PROMETH$_2$O

20IND06 PROMETH2O

WP1: Improved trace water measurement methods and techniques up to M27 Status Report M28-M36 Planning

EMPIR EURAMET
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)

- ❑ Task 1.1: Development and improvement of optical analyzers
- ❑ Task 1.2: Validation of the measurement methods and techniques
- ❑ Task 1.3: Recommendation of transfer standard(s) for a future CIPM comparison in the trace water range -65 °C to -105 °C (5 ppm to 5 ppb)

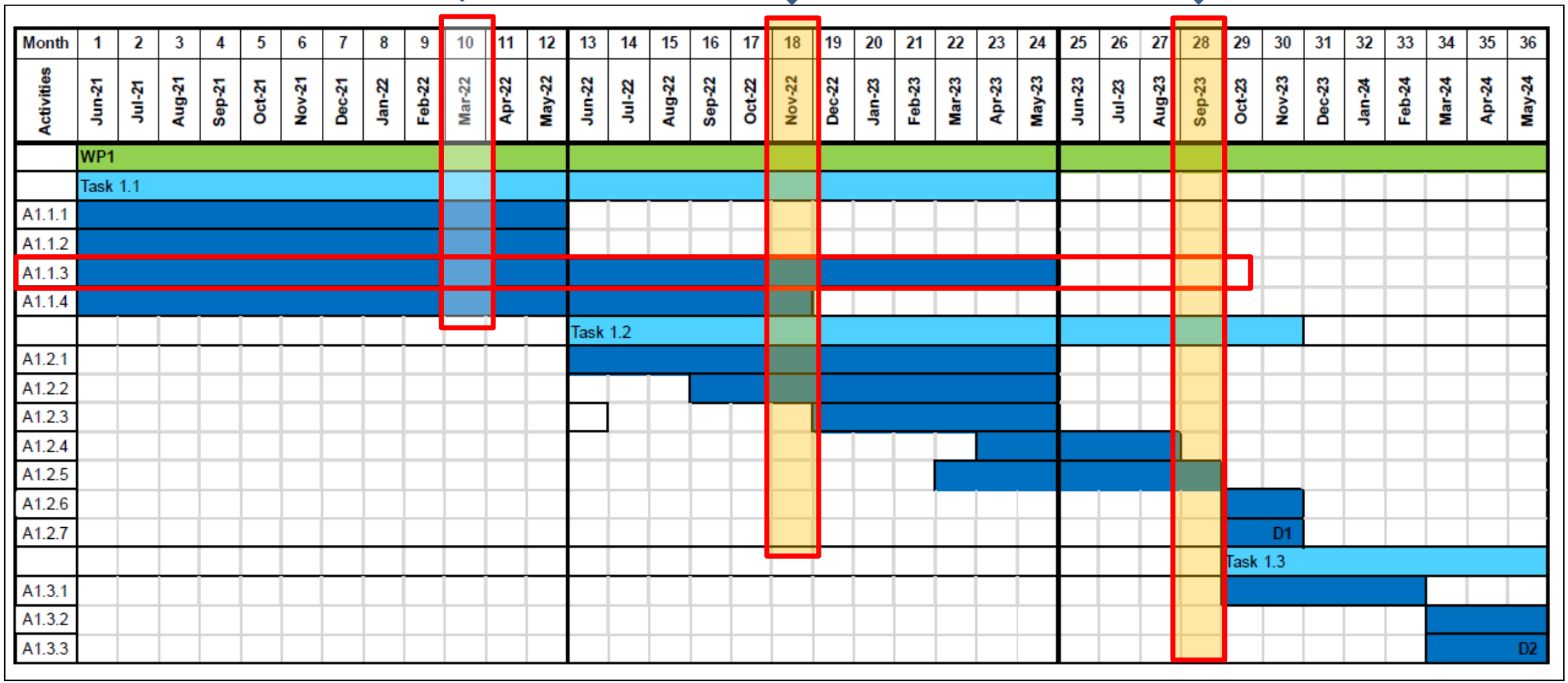
Task 1.1: Development and improvement of optical analyzers

Task 1.1

M9 (web) meeting

M18 meeting at VSL

M27 WEB meeting



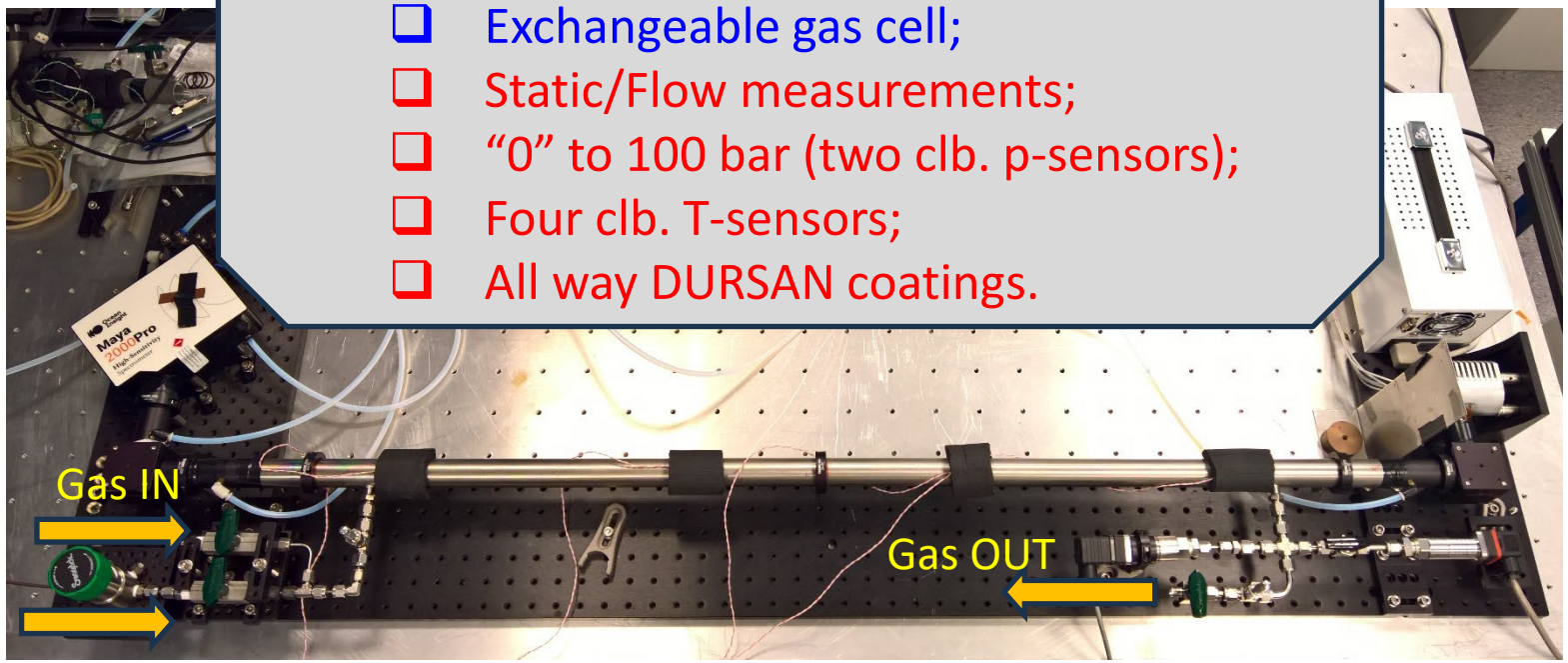
A1.1.2

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

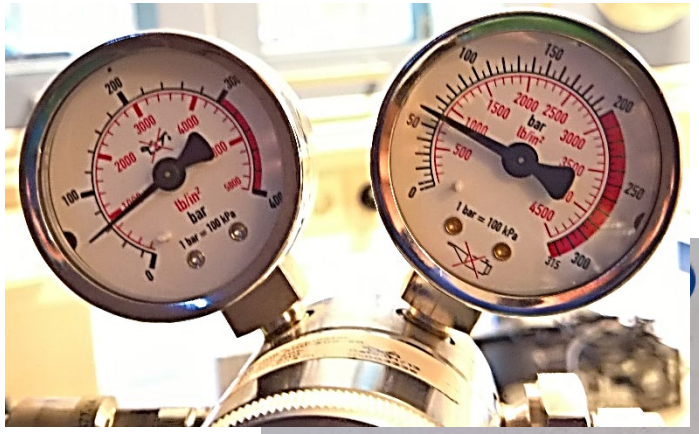
With an input from Alexander Fateev

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**

- Modular system;
- Exchangeable gas cell;
- Static/Flow measurements;
- “0” to 100 bar (two clb. p-sensors);
- Four clb. T-sensors;
- All way DURSAN coatings.



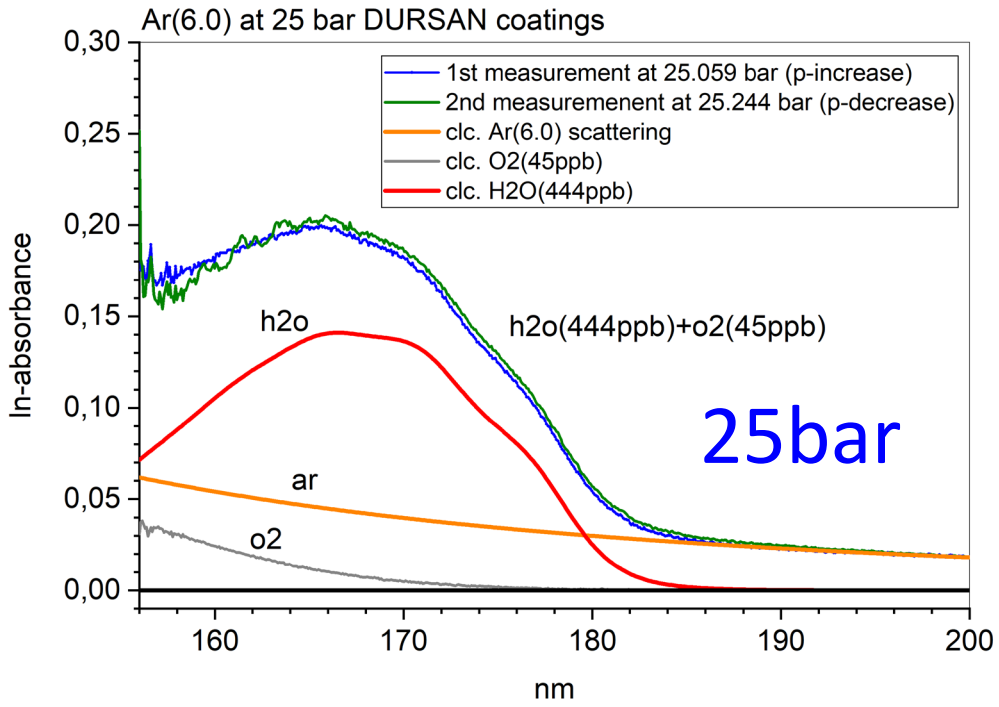
- Gases: Ar, N2, H2, CH4, etc.
- Two gas inlets;
- Ar or N2 purge;
- Measurement time per 1x data set can be in ms;
- Spectral range limited by cut off sapphire windows;
- Can be used with other spectrometer, windows and light-source: extended spectral range version.

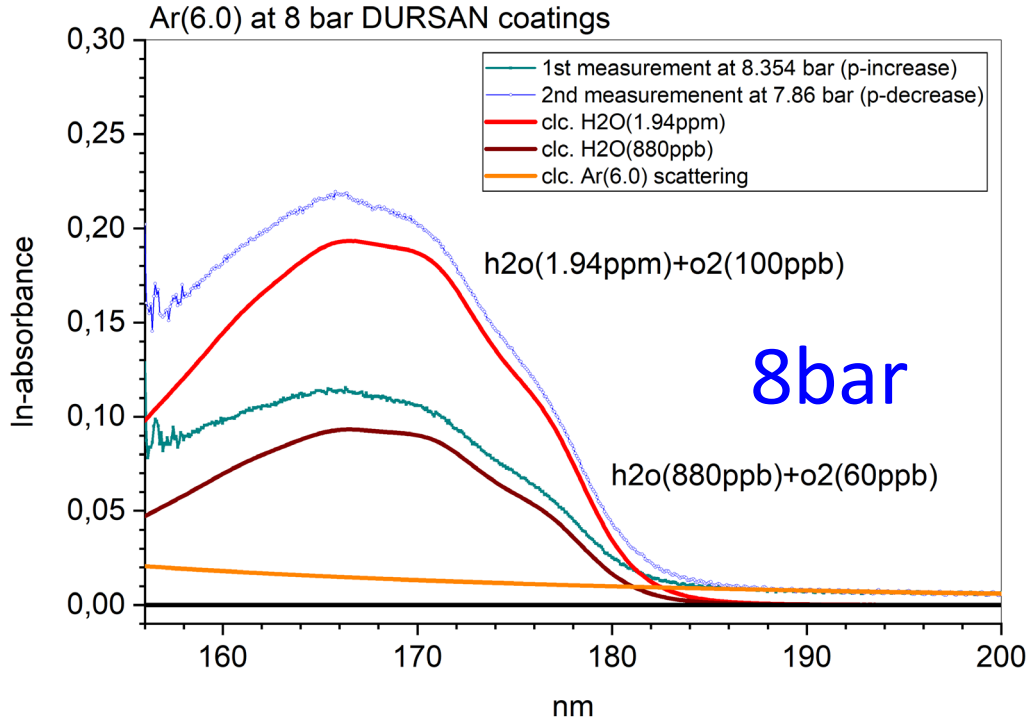


- Ar(6.0) commercial from AL (cylinder with reduction valve in 200bar/out 200bar)
- Ar(6.0) purge of whole system in 6 hrs. (cylinder-cell path)
- Ar(5.0) purge for optics
- 1 bar → 8 bar → 25 bar → 50 bar → 75 bar → 50 bar → 25 bar → 8 bar → 1 bar measurement sequence
- In flow measurements
- 10 min to 40 min waiting before next measurement

Towards industrial applications

A1.1.2

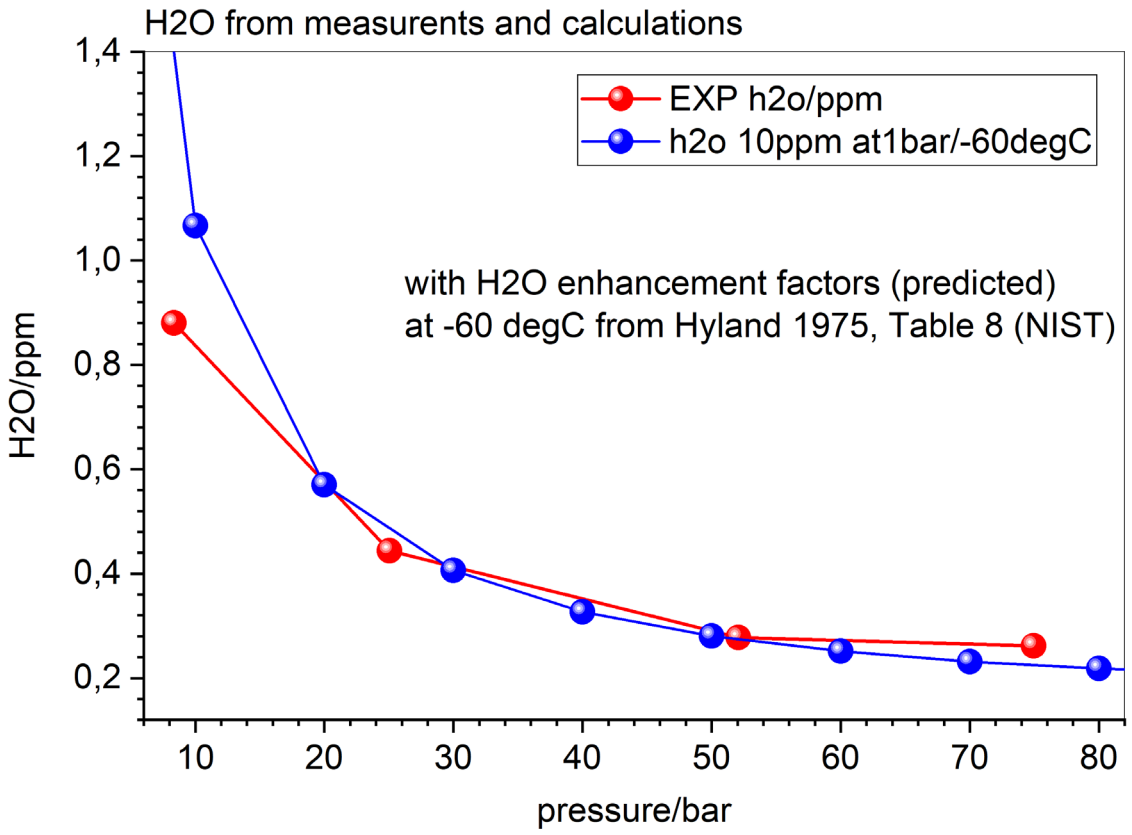




- H2O+O2+Ar dominated
- Pressurizing (up): 1 bar → 8 bar → 25 bar → 50 bar → 75 bar
- De-pressurizing (down): 75 bar → 50 bar → 25 bar → 8 bar → 1 bar
- Good agreement (reproducibility, up/down), except 8 bar case: H2O release (25 bar → 8 bar and wait ca. 20 min)

Enhancement factors and trends

A1.1.2



Pressure in cell/bar	H2O/ppb	O2/ppb
8	880	60
25	444	25
50	278	24
75	265	35
8 (25→8 bar step)	1940	100

- H2O and O2 concentrations correlate with p-change
- Measured H2O can be well fitted with use Hyland 1975 H2O predicted enhancement factors (10ppm/-60deg): possible H2O traces from reduction valve
- H2O release from pressure reduction step in low-pressure range (< 25 bar)
- Method can be used for enhancement factor developments

A1.1.3

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

With an input from Humbet Nasibli

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**

Primary Standards For Trace Water

1-Pressure Primary Humidity Generator

- ❑ Frost-point temperature: -80 °C to -20 °C
- ❑ Water vapor amount fraction: **0.33 ppm to 770 ppm**
- ❑ Pressure: 1000 hPa

Humidity Generator System

- ❑ **-80°C FP to +20°C DP**
- ❑ **Uncertainty: 0.23°C**

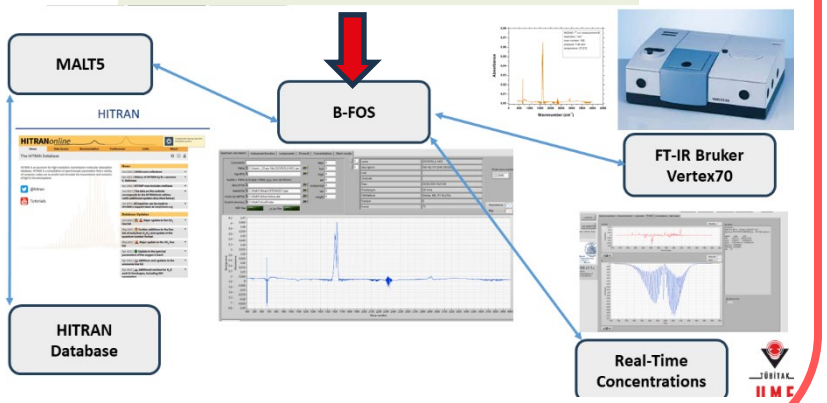
Bruker Vertex70 with Pike Long Path Gas Cell

FT-IR-Based NO/N2 Measurements

PRO MET H2O

TÜBİTAK UME

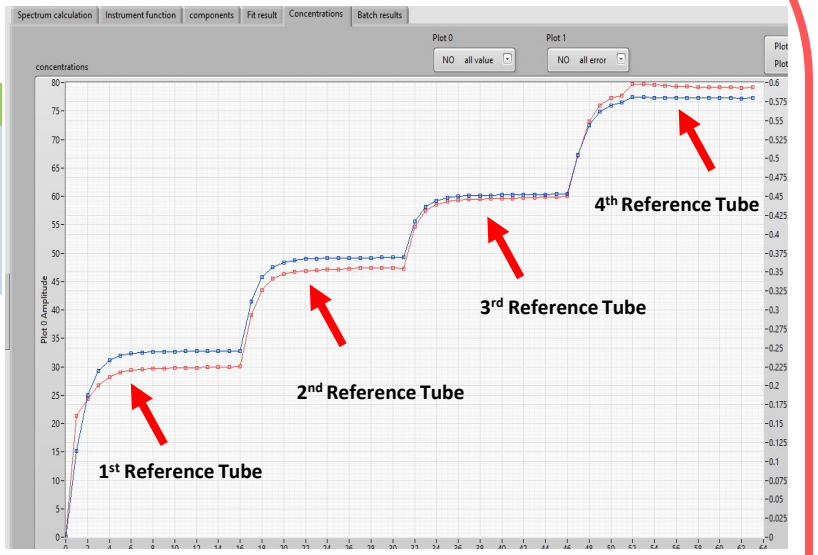
BIPM CBKT on-line FT-IR Analysis for Gas Standards



Measurement Series of the Mole Fraction NO/N2

Reference Cylinder Value

Cylinder Number	Component	Value(µmol/mol)	Uncertainty(µmol/mol)
D115410	NO/N2	29.92	0.24
D115718	NO/N2	44.99	0.36
D115603	NO/N2	54.87	0.44
D115409	NO/N2	70.0	0.6



D115410-NO/N2 (29.92 ppm)	D115718-NO/N2 (44.99 ppm)	D115603-NO/N2 (54.87 ppm)	D115409-NO/N2 (70.0 ppm)
31.07798	47.56519	59.23814	76.52151
31.92559	48.37196	59.69894	77.51005
32.31313	48.77173	59.94986	77.42642
32.50566	48.95999	60.08033	77.33112
32.59675	49.05537	60.076	77.31017
32.64626	49.10955	60.16478	77.28785
32.67745	49.13665	60.21277	77.27267
32.69862	49.14479	60.21499	77.27042
32.71064	49.18851	60.26925	77.27349
32.73185	49.19058	60.29693	77.24984
32.73741	49.20251	60.31909	77.24976
32.73386	49.2125	60.34221	77.23634
32.75005	49.20481	60.40725	77.30295

FT-IR Vertex 70 BFOS Measured Values

INVERSE EVALUATION			
x-values	Uncertainties associated with x-values	y-values	Uncertainties associated with y-values
54.835	0.132858759	60.2384	0.03466665

GRAVIMETRIC VS ANALYSIS			
	x (ppm)	u (ppm)	u (%)
REF	54.87	0.22	0.40%
FTIR	54.84	0.13	0.24%
LHS	0.03	PASSED?	YES
RHS	0.51		

$$|x_{det} - x_{pas}| \leq 2\sqrt{u^2(x_{det}) + u^2(x_{pas})}$$

XLGENLINE VERSION NO ANALYSIS

	D115410-NO/N2 (29.92 ppm)	D115718-NO/N2 (44.99 ppm)	D115603-NO/N2 (54.87 ppm)	D115409-NO/N2 (70.0 ppm)
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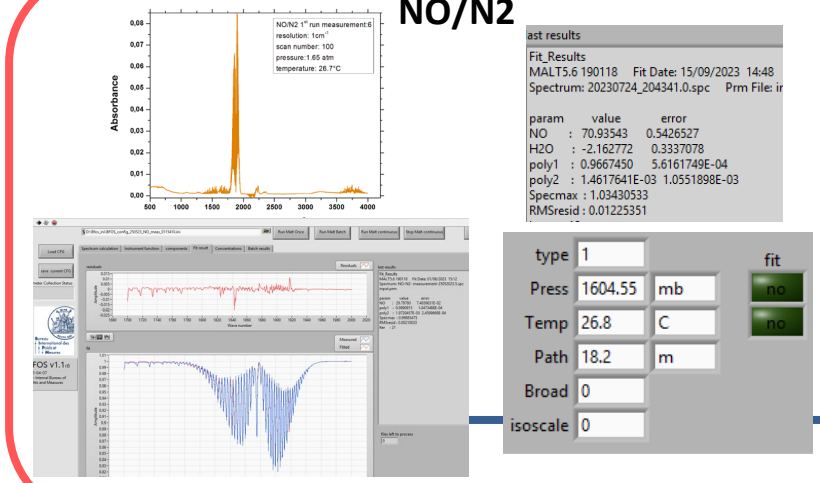
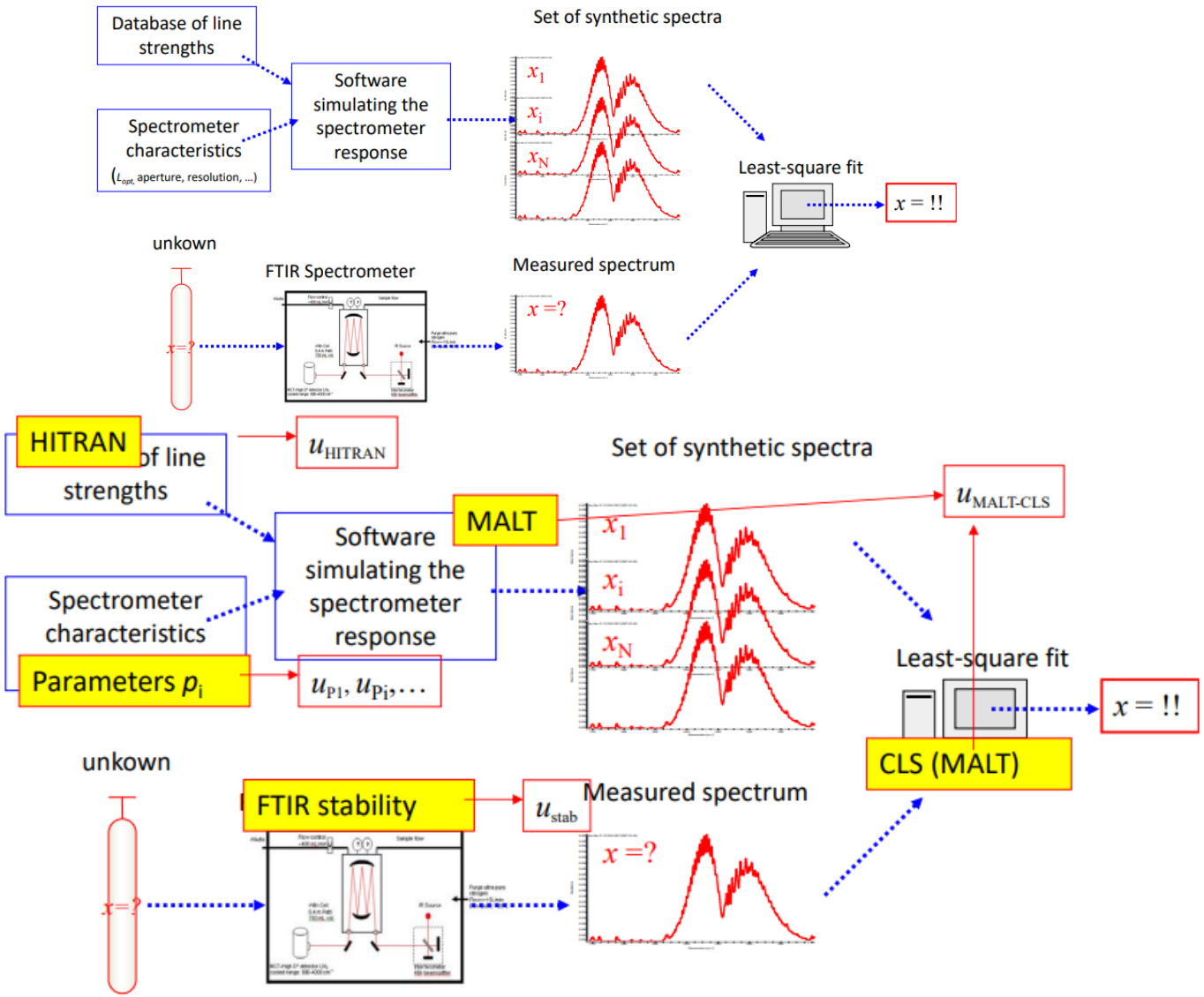
11	32.73741	49.20251	60.31909	77.24976
12	32.73386	49.2125	60.34221	77.23634
13	32.75005	49.20481	60.40725	77.30295
14				
15				
16				
17				
18				
19				
20				
DATA # used	10	10	10	10
AVG, y	32.679	49.141	60.238	77.278
stdev	0.08	0.08	0.11	0.03
RSD, %	0.24	0.16	0.18	0.04
u(y)	0.024	0.026	0.035	0.009
u(y), %	0.07	0.05	0.06	0.01

NO/N2



FT-IR Uncertainty Budgets

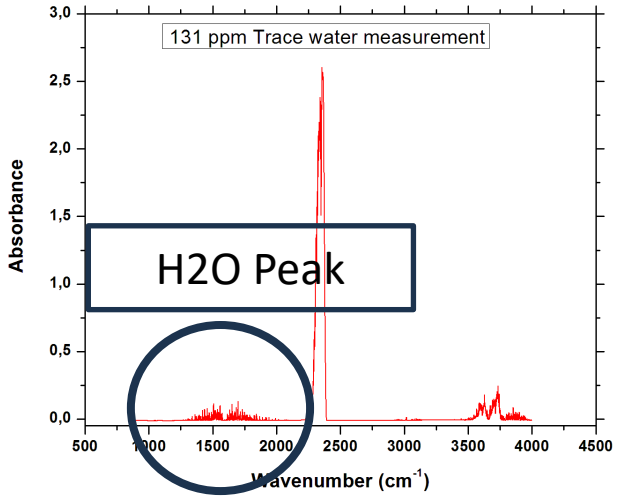


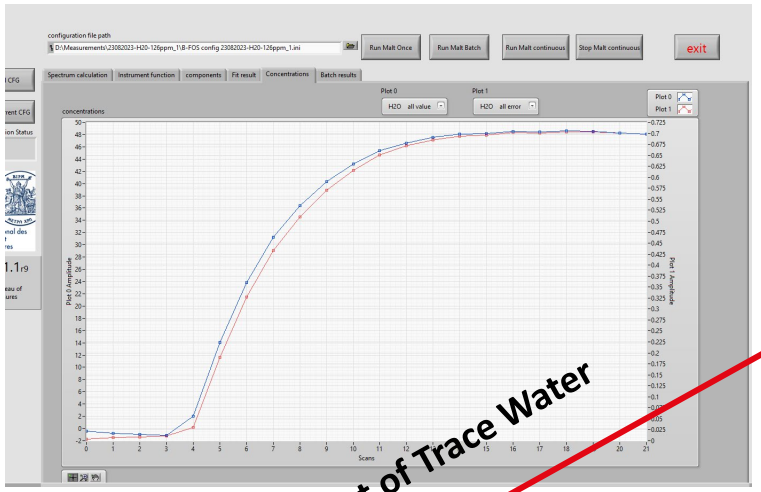
Uncertainty Components

- Uncertainty associated with database parameters
- Allan variance study of the FTIR response
- MALT-CLS uncertainty (includes FTIR parameters uncertainty)

- **The system, optimized through reference gas measurements (NO/N2, NO2/N2, CO2/Syn.Air) will now be used to detect trace amounts of water.**

FT-IR-Based Trace Water Measurements





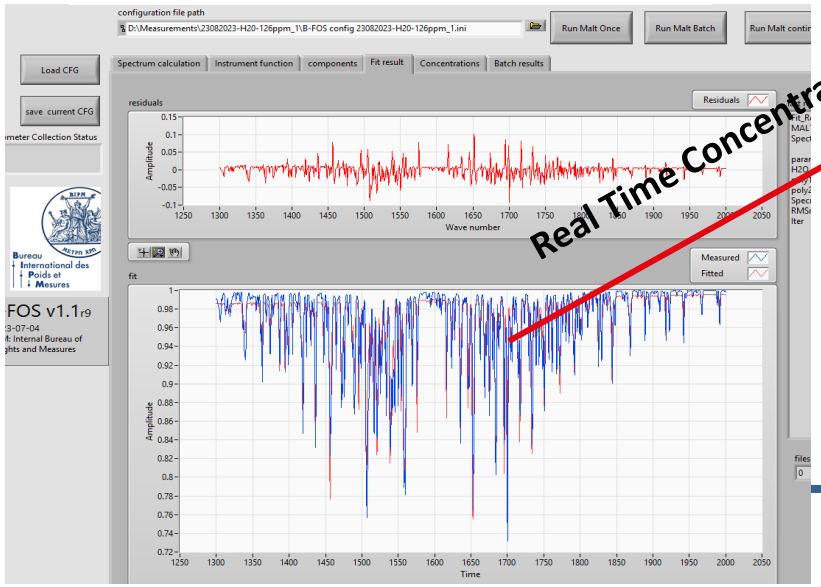
last results

Fit_Results
MALT5.6 190118 Fit Date: 12/09/2023 14:09
Spectrum: 20230823_154801.0.spc Prm File: input.prm

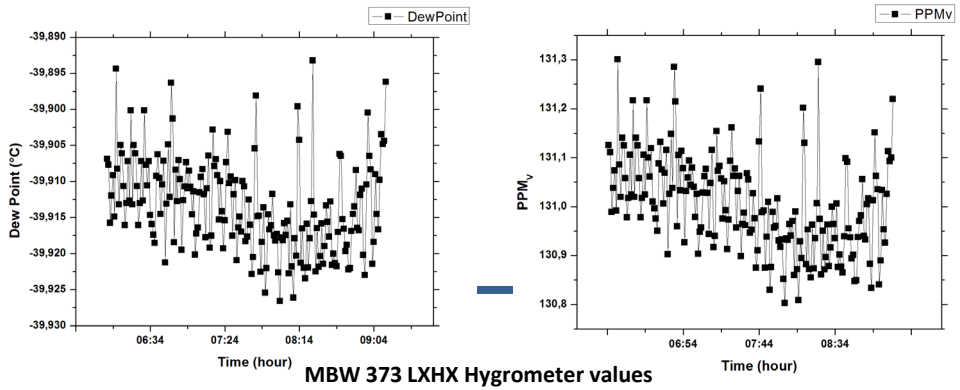
param	value	error
H2O	48.10364	0.6978567
poly1	0.9910291	5.2257482E-04
poly2	6.8698027E-03	1.0952320E-03

Specmax : 0.98816133
RMSresid : 0.01663516
Iter : 21

Real Time Concentration Measurement of Trace Water

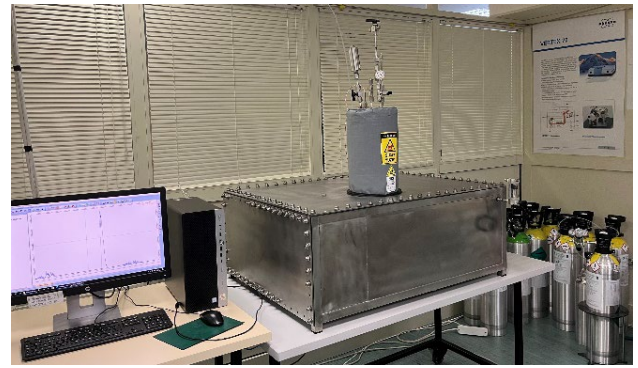


At the moment, we performed a few measurements with dry air.
The current system allows one to reach 330 ppb.
Several measurements in the range from 5 ppm to 130 ppm have been demonstrated that there is an offset in the fitting results.



MBW 373 LXHX Hygrometer values

A new stainless steel box has been manufactured and installed. These days, we are purging it with pure nitrogen; maybe in one or two days, we will start the final measurements.



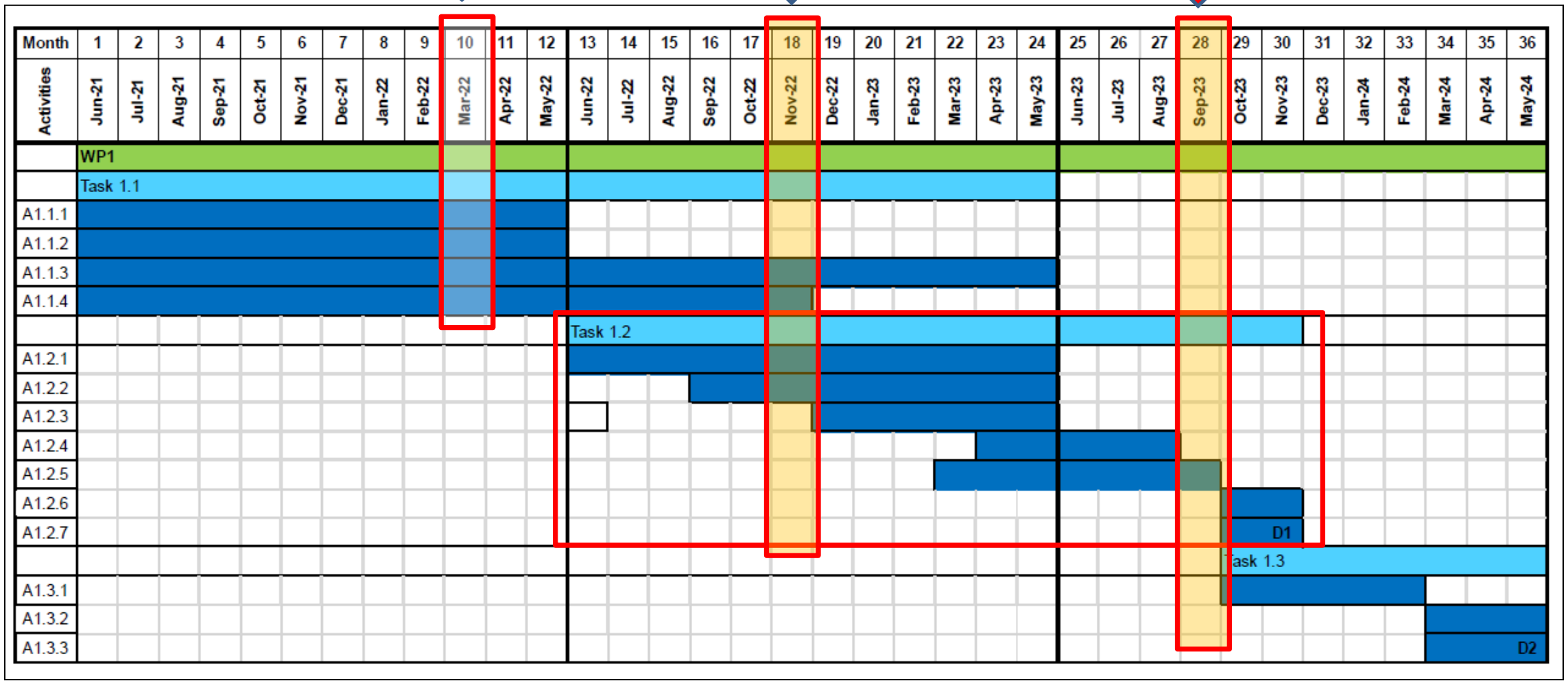
Task 1.2: Validation of the measurement methods and techniques

Task 1.2

M9 (web) meeting

M18 meeting at VSL

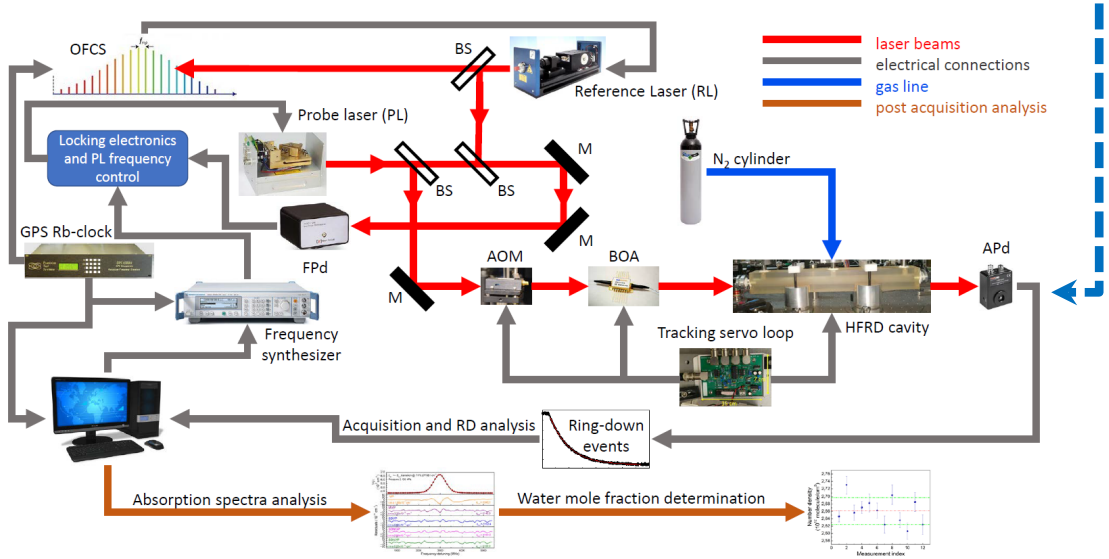
M27 WEB meeting



A1.2.1 M24	**Validation and inter-comparison of the CC-FS-CRDS spectrometer with a reference humidity generator.**	**SUN & INRIM**

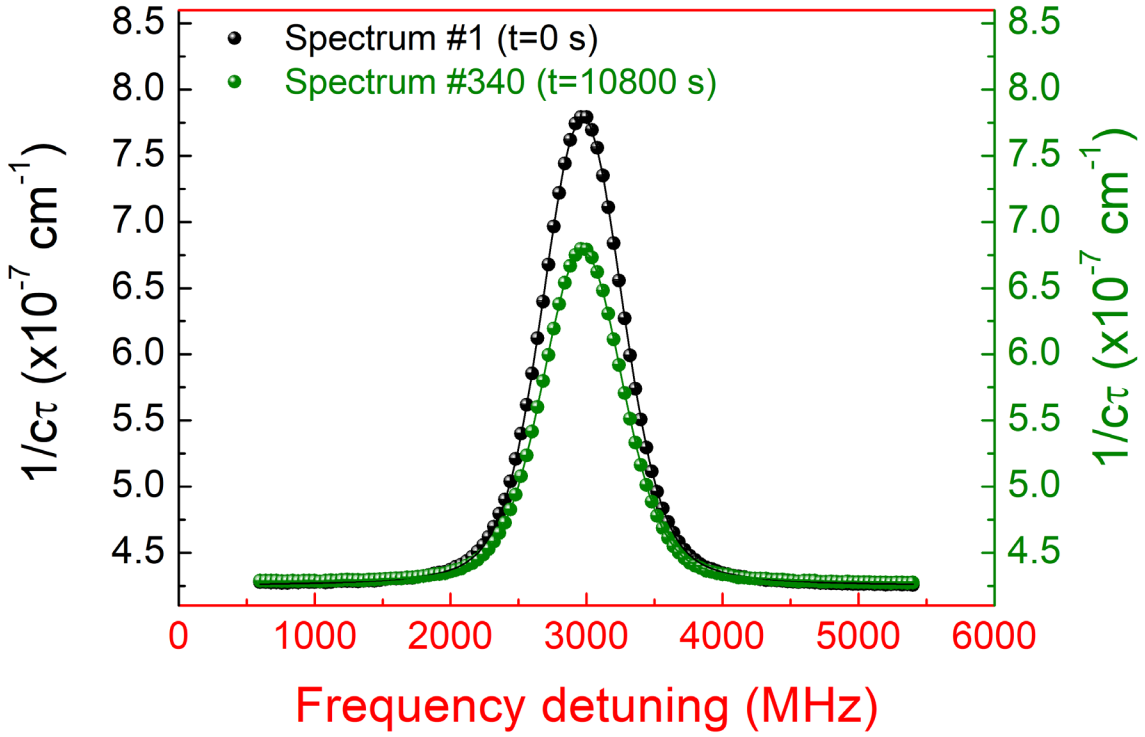
With an input from Antonio Castrillo

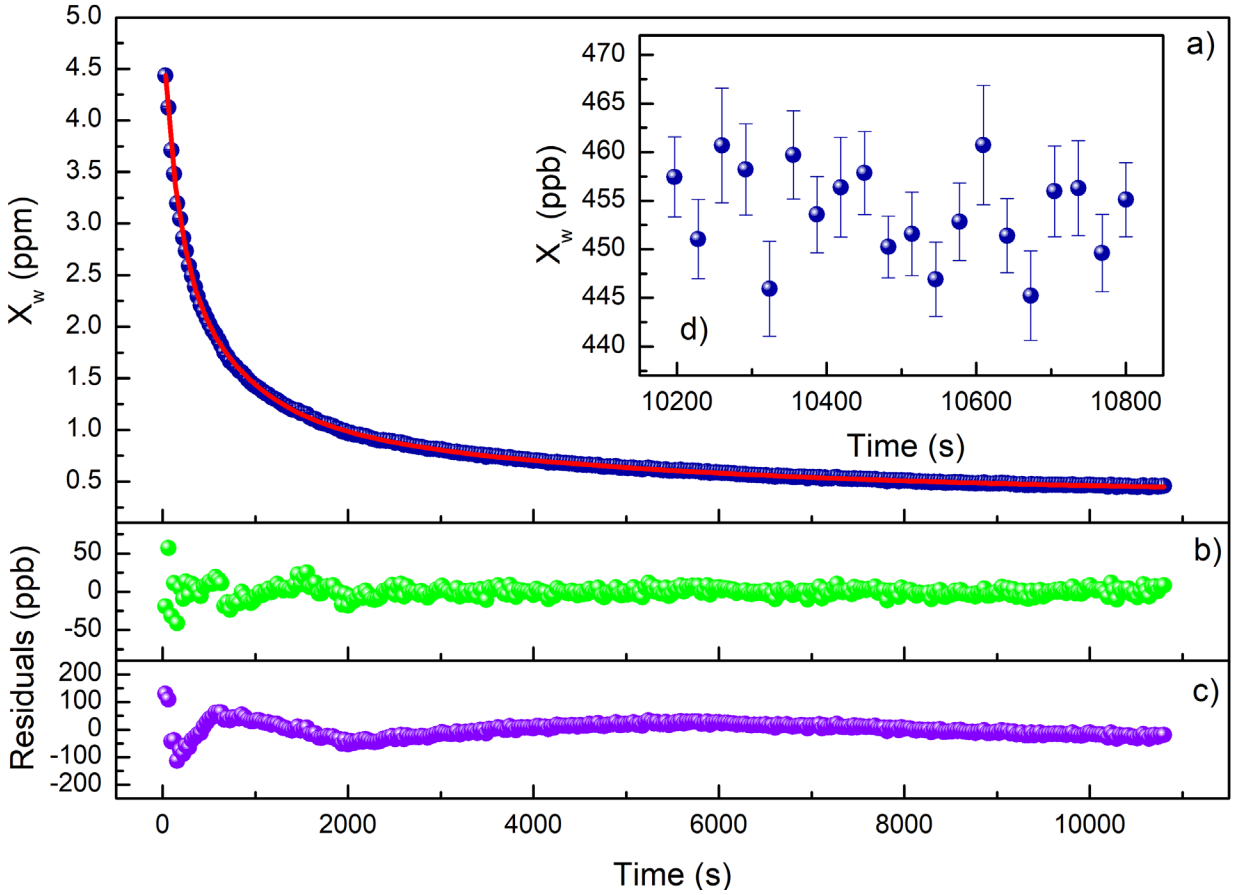
Comparison & validation



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

New reproducibility tests

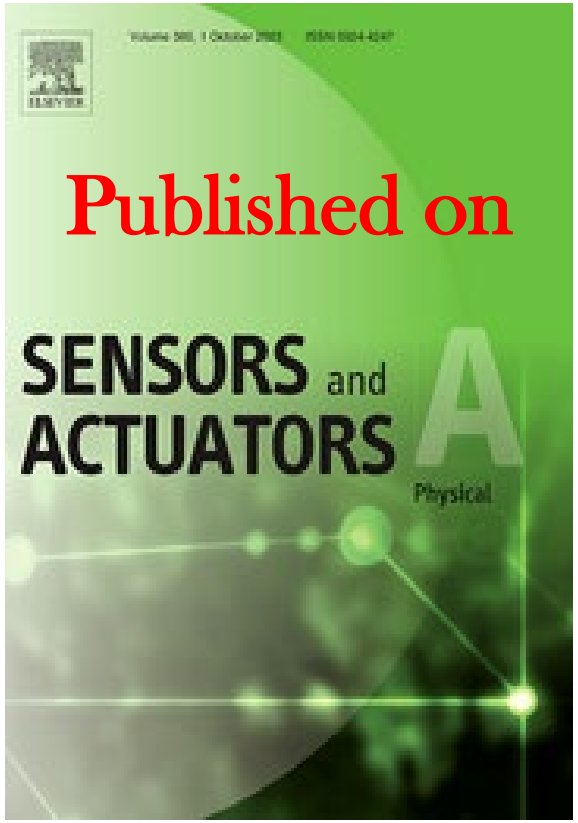




$$x_W(t) = x_{W_\infty} + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}$$

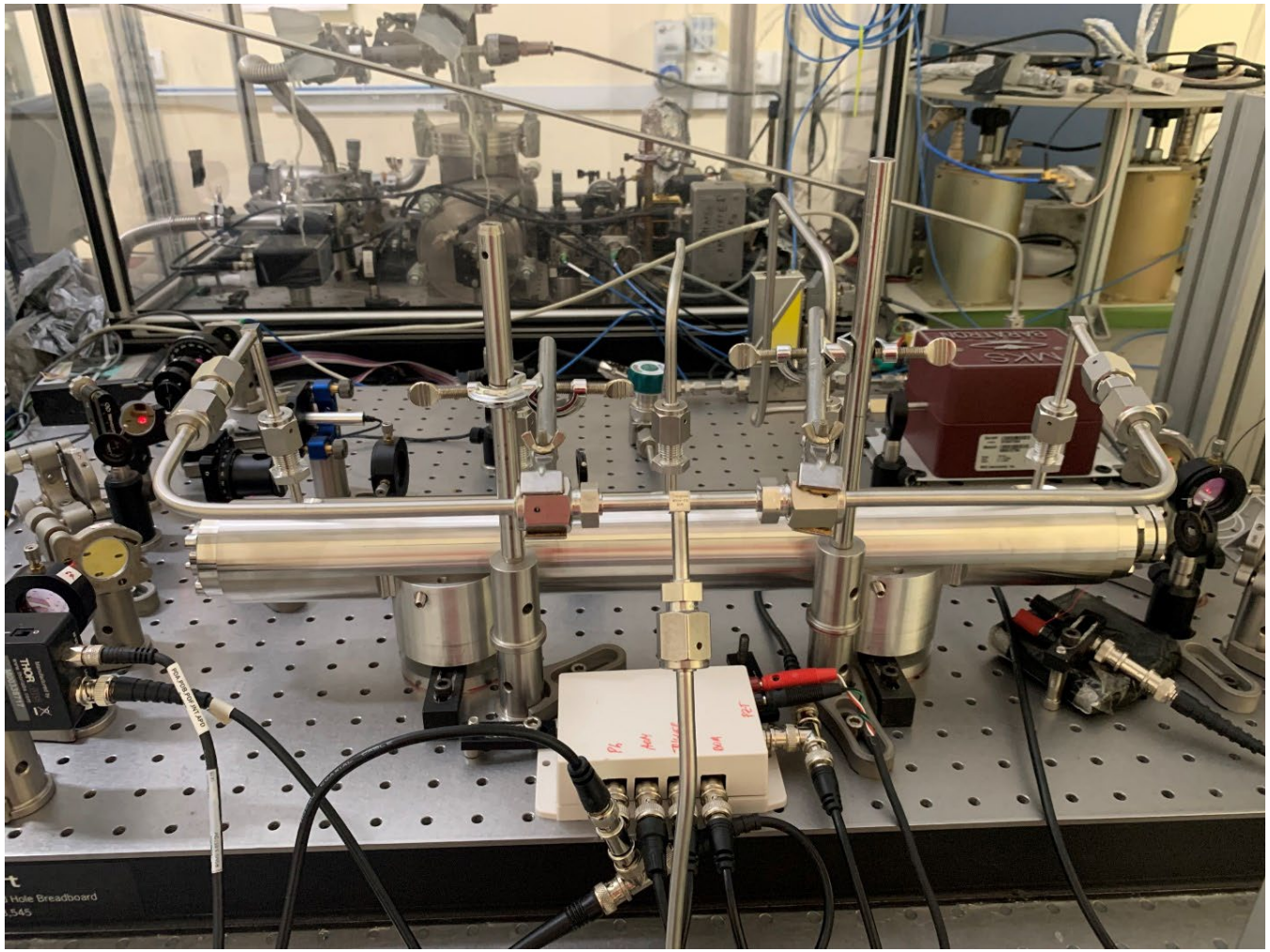
$$x_{W_\infty} = (382 \pm 5)\ ppb$$

Refined uncertainty budget



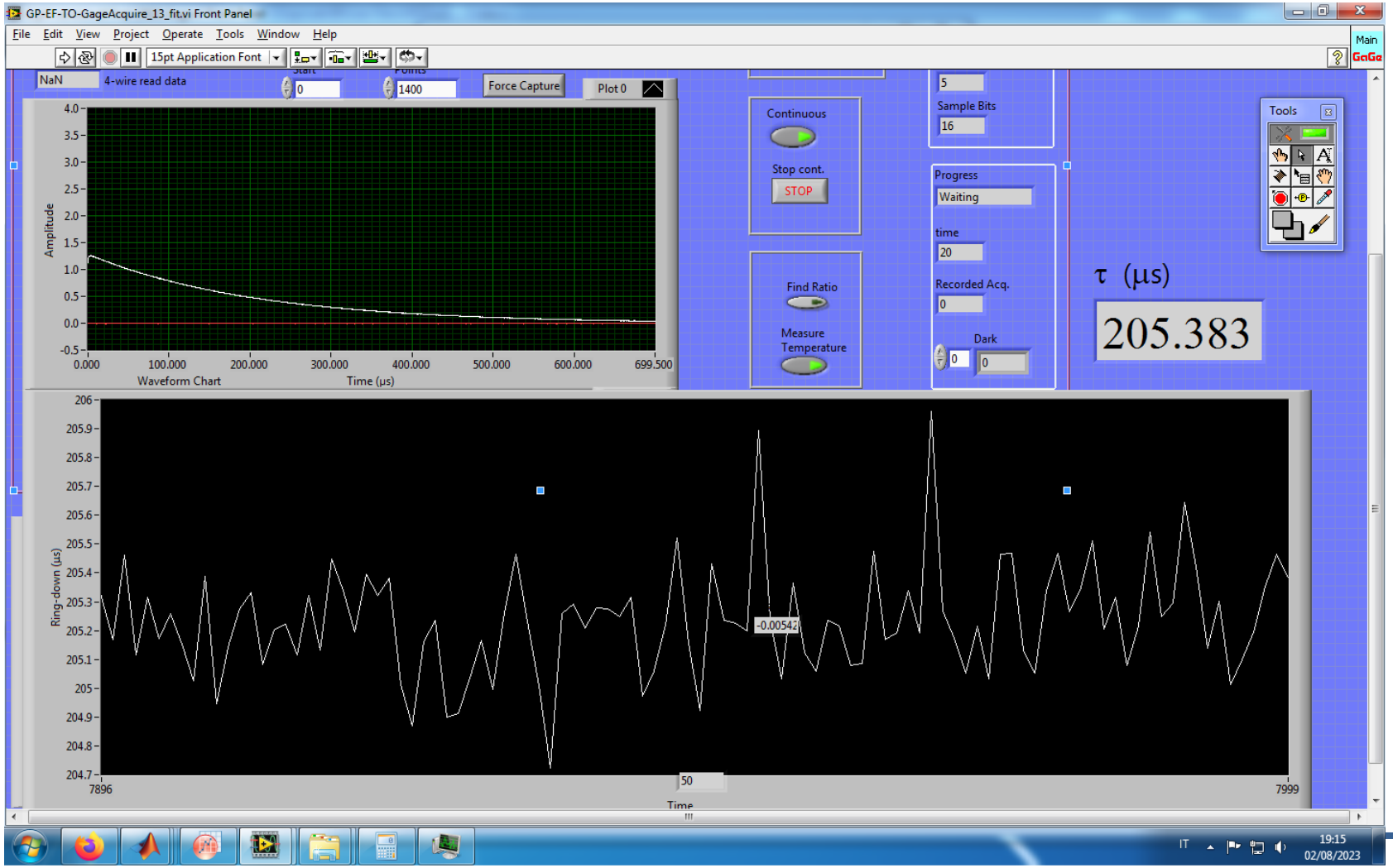
Contribution (k=1)	Type A (%)	Type B (%)
Statistical	1.3	
Line strength		0.3
Linearity frequency scale		Negligeable
Laser scan width		0.1
Horizontal resolution		0.2
Integration time		0.04
Temperature		0.07
Pressure		0.05
Line shape model		0.1
Partition function		0.04
Overall uncertainty	1.4 %	

New cavity spacer: installed 1st week of August 23



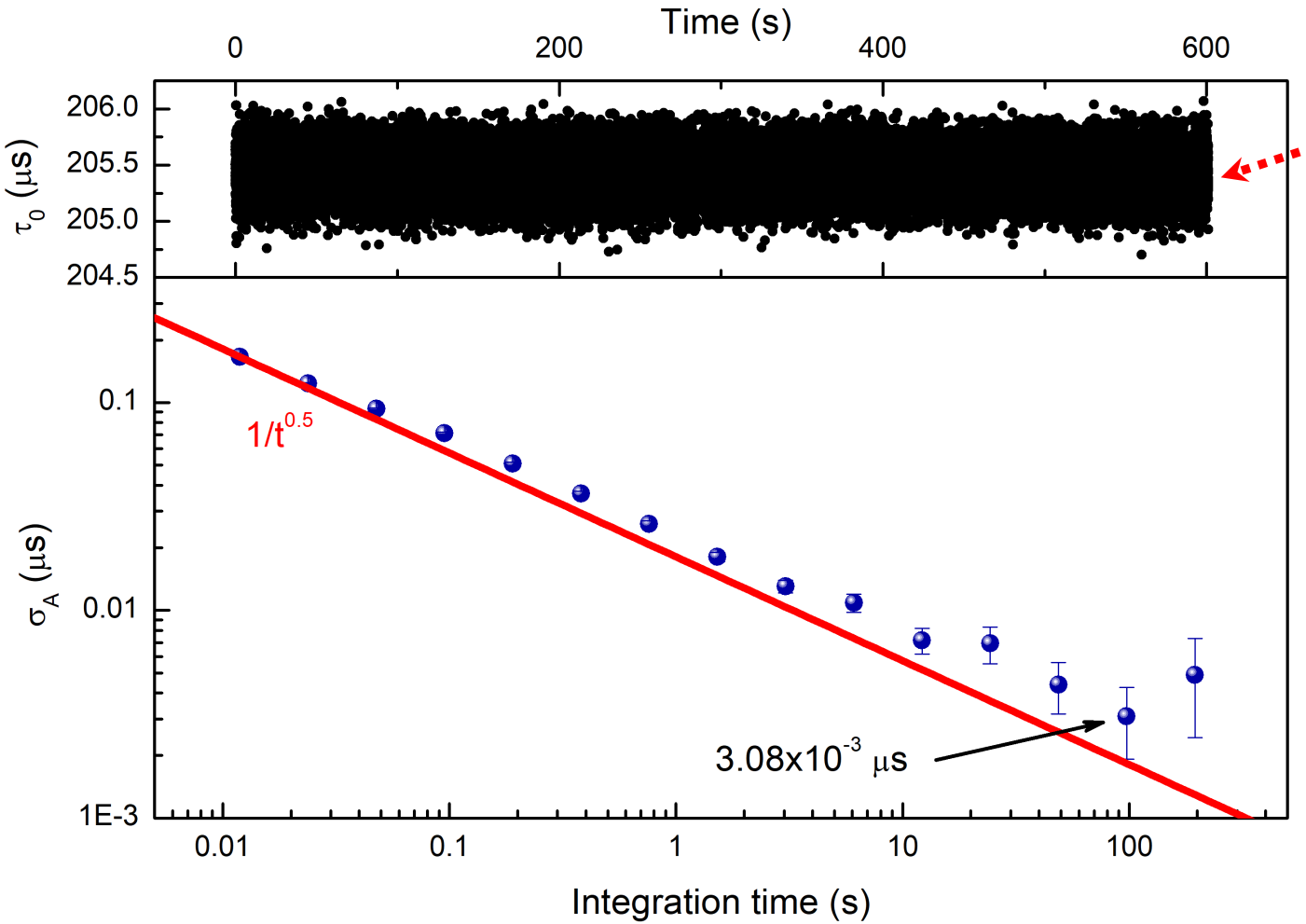
- Electrically polished 316-L stainless-steel;
- Internal surface minimization (ϕ_{int}=8 mm);
- All VCR-type metal-gasket fittings;
- Made by SAES RIAL Vacuum (Italy);
- Delivered during the second week of July (2 months of delay);
- Included in the CC-FS-CRDS during the first week of August;

New cavity mirrors (on the new spacer)



About 200 µs of ring-down time under vacuum conditions (about a factor 2 higher as compared to previous configuration).

New cavity mirrors



$\tau_0 \approx 205\ \mu s$

$LOD = 62\ ppt$

@ 100 s integration time

A1.2.1 (M24) + 5-6 months of delay (= M30):

New cavity spacer → validation against INRIM traveling standard during the next 2-3 months [in coincidence with the end of activity 1.2.6 (D1)].

M27 outputs

Contributions to conferences:

- **C-PASS 2023** CONFERENCE ON PHOTONICS FOR ADVANCED SPECTROSCOPY AND SENSING, 3-8 September 2023, Castellaneta M. (ITALY).
  INVITED TALK: «Comb-assisted frequency-stabilized cavity ring-down spectroscopy: application to ultra-sensitive detection of water vapor».
- **EGAS54** Conference if the European Group on Atomic Systems, 19-22 June 2023, Strasbourg (France)
  Poster: «Lamb-dip cavity ring-down spectroscopy of acetylene at 1.4 μm».

Contributions to journals
(funding from PROMETH2O, EURAMET repository OK):

A. Castrillo *et al.* "On the $^{12}C2H_2$ near-infrared spectrum: absolute transition frequencies and an improved spectroscopic network at the kHz accuracy level" *Phys. Chem. Chem. Phys.*, **25**, 23614-23625 (2023), https://doi.org/10.1039/D3CP01835K;

E. Fasci *et al.* "Water vapor concentration measurements in high purity gases by means of comb assisted cavity ring down spectroscopy" *Sensors and Actuators A: Physical*, **362**, 114632, (2023), https://doi.org/10.1016/j.sna.2023.114632 .

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,

- A state of the art **chilled-mirror hygrometer (PI MBW SLX)** was provided by Qrometric to INRIM
- INRIM performed a calibration of the hygrometer in the frost point temperature range from -100 °C to -20 °C
- **Deviations from the reference value were within the expanded measurement uncertainty from -90 °C to -20 °C, slightly higher at -100 °C**
- **Comparable results were obtained by comparing the SLX calibration against the PHG developed by Qrometric**
- Long purging procedure required (≈ 1 week) for the hygrometer and connection tubing, using a ultra dry gas (T_{fp} < -100 °C), before starting the calibration at the lowest frost-point temperature (-100 °C)
- Long response time of the hygrometer before equilibrium at T_{fp} = -100 °C and -90 °C (> 40 h), much shorter at -75 °C (≈ 18 h) and especially at -20 °C (≈ 6 h).

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

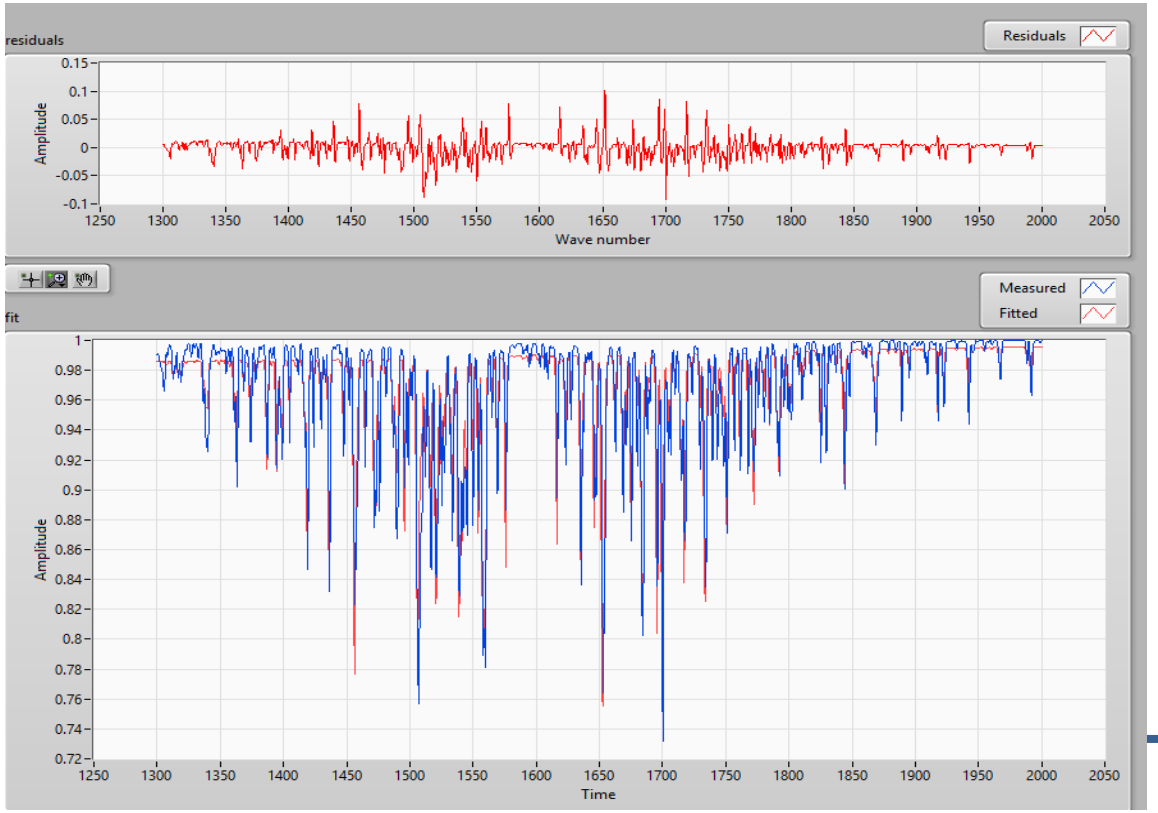
- Not active (CE-FM development paused)

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

- Intercomparison Far-UV system against FPG generator at Qrometric site in UK
- 1 bar and pressurized FPG versions
- Ar and or N2 flows with ppm/ppb H2O levels
- Planned/confirmed for Week 48, M30 (end of November)

A1.2.5

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**

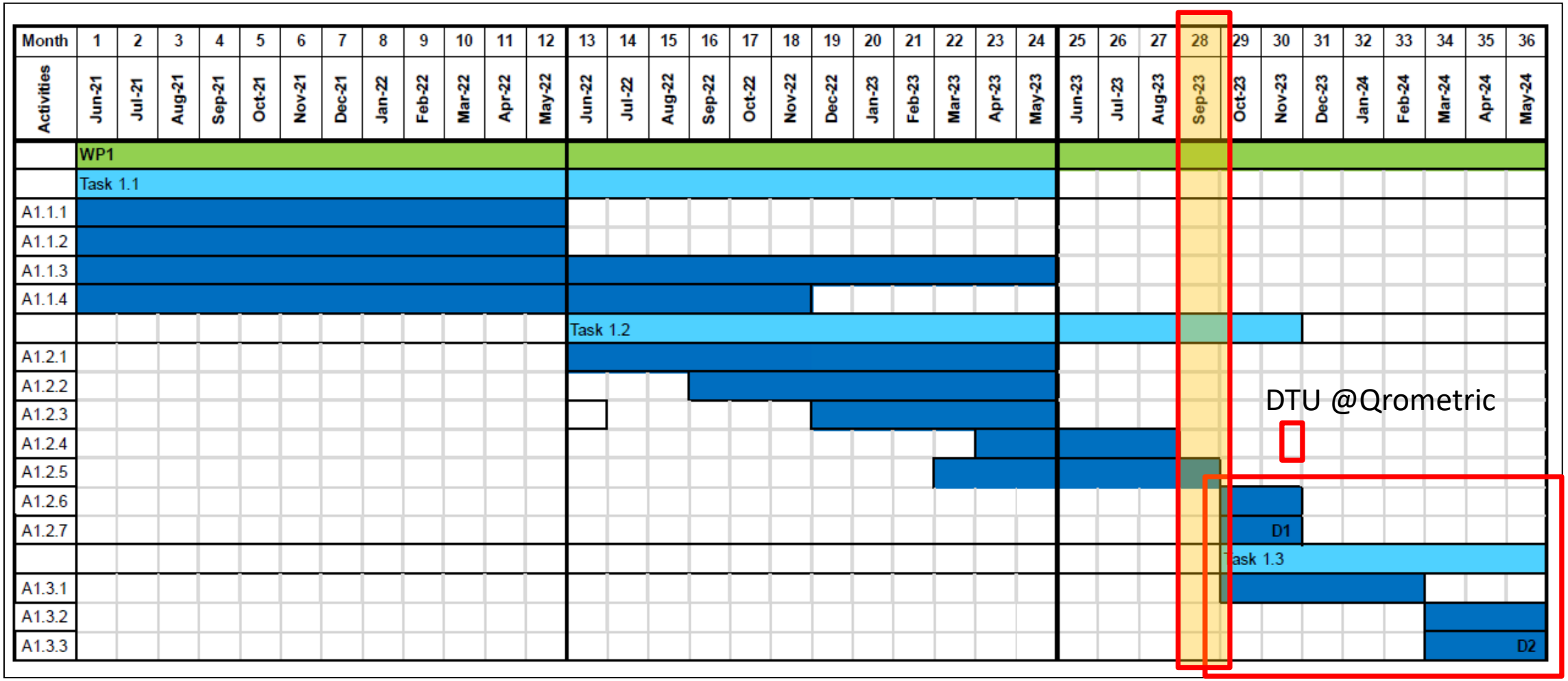


- **Few measurements with dry air. The current system allows one to reach 330 ppb.**
- **Several measurements in the range from 5 ppm to 130 ppm have been demonstrated that there is an offset in the fitting results.**
- **A new stainless steel box has been manufactured and installed. These days, we are purging it with pure nitrogen; maybe in one or two days, we will start the final measurements.**
- **DTU and TUBITAK discussed the measurements and databases.**

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

WP1: Next 9 months

M27 WEB meeting



Task 1.2: A1.2.6-A1.2.7

- ❑ **Summarize results/developments in WP1**
- ❑ **Start Report writing (from October 1st): DTU collects inputs**
- ❑ **Submit Report to comments (before X-mas)**
- ❑ **Submit Report as D1 by M32 (middle or end of January 2024)**

A1.2.6 M30	DTU, SUN, MBW, INRIM, TUBITAK, and Qrometric will analyse the results for the CC-FS-CRDS spectrometer (A1.2.1), high-quality CMH (A1.2.2), CE-FM spectroscopy hygrometer (A1.2.3), far-UV system (A1.2.4), and FTIR system (A1.2.5) and produce a report and recommendations on measurement methods and techniques for water traces measurements in industrial environments 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,** SUN, MBW, INRIM, TUBITAK, Qrometric

A1.2.7 M30	DTU, SUN, MBW, INRIM, TUBITAK, and Qrometric will review the report from A1.2.6 and will send it to the coordinator. Once the report has been agreed by the consortium, the coordinator on behalf of SUN, MBW, INRIM, TUBITAK, and Qrometric, will then submit it to EURAMET as **D1**: '*Report and recommendations on measurement methods and techniques for trace water measurements in industrial environments in the amount fraction range between 5 parts in 10^6 (5 ppm) and 5 parts in 10^9 (5 ppb) (-65 °C and -105 °C frost point) with relative standard uncertainty between 3 % and 8 %, from upper to lower range, respectively.*'	**DTU,** SUN, MBW, INRIM, TUBITAK, Qrometric

A1.2.6 M30	Report and recommendations on measurement methods and techniques for water traces measurements in industrial environments (deliverable D1).	DTU, SUN, MBW, INRIM, TUBITAK, Qrometric

- We can give only partial recommendations: see uncertainty budget and M27 report.
- Further recommendations will be provided, if necessary, after the comparison of CC-FS-CRDS against the travelling standard provided by INRIM, namely as soon as activity 1.2.1 will be completed.

Recommendation of transfer standard(s) 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	DTU, with the support of INRIM, PTB, and TUBITAK, will select a subset of instrumentation [e.g. CRDS spectrometer (A1.2.1), high-quality CMH (A1.2.2)] suitable as precision transfer standard(s) for a CIPM inter-comparison, considering instruments accuracy, reproducibility, stability and ability to handle gas matrices effects. The analysis will use the report from A1.2.6 and the information from A2.1.1 and A2.1.3.	DTU, INRIM, PTB, TUBITAK
A1.3.2 M36	INRIM, PTB, TUBITAK and DTU will use the results from A1.3.1 to write a recommendation report containing proposed instruments selected as transfer standards in the trace water range -65 °C to -105 °C (5 ppm to 5 ppb) on the basis of accuracy, reproducibility, stability and ability to handle gas matrices effects for a future CIPM inter-comparison in the trace water range.	**INRIM**, PTB, TUBITAK, DTU
A1.3.3 M36	INRIM, PTB, TUBITAK, and DTU will review the report the report from A1.3.2 and will send it to the coordinator. Once the report has been agreed by the consortium, the coordinator on behalf of INRIM, PTB, TUBITAK and DTU, will then submit it to EURAMET as D2: *'Report on the "Recommendation of transfer standards for a future CIPM comparison in the frost-point temperature range -65 °C to -105 °C (5 ppm to 5 ppb)"'*.	**INRIM**, PTB, TUBITAK, DTU

First priority (Feb. 2024)
Based on **A1.2.6** + input from INRIM (A2.1.1) and PTB (2.1.3)

A1.3.2 & A1.3.3:
Start March 2024 (M34)

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Thank you for your attention

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