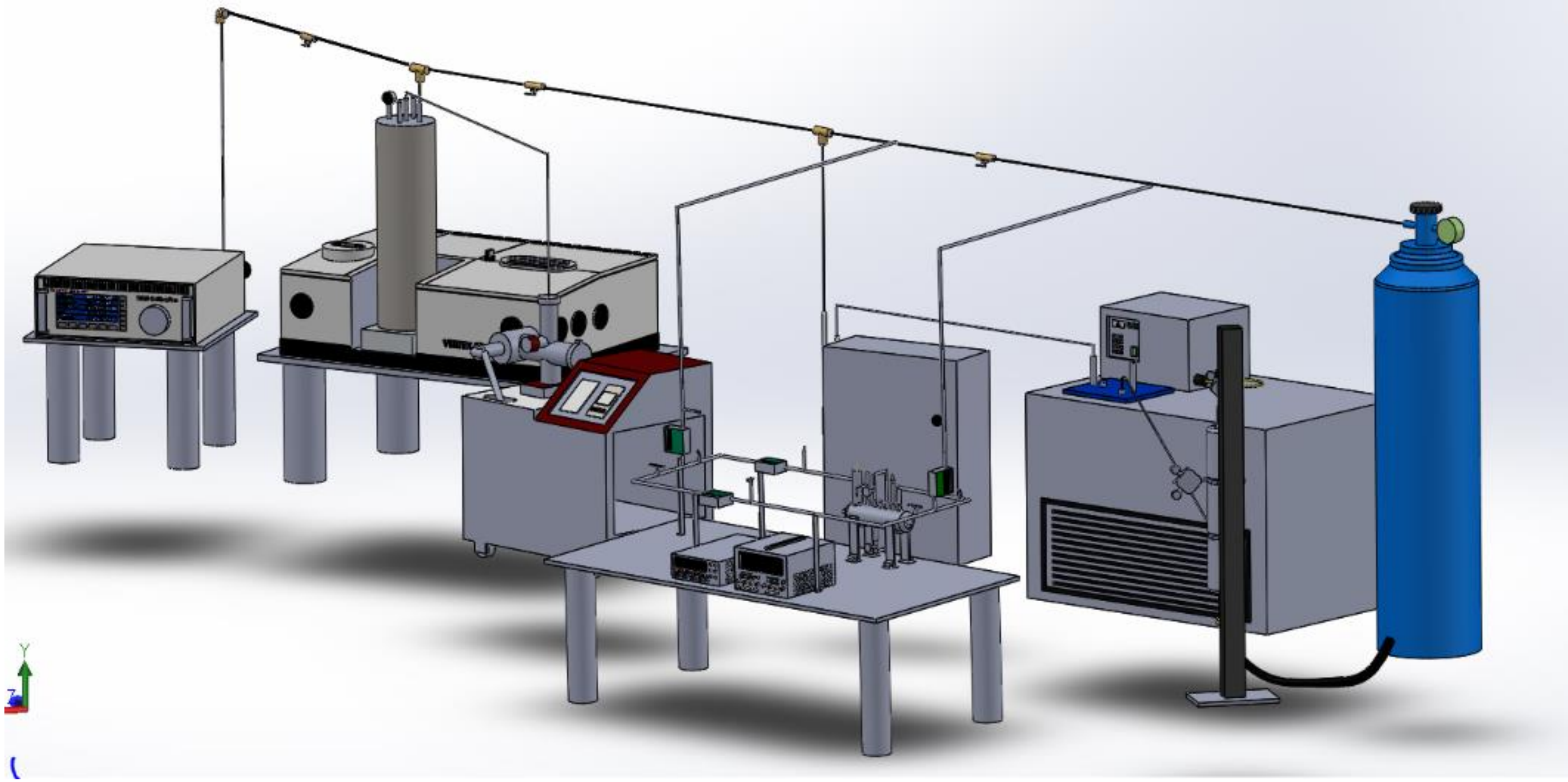
- ✓ A new multi-pass gas cell and the related interfaces were integrated into the existing FT-IR spectrometer system;
- ✓ A new MCT detector were installed into the **Bruker Vertex 70 FT-IR** spectrometer and the system was integrated with a multi-pass gas cell.
- ✓ A gas supply system for measurements in the FT-IR spectrometer has been constructed;
- ✓ A purging system for the optical path has been constructed;

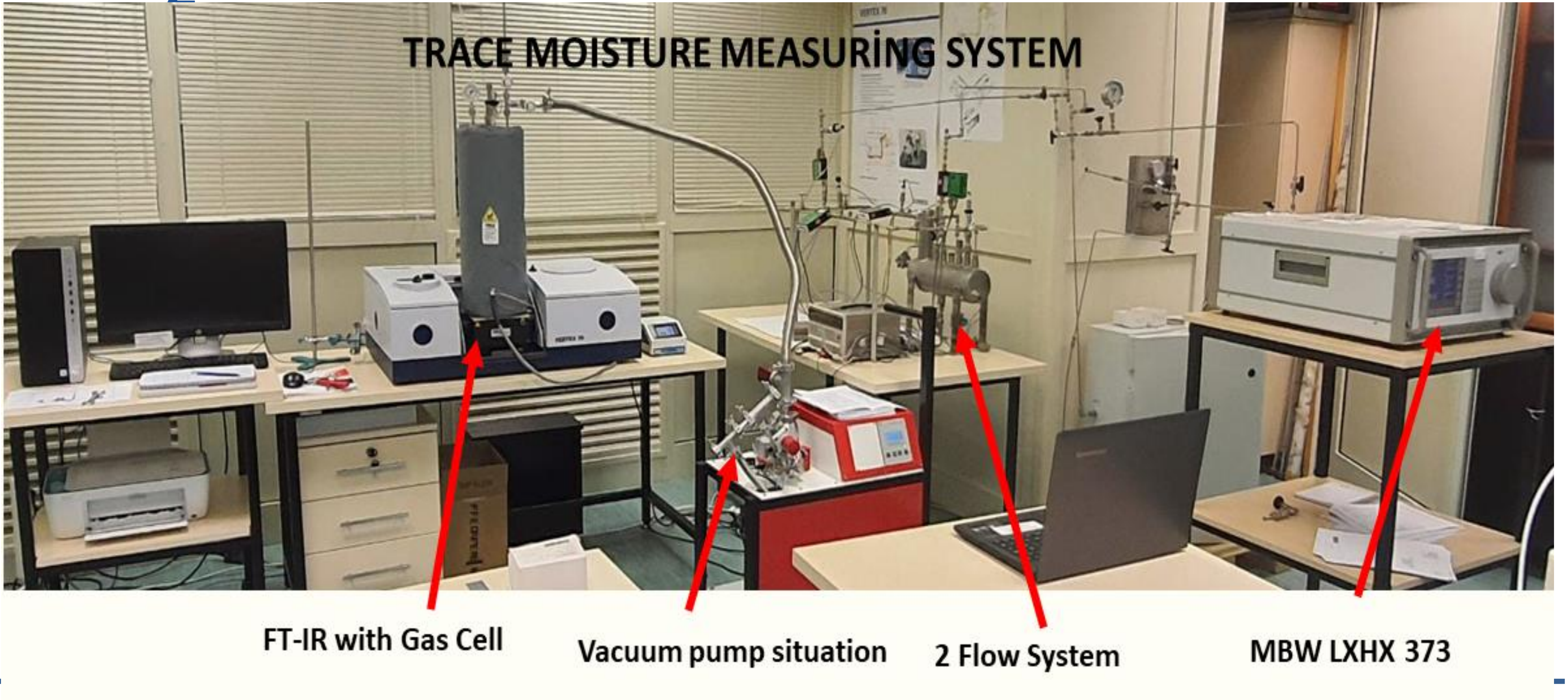
- ❑ The full metrological characterization of the system is under way;
- ❑ Measurement uncertainty budget is under the preparation.

- Currently, the measurements with **conditioned Air at 1 bar** is ongoing;
- Preliminary measurements are **satisfactory** but the measurement system still **needs improvements**;
- A PhD student has involved into this Project. Trainings are on-going on the subjects: humidity and moisture metrology, measurement uncertainty and FT-IR spectrometry.

Trace Moisture Measuring System

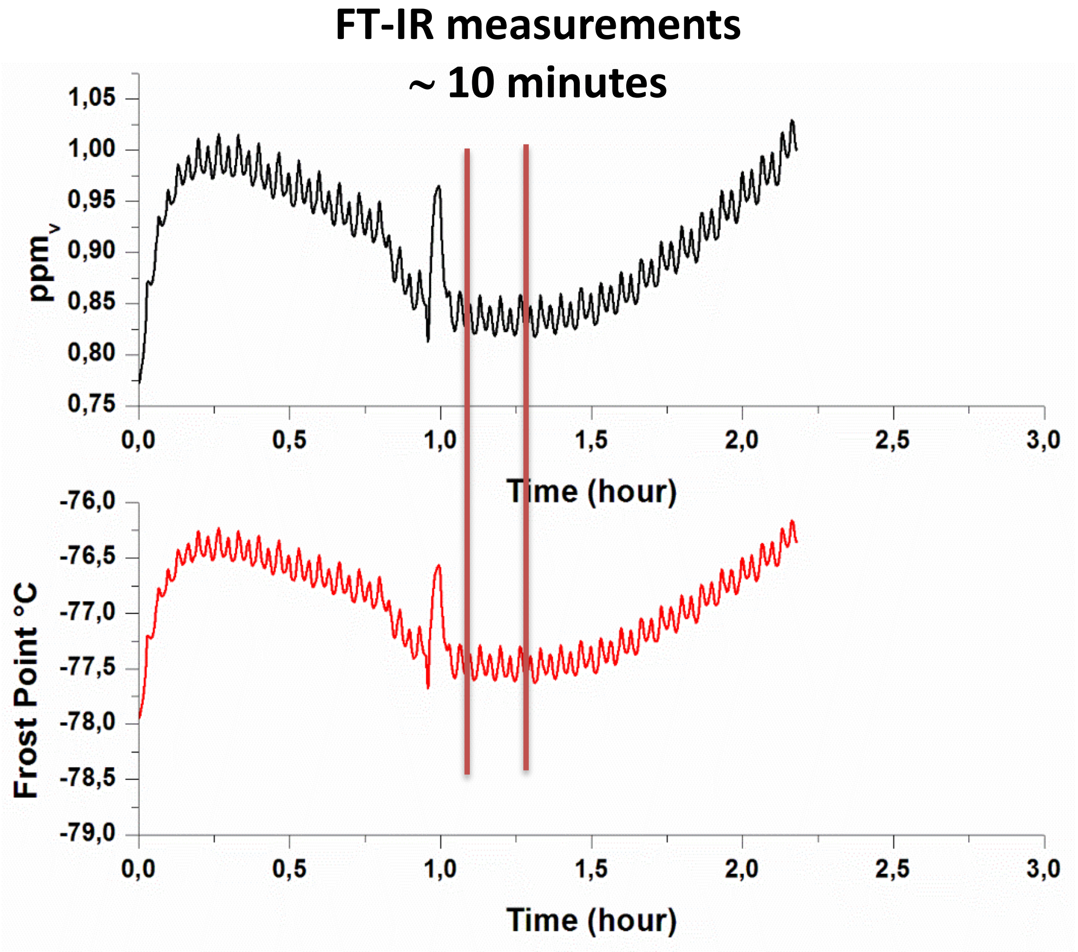
- Drying Unit was integrated into 2F humidity generator.
- Measurements conducted simultaneously by FT-IR and DPHM.
- System is under vacuum to prevent ambient effects.
- FT-IR system purged with N_2.

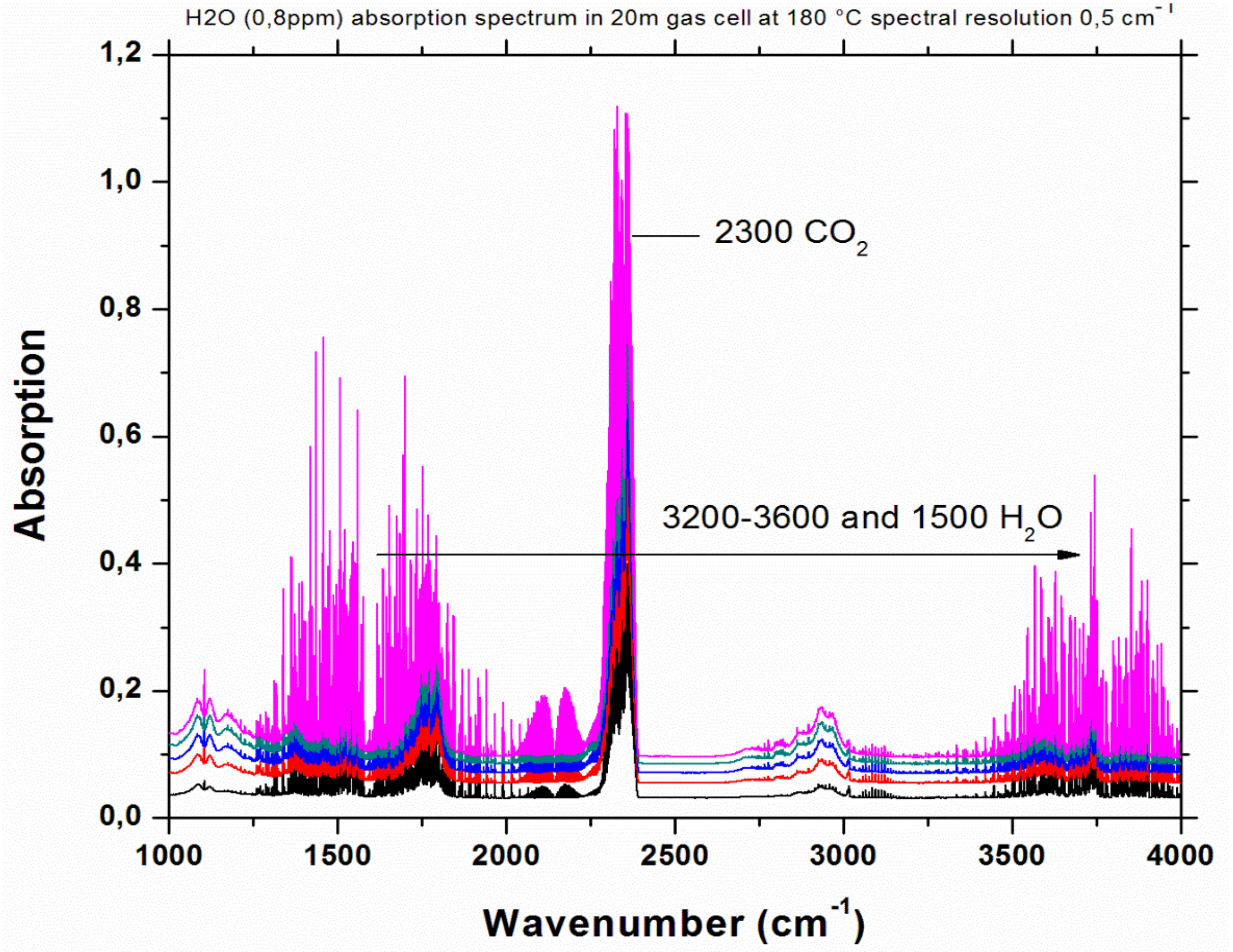



TRACE MOISTURE MEASURİNG SYSTEM
FT-IR with Gas Cell
Vacuum pump situation
2 Flow System
MBW LXHX 373

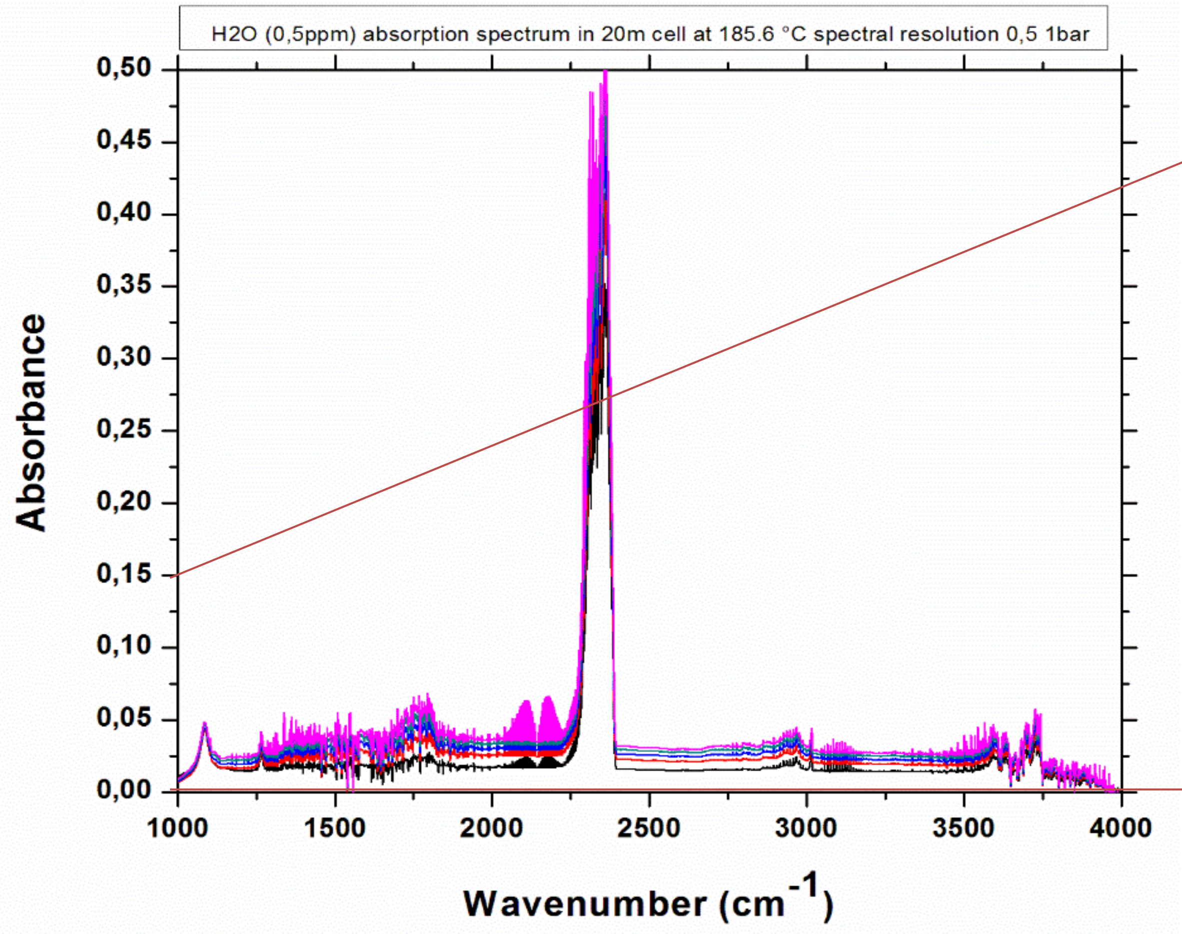
A1.1.3 FTIR vs. DPHM

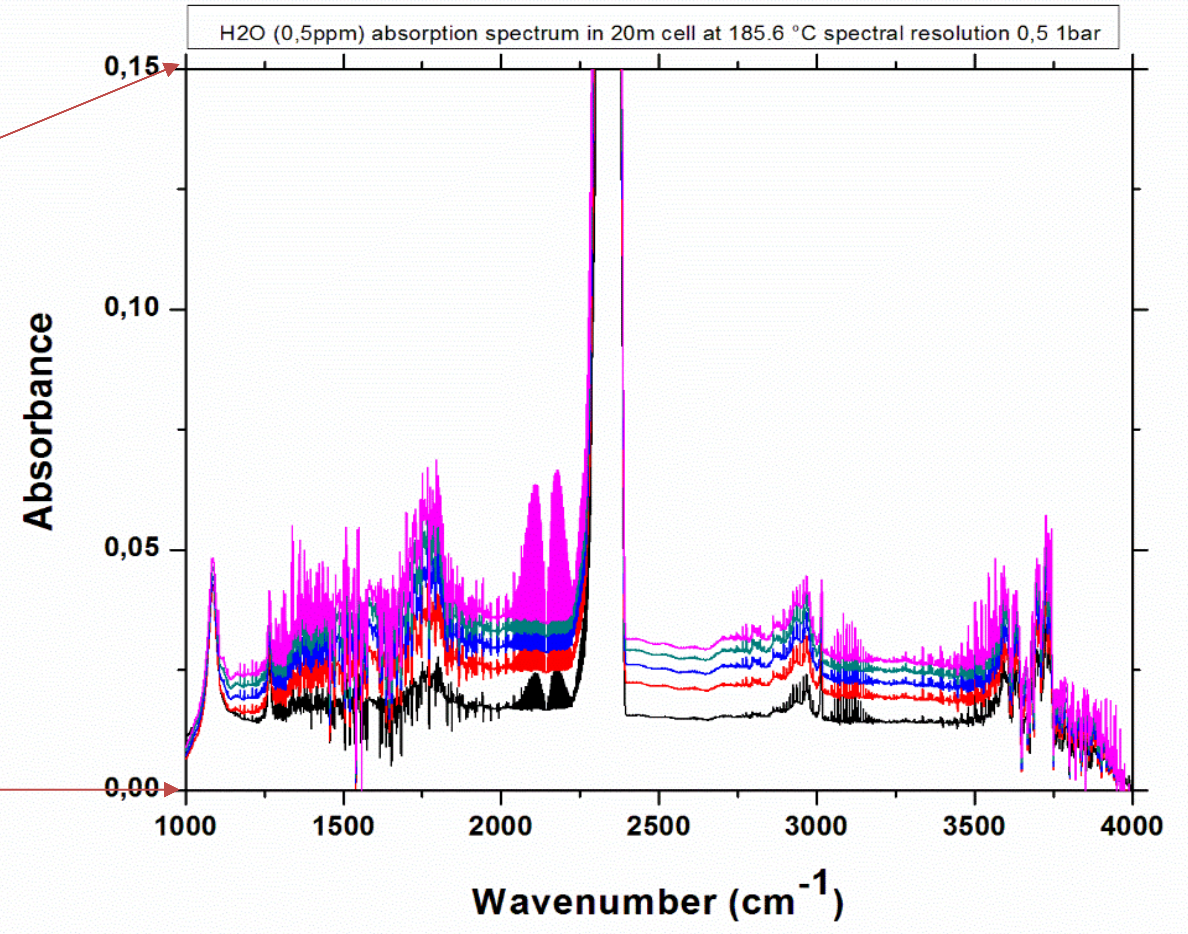
Measurement results from both DPHM and FT-IR at 0.8 ppm (-75°C)(20m cell)





A1.1.3 FTIR Measurement results





FT-IR measurements (20 m cell), system is under vacuum for 3 days at 185 °C

A.1.1.4

Develop a **NIR** cavity-enhanced frequency-modulated **(CE-FM)** spectroscopy hygrometer

With an input from Ned Hawes

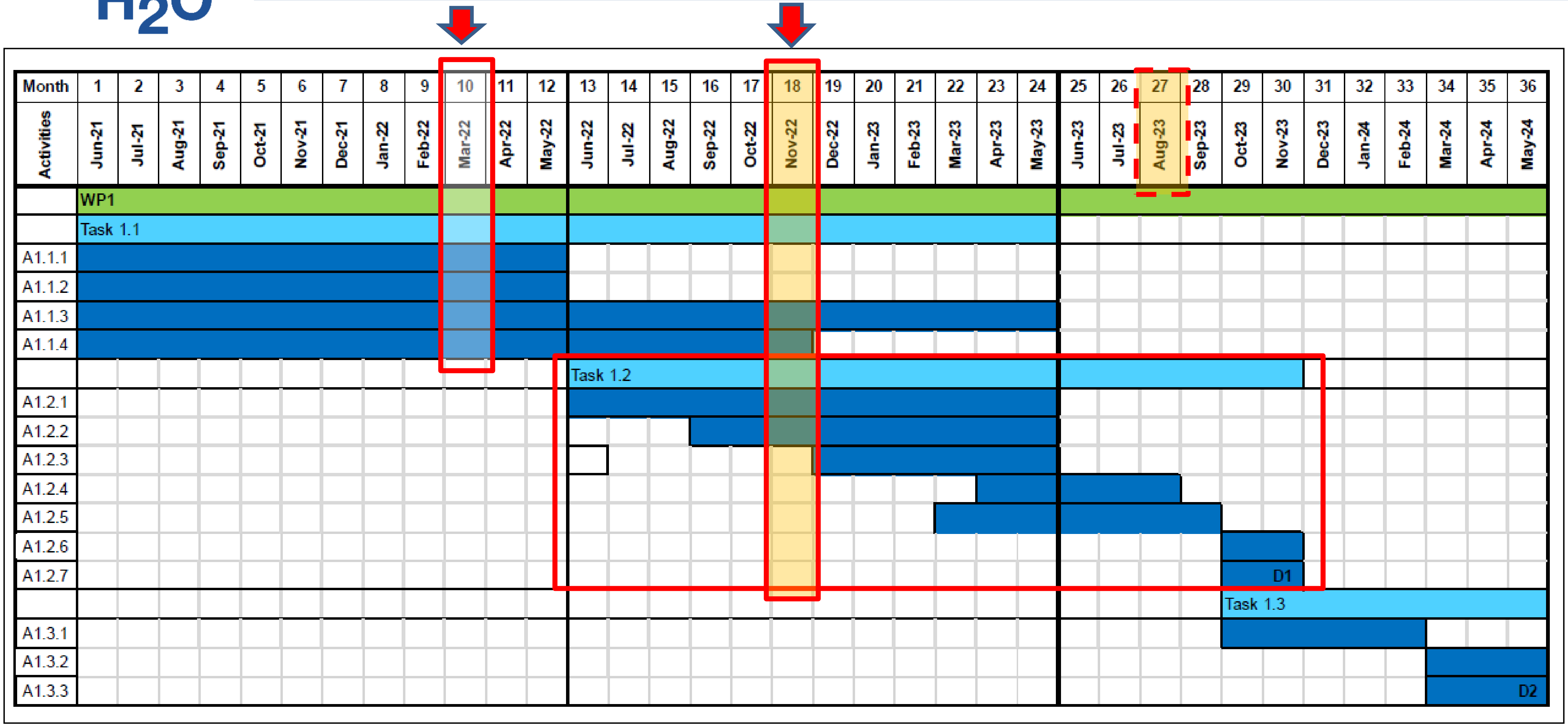
- ?

Task 1.2: Validation of the measurement methods and techniques

Task 1.2

M9 (web) meeting

M18 meeting at VSL

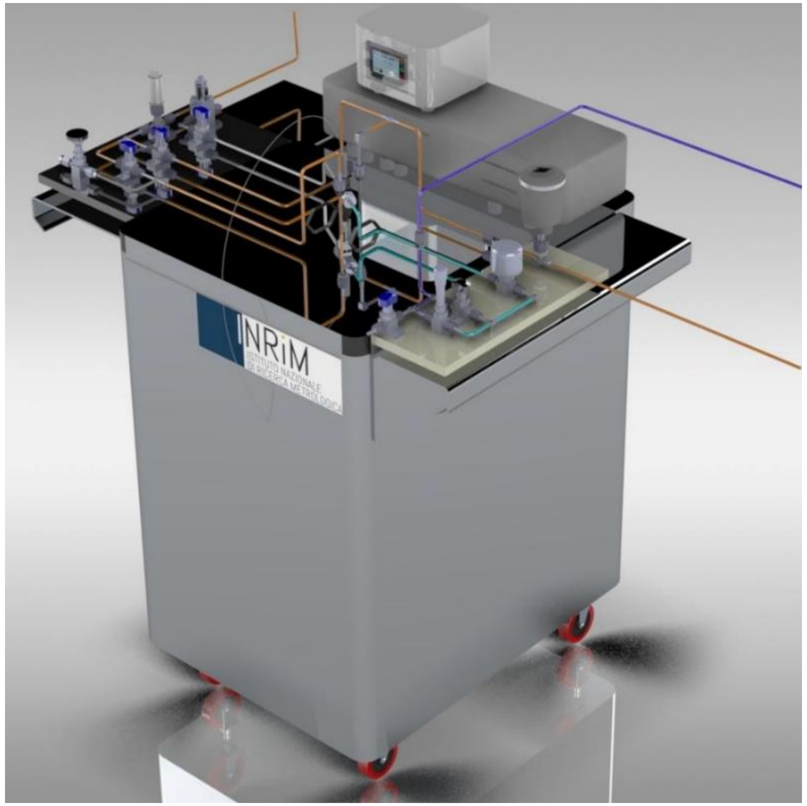


A1.2.1

A1.2.1 M24	SUN will validate and perform an inter-comparison of the CC-FS-CRDS spectrometer developed in A1.1.1 with a reference humidity generator. Because the CC-FS-CRDS system use requires a self-reference optical frequency comb which is not transportable, the system validation will be done in the same laboratory where it was developed. SUN, with the support from INRIM, will assess the performance, possible gas matrices effects on the measurements and measurements uncertainties of CC-FS-CRDS spectrometer in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**SUN**, INRIM

- ✓ **INRIM loaned to SUN a calibrated CRDS analyser (HALO RP Trace H2O) in May 2022 to support SUN in the assessment of the CC-FS-CRDS.**

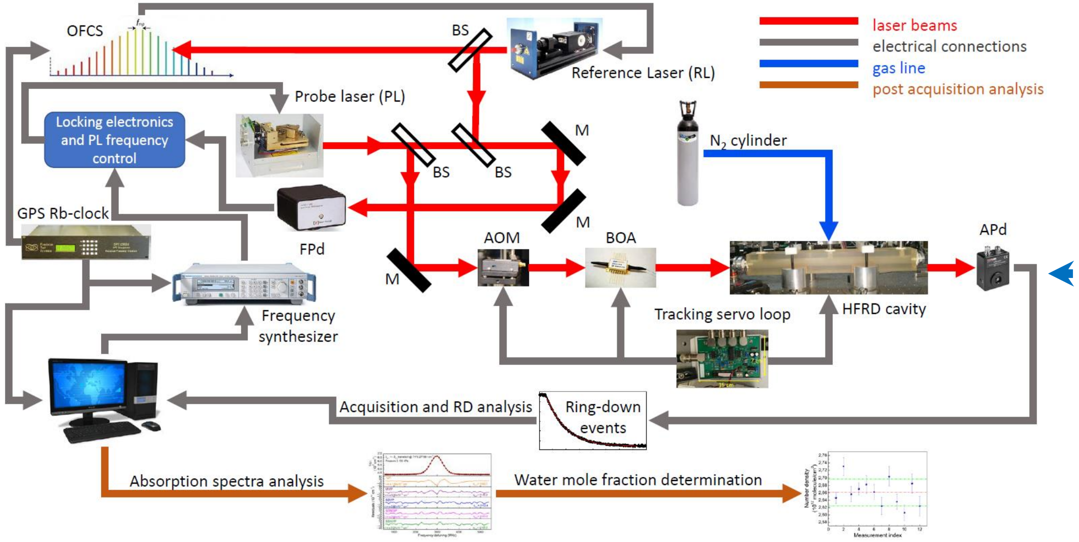
LFP HUMIDITY GENERATOR



- 2-pressure, single-pass humidity generator
- **Frost-point temperature between -105 °C and -20 °C**
- **Water vapour mole fraction between 5 ppb_v and 1038 ppm_v @1000 hPa**
- **Pressure: 200 hPa to 5000 hPa**
- Carrier gas: Nitrogen, Argon

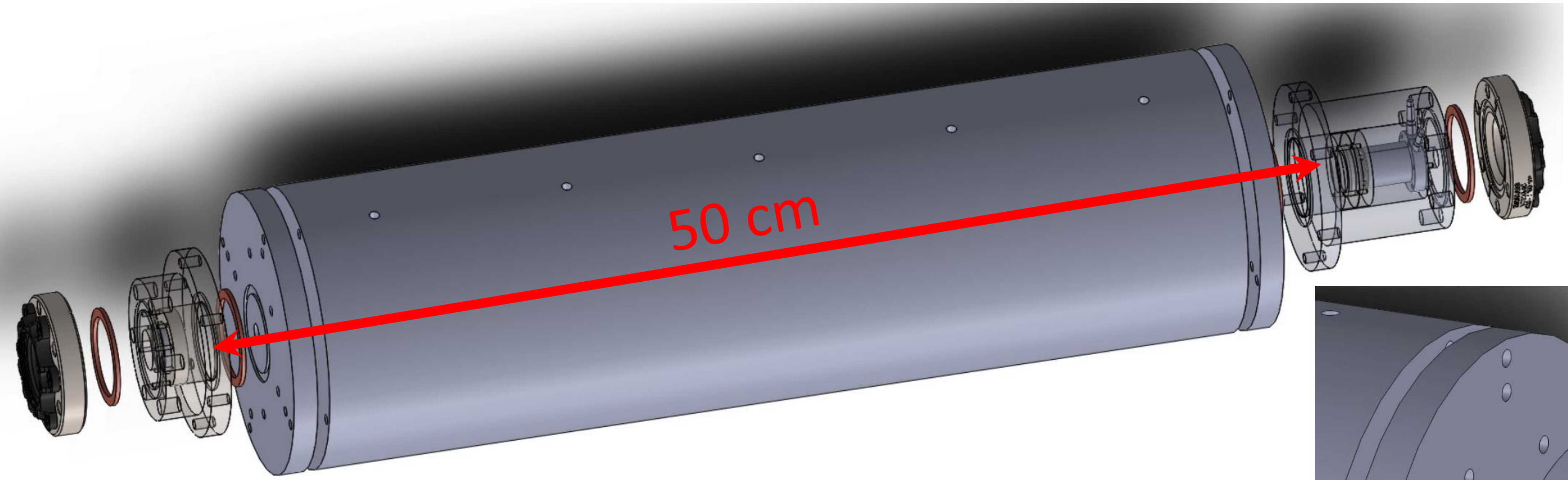
A1.2.1 CC-FS-CRDS comparison & validation: preliminary tests

So far, limited success in the comparison: sticking of water molecules on the cavity walls!

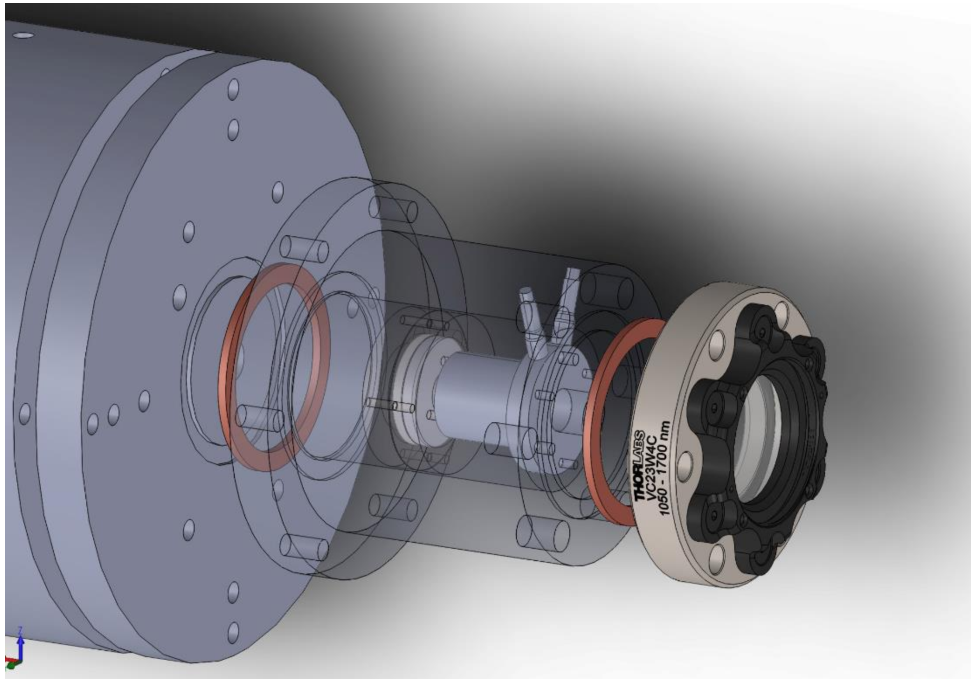


Tiger Optics CRDS analyzer traceable to INRIM humidity standards (with Vito & Rugiada)

A.1.2.1 CC-FS-CRDS: Design of a new cavity spacer: 1^{st}

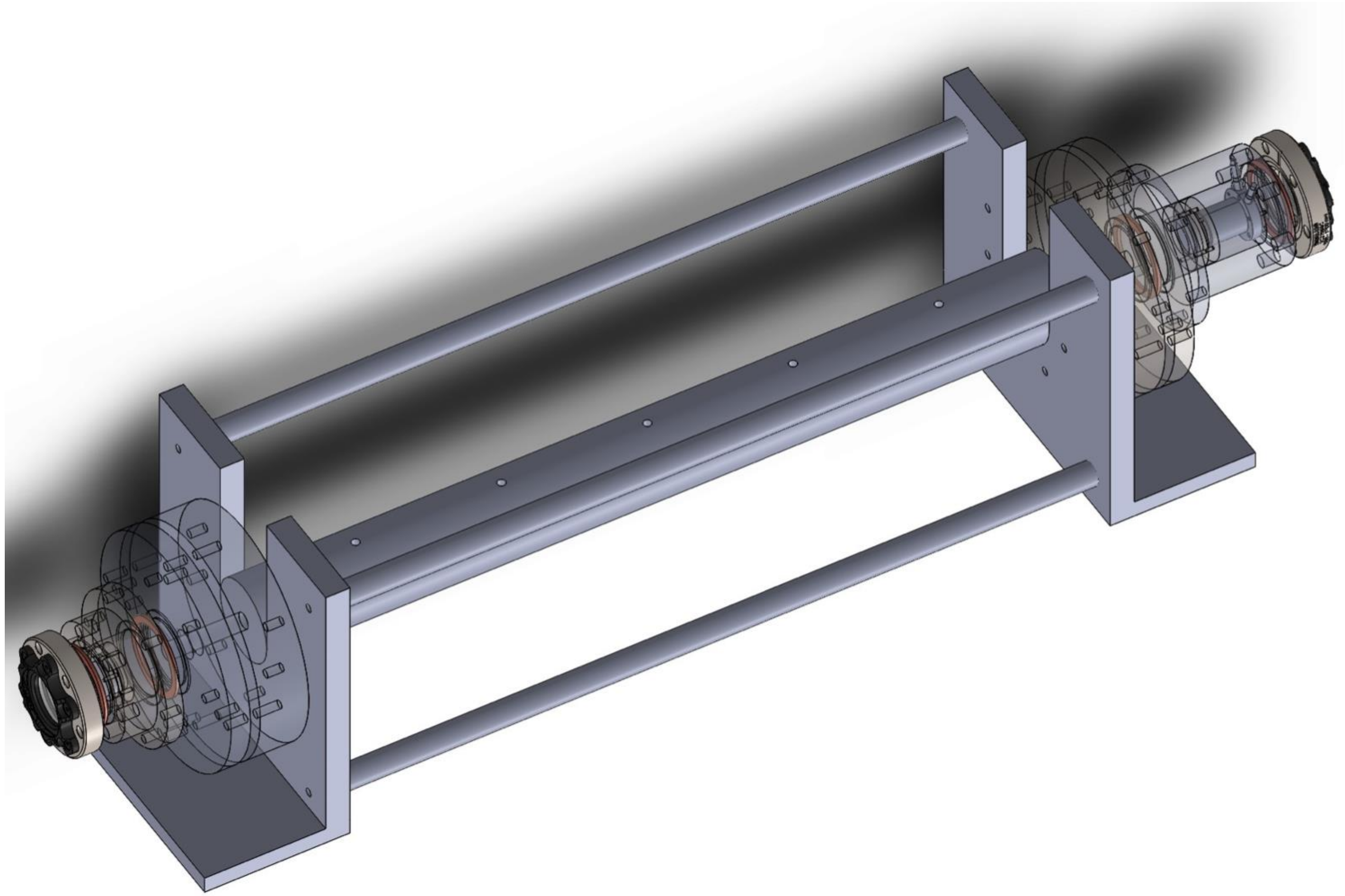


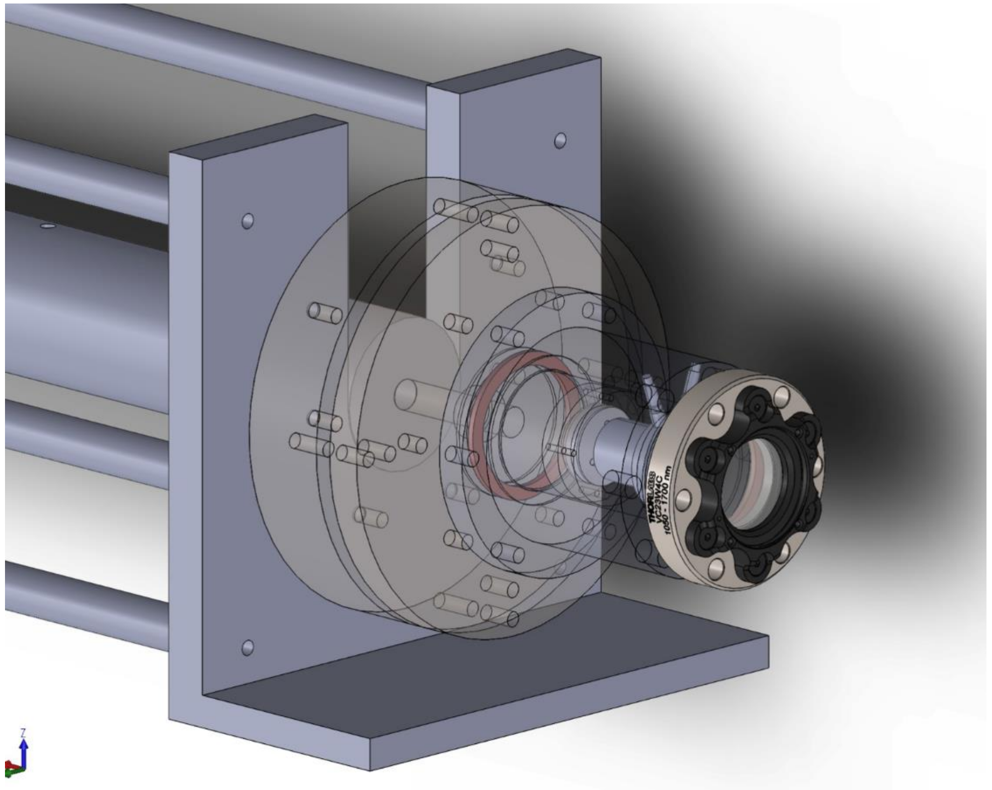
New mirrors (higher R!)



- Electrically polished 316-L stainless-steel;
- Internal surfaces minimization (ϕ_{int}=10 mm);
- No glue;
- No Viton O-ring;
- Stainless-steel enclosed, 3 piezo actuators;
- Dursan coating to minimize water stickling.

A.1.2.1 CC-FS-CRDS: Design of a new cavity spacer: 2nd



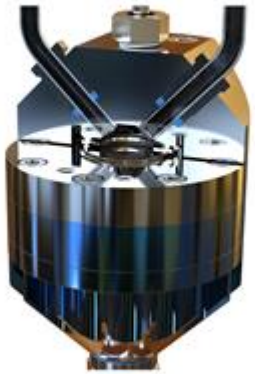


During the realization of the new spacer, a simpler approach:

- Validation of new cavity spacer in the next 6-9 months

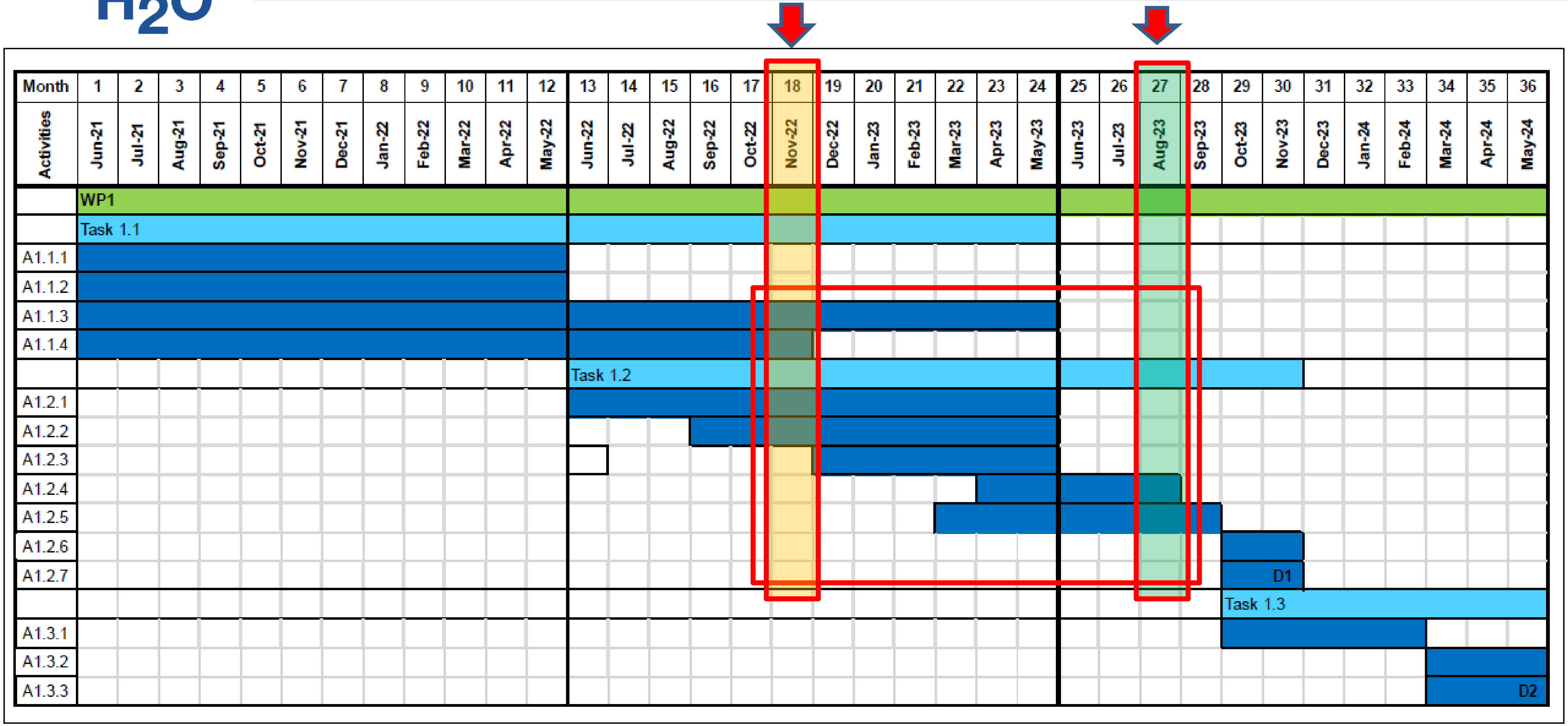
A1.2.2 M24	Qrometric, MBW and INRIM will validate and perform an inter-comparison of a commercial high-quality CMH for ultra-low frost-point measurements (5 ppb/-105 °C) with trace water generator improved in A2.1.1. Qrometric, MBW and INRIM will assess the performance, and possible gas matrices effects on the measurements and measurements uncertainties of high-quality CMH in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**INRIM**, MBW, Qrometric,

- ✓ **INRIM** purchased a **SLX CMH** from MBW Calibration. At the moment the chilled mirror hygrometer is under assessment.



WP1: Next 9 months

M18 meeting at VSL



A1.1.2 M12	DTU will develop a compact and transportable far-UV system for trace water vapours measurements in Ar, N_2 and H_2 from 5 ppm to 5 ppb with standard relative uncertainty between 3 % and 8 % and operation pressure up to 1 MPa.	**DTU**

Small improvements & add-ons:

- ❑ **KISTLER (100bar)/TC (accredited) calibration**
- ❑ **DURSAN coatings for Ø 3mm + Swagelok valve + Fittings (inlet side) for industrial trials**
- ❑ **H_2O-measurements (50bar-60bar) at lower ABS**

A1.1.3 M24	TUBITAK will improve the existing FTIR-based trace water measurements in N_2 and Ar from 5 ppm to 50 ppb with standard relative uncertainty between 3 % and 8 % and operation pressure up to 1 MPa. The existing high-resolution FTIR system will be upgraded with a new pump system and a new multi-pass gas cell to enable water vapor measurements down to 50 ppb and operating pressure in the cell up to 1 MPa.	**TUBITAK**

- **On-going FTIR-system improvements: Filter, etc.**
- **More H_2O-measurements.**

A1.2.1 to A1.2.3

A1.2.1 M24	SUN will validate and perform an inter-comparison of the CC-FS-CRDS spectrometer developed in A1.1.1 with a reference humidity generator. Because the CC-FS-CRDS system use requires a self-reference optical frequency comb which is not transportable, the system validation will be done in the same laboratory where it was developed. SUN, with the support from INRIM, will assess the performance, possible gas matrices effects on the measurements and measurements uncertainties of CC-FS-CRDS spectrometer in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**SUN**, INRIM

- Next steps to be planned between SUN and INRIM

A1.2.2 M24	Qrometric, MBW and INRIM will validate and perform an inter-comparison of a commercial high-quality CMH for ultra-low frost-point measurements (5 ppb/-105 °C) with trace water generator improved in A2.1.1. Qrometric, MBW and INRIM will assess the performance, and possible gas matrices effects on the measurements and measurements uncertainties of high-quality CMH in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**INRIM**, MBW, Qrometric,

- Would Qrometric join this activity at M19 (December 2022)?

A1.2.3 M24	Qrometric with support from INRIM and MBW will validate and perform an inter-comparison of the cavity-enhanced frequency modulated (CE-FM) spectroscopy hygrometer developed in A1.1.4 with a reference trace water generator. Qrometric, INRIM, and MBW will assess the performance, and possible gas matrices effects on the measurements and measurements uncertainties of in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**Qrometric**, INRIM, MBW

- Activity starts in December 2022
- Further steps will be discussed (web)

PRO MET H_2O

A1.2.4

A1.2.4 M27	DTU and Qrometric will validate and perform an inter-comparison of the far-UV system developed in A1.1.2 against a traceable transfer standard water analyser (e.g. CE-FM from A1.1.4 or CMH from A1.1.2). DTU and Qrometric will assess the performance, and possible gas matrices effects on the measurements and measurements uncertainties in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**DTU**, Qrometric

- **Activity starts in April 2023;**

- **Option 1: FPG (max 1.5 bar) shipment to DTU;**
- **Option 2: measurements at INRIM om LFP generator (5 bar);**
- **To be further discussed (web)**

A1.2.5 M28	TUBITAK will validate the upgraded FTIR system from A1.1.3 regarding in house reference humidity generator and gas mixtures. TUBITAK will assess the performance, and possible gas matrices effects on the measurements and measurements uncertainties in the amount fraction range between 5 parts in 10^6 (5 ppm) and 50 parts in 10^9 (50 ppb) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.	**TUBITAK**

- ❑ **Activity starts in March 2023**

- ❑ TUBITAK will perform validation measurements of the upgraded FTIR system (in Task 1.1) by means of its the reference humidity generators;
- ❑ The targeted water concentration to be measured is between 5 ppb and 5 ppm at pressures up to 1 MPa;
- ❑ Performance analysis of the used methods and thoroughly study of measurements uncertainties will be investigated and assessed at TUBITAK.

WP1: Next 9 months

PROMETH2O

Thank you for your attention

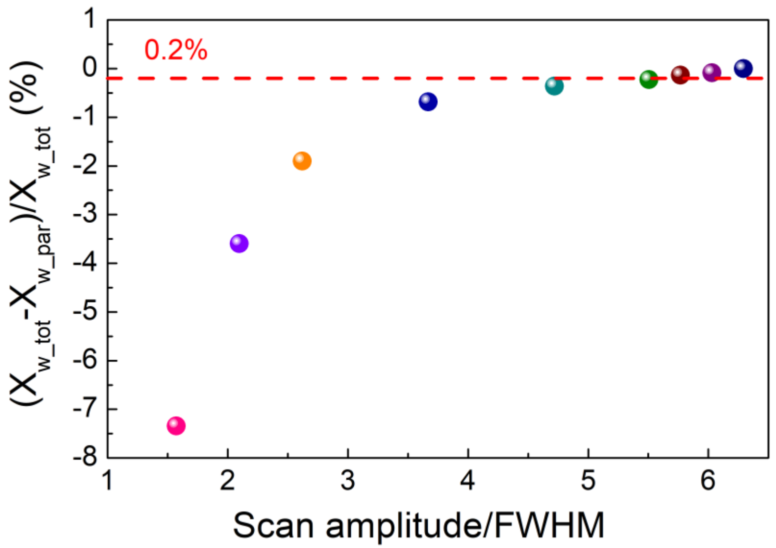
EMPIR EURAMET
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

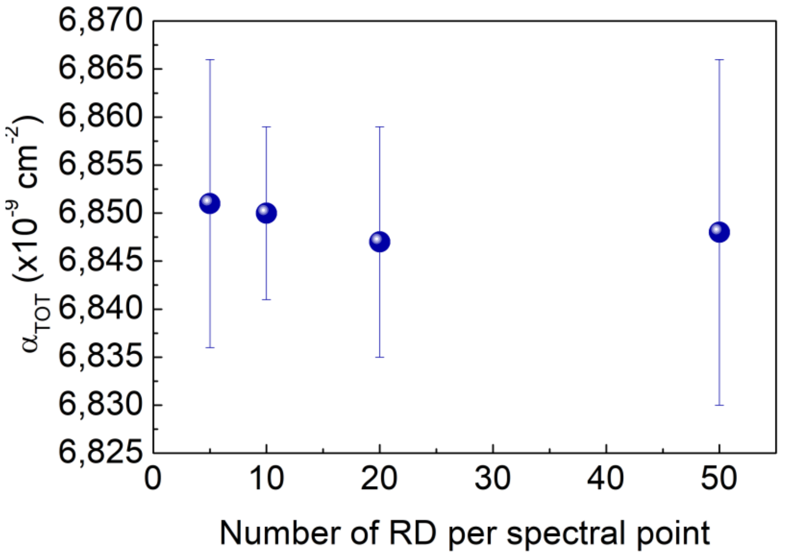
Extra slides

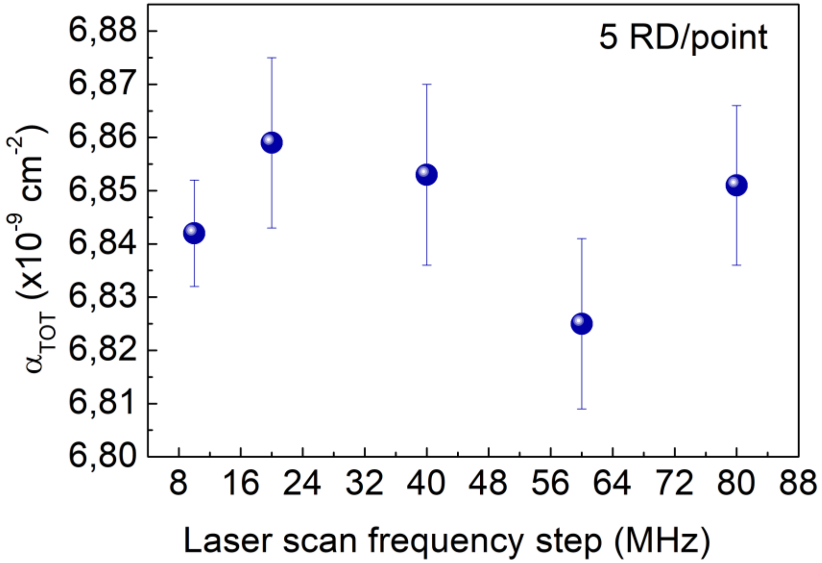
The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

CC-FS-CRDS: Dependence of x_W on experimental parameters

#RD/spectral point



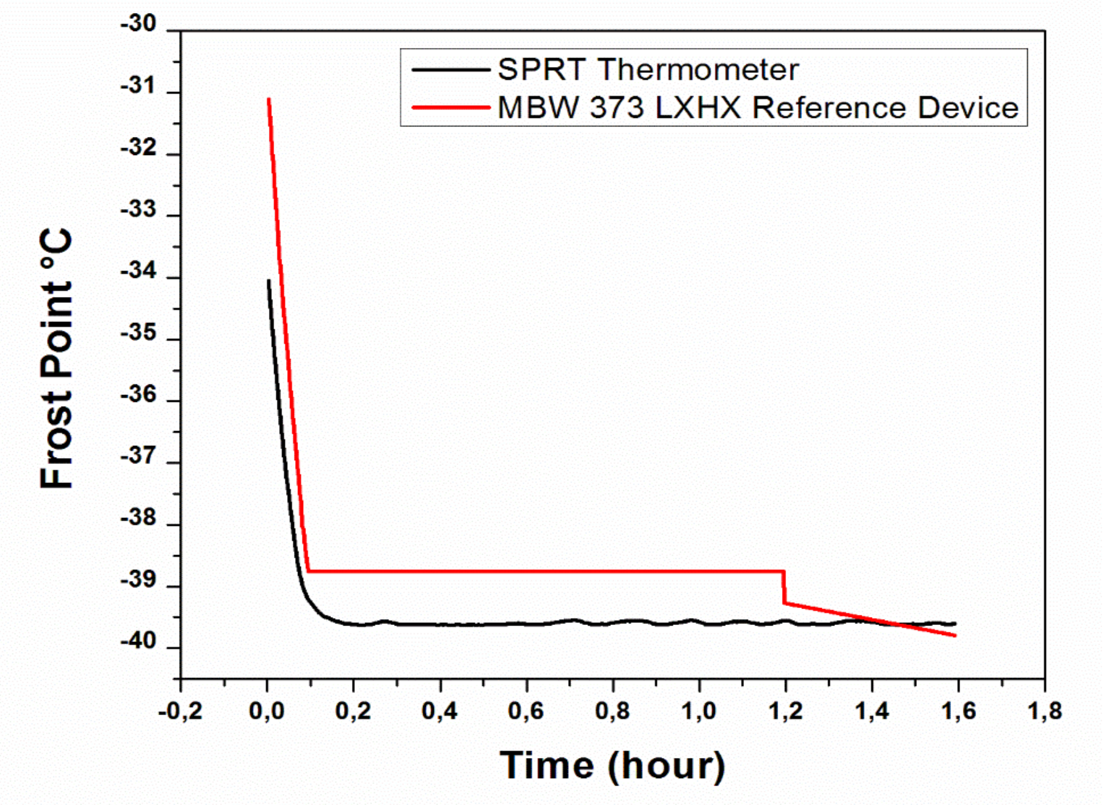


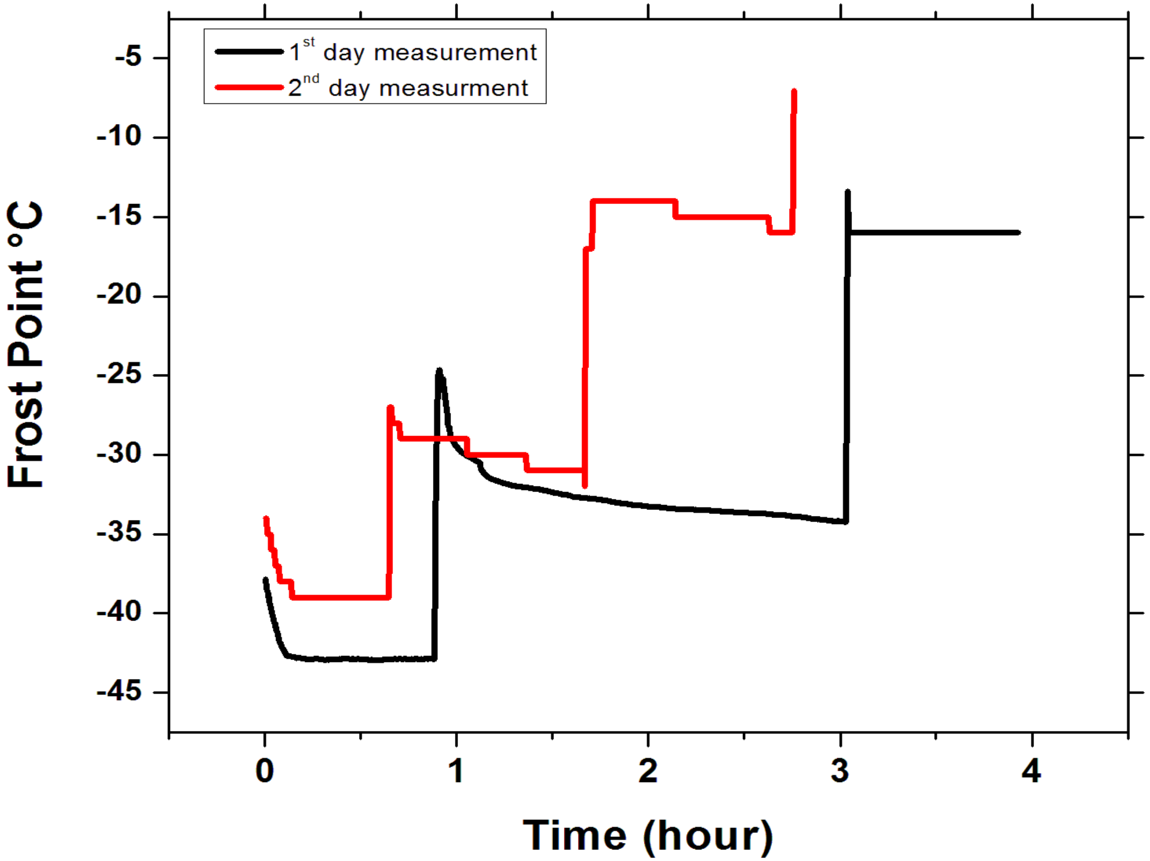


Amplitude of the laser scan

Frequency step

Characterization of Liquid Bath – Before Drying Unit

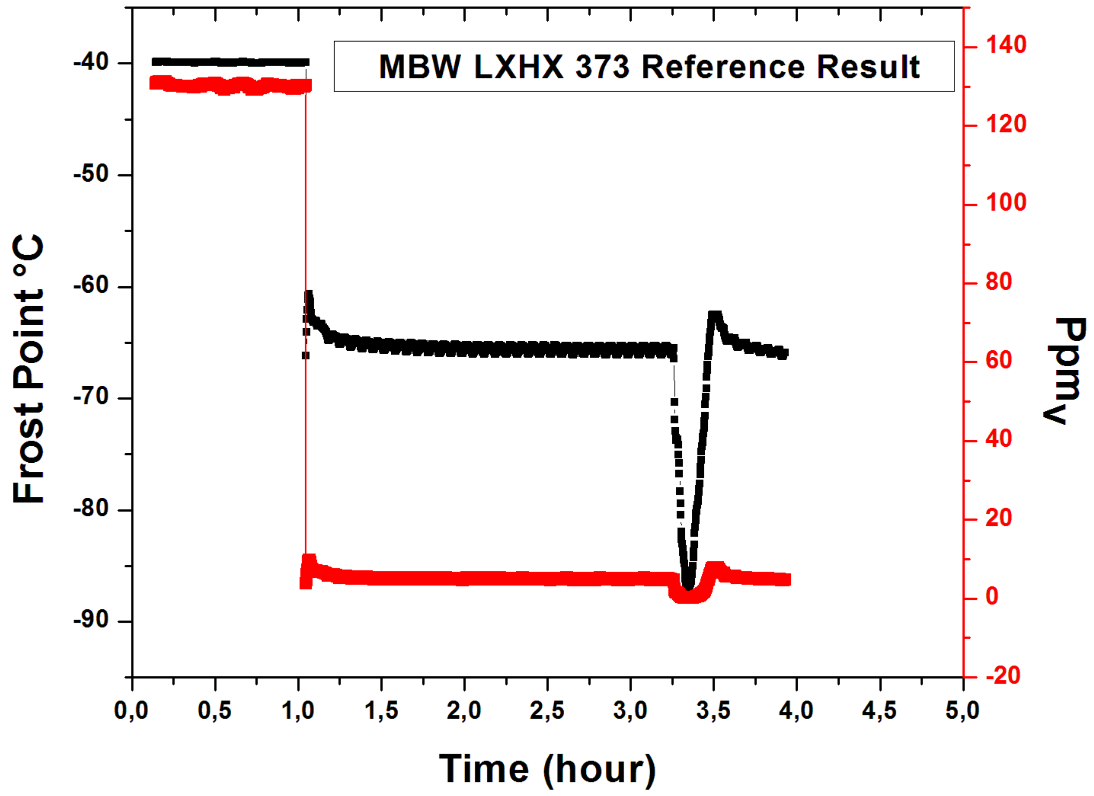




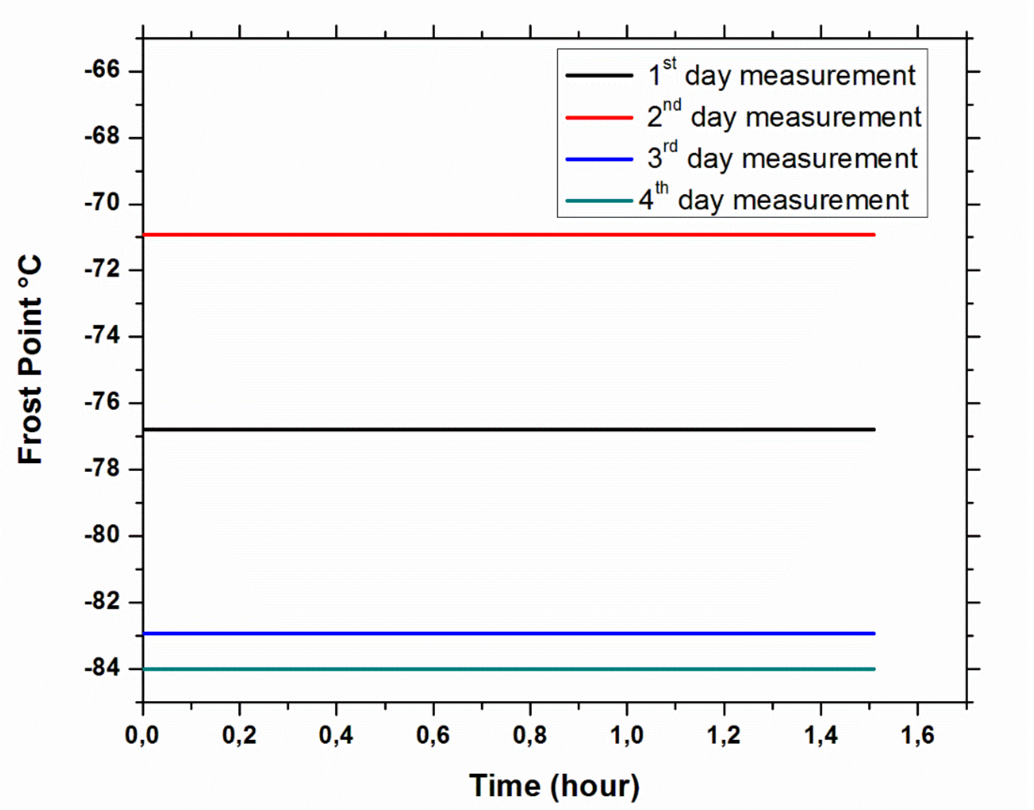
The stability graph of the bath temperature at -40°C measured both by SPRT and DPHM. Drying Unit is fed by the air obtained from the liquid bath.

Mixing the dry air at -40 °C in 2F humidity generator.

Characterization of dry air



FP and ppm values of dry air obtained by using Lauda Bath and PSD4 Dryer Unit.



Graph shows the dry air stability measurement results obtained from DPHM at -75 °C. Output of the drying unit.

TUBITAK UME Future Plans …

- System improvements: Filter, etc.

- TUBITAK UME **Humidity and Gas Metrology Laboratories** will participate a training held by BIPM:

  UME - BIPM Knowledge Transfer Online Training – FT-IR for Gas Standards under

  CBKT Project: Metrology for Clean Air – FTIR for Gas Standards: on-line knowledge transfer programme.

  Course Content:

  Interpretation of FTIR spectra for gas analysis. Application of FTIR measurement techniques for a number of key air quality gases: NO/N_2 over the range 30 µmol/mol to 70 µmol/mol, NO_2/N_2 over the range 2 µmol/mol to 15 µmol/mol, and CO_2 over the range 380 µmol/mol to 480 µmol/mol.

TUBITAK UME – Task 1.3 / A1.3.1 & A1.3.2

WP1: Improved trace water measurement methods and techniques

Task 1.3: Recommendation of transfer standards for a future CIPM comparison in the trace water range -65 °C to -105 °C (5 ppm to 5 ppb)

Activity number	Activity description	Partners (Lead in bold)
A1.3.1 **M33**	INRIM, PTB, TUBITAK and DTU will review the results of validation and inter-comparison work in the Task 1.2. A selection of instrumentation suitable for use as a transfer standard in the ultra-trace water range taking into account instrument(s) accuracy, reproducibility, stability and ability to handle gas matrices effects will be made.	**DTU**, INRIM, PTB, TUBITAK
A1.3.2 **M36**	INRIM, PTB, TUBITAK and DTU will use the results of the A1.3.1 to write a recommendation report for a future CIPM inter-comparison in the trace water range **(deliverable D2)**.	**INRIM**, PTB, TUBITAK, DTU

- TUBITAK will share the results of the validation measurements and review the results of other participants to summarise the findings in Task1.1 and 1.2;
- TUBITAK will contribute to the recommendation report for a future CIPM inter-comparison in the trace water range.