Lab protocol for discrete GHG sample injections using the Li-COR 7820 (TG20: N2O) and Li-COR 7810 (TG10: CO2 + CH4)

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Conceptual framework:

The Open-loop method used in this protocol is described in depth in the manufacturers technical note available in the website. Fundamentally, a baseline is established using a gas carrier of known GHG concentration (synthetic air, only trace CO2, CH4 and N2O expected), small volume samples are injected into the carrier gas stream and a peak in the analyzer signal is produced. The area under the peak is proportional to the amount of GHG injected with the sample ([ppm]*ml) in relation to the baseline concentration in the carrier gas. After applying a calibration factor obtained using a reference gas of known GHG concentration, the concentration of GHG in small-volume samples can be calculated from the peak-area and the injected volume.

Guideline for Volume injection:

The injected volume range that creates a linear response has been determined to be between 0.1 and 1ml for the TG-20 Licor (N2O), also for TG-10 Licor (CO2+CH4).

For TG-10 Licor (CO2+CH4), depending on the sample CH4 concentration, we might have artefacts in the CO2. If we encounter negative CO2 peaks with very high CH4 in the sample, the volume injected should be progressively lowered (1ml, 0.8ml, 0.4ml, 0.2ml, 0.1ml) until we observe a consistent response in CO2 without negative peaks.

As long as the instrument signal is not saturated (>100 ppm N2O, >100 ppm CH4 and >10,000 ppm CO2, virtually impossible for field samples,) and no artefacts are seen, using an injection volume of 1ml maximizes the sensitivity and signal-to-noise ratio.

Discrete gas samples are stored and sampled from pressurized exetainers (typically 20-25ml of atmospheric-pressure gas are forced into a 12ml capacity exetainer), this reduces the risk of contamination. However, given that the signal in the instruments is proportional to the amount of gas (number of molecules) injected, it is imperative that injections of known volume (1-ml usually) are carried out at atmospheric concentration. Thus the syringe stopcock must be open to ambient pressure for 5-10 seconds to allow excess gas to escape and ensure that we are actually injecting at atmospheric pressure.

Excess Air Flow regulation:

The flow-meter in air bottle must be adjusted to a flow of 350-375 L/min. This excess flow ensures stable baseline (the Licors only take 250L/min, the excess flow is vented through the T tube) while minimizing the synthetic air usage. The 2-stage regulator must be set to an output pressure of ~ 0.2 bars (precision not critical).

Useful documentation:

LI-COR 7820 Instrument manual: 7820-Instruction-Manual-19432.pdf | Con la tecnología de Box

Scripts for processing data:
https://github.com/MCabreraBrufau/Measuring_discrete_GHG_samples_with_Licor

Equipment & location:

- Li-COR 7820 (TG20) portable analyzer for N2O
- Li-COR 7810 (TG10) portable analyzer CO2 +CH4
- 1ml glass syringes, 3-way stopcocks, single use needles
- Synthetic Air cylinder and Tubing (including injection port)
- Dedicated Li-COR laptop (preferentially, but any other laptop with wifi can be used).
- Tablet (if 2 instruments are used in series)
- Exetainers with samples

*Note on Air supply: LiCOR says "The carrier gas must be non-zero CH_4 gas in air because the analyzer uses the CH_4 absorption line for parameter optimization during the gas concentration measurement." Although using Synthetic air causes negative baselines (for CH4 and N2O), we have tested that for this application the measurements are accurate and reliable using regular synthetic air (either it has enough trace amounts of CH4 or internal corrections are fast-enough when CH4 concentration increases due to injection.

Summary Steps:

1. Setup and turn on Licor and connect pc:
    a. WIFI: **TG20-01377** Password: ***licorenv***
    b. Navigate to: **http://192.168.10.1**

*For TG10 Licor, the password and URL are the same, but make sure you are connected to the correct WIFI (that of TG10).

2. Write down initial air cylinder pressure.
3. Prepare Injecciones_Licor_yyyymmdd.xlsx. Remember to log any event and potential changes to remarks.
4. Record **lab_baseline** and prepare exetainers with standards (lab-air and 6ppm-standard).
5. Open air supply and record **loop_baseline**
6. Perform injections keeping to the pattern:
    - Standard injections: **6ppm-1_1** and **aire-1_1**
    - Batch of 10 samples
    - Standard injections: **6ppm-2_1** and **aire-2_1**
7. Export data and save excel with injection records.
8. Close air supply, write down final air cylinder pressure, close cylinder.

*Standard injections and baseline measurements are not strictly required, but it is good practice. Ambient air "standards" come with a lot of variability and potential biases between lab_baseline and aire-x samples, we do not use them anymore.

Detailed Step by step:

IMPORTANT NOTE: This step by step describes the usage of a single instrument (TG20, N2O), if both TG10 and TG20 are used in series, most steps are the same, but you will have to:

- Connect the outlet of TG10 to the inlet of TG20, i.e. TG10 receives the injection first, then the gas passes to the TG20 (there might be pressure issues if they are in the opposite order).

- Start and end the remark in each instrument separately (using another tablet or another laptop for the TG10).

- In excel notes, log observations for each instrument separately into the appropriate columns. Additionally, also in excel, explicitly say that 2 instruments were used, write down their upstream-downstream positions, and make sure to clearly note the times for corrections in the excel (2 instruments have slightly different times). The current approach is to always refer the times to the TG20 time, writing down the time-delay between the instruments in the excel once per day.

Setting up the Li-COR

1. Position the Li-COR in GC lab bench. Connect to an electrical outlet in wall. Turn on the analyzer by pressing the side button. It will begin the warmup cycle (30 min).

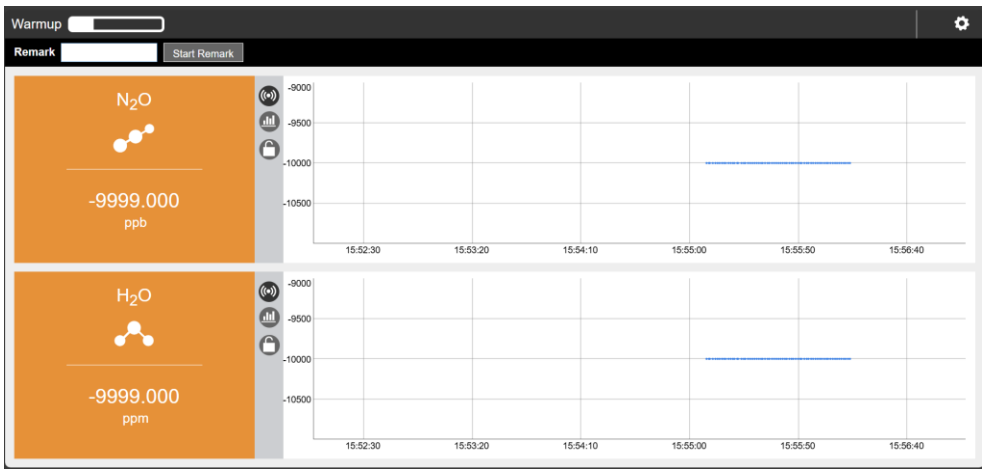
2. Open the air cylinder main valve (with the regulator closed). Log the cylinder pressure in the Air consumption Log.

3. Turn on the laptop, connect to Li-COR WIFI, and open the web-based application.
    a. Connect to network

        -WIFI: **TG20-01377**

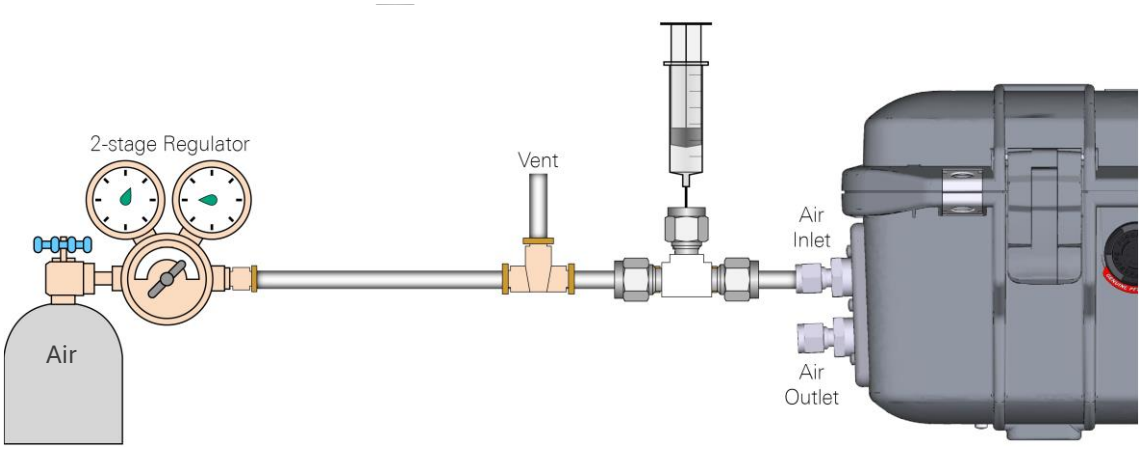
        -Password: ***licorenv***

    b. Using web browser Firefox/Chrome/Safari, enter the Fixed IP address in the explorer tab: **http://192.168.10.1**



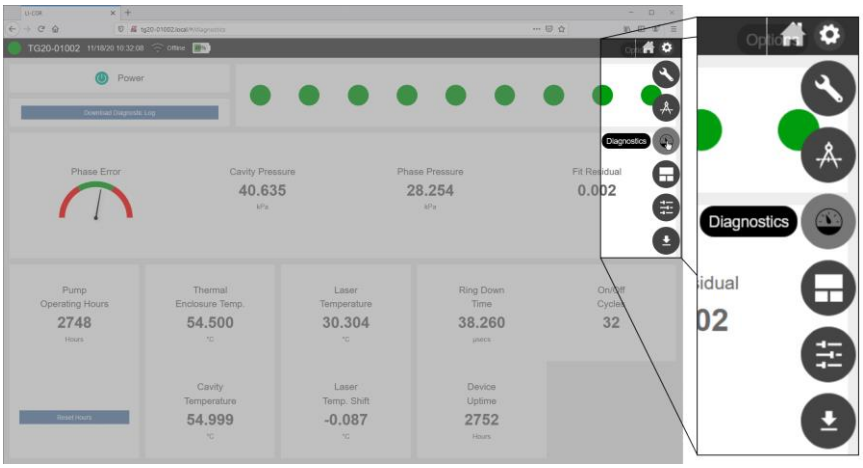
Window of web browser connected to Licor App, showing warmup cycle progress in top-left corner.

4. While the instrument warms up, you can connect the tubing that is connected to the Air cylinder with the air supply closed (the vent tube avoids Li-COR experiencing drops in pressure while connecting). With the regulator closed. **DO NOT** open the regulator during Li-COR warmup cycle.



Scheme of the plumbing setup for discrete injections.

5. Wait until the instrument finishes the warmup cycle. You can track the Li-COR warmup progress in **Options > Diagnostics**, only when all lights have turned green, the instrument has reached operating conditions.



Diagnostics window: all green lights means instrument ready.

6. Log every sample and comment during the session in an excel file in the laptop called Injecciones_Licor_yyyymmdd.xlsx. Every remark and event should be clearly identified for later processing of data. If a modification in remarks is necessary, always identify it with the time-span of modification by writing down the Licor time (hh:mm:ss-hh:mm:ss). Avoid vague observations like “incorrect end-time”, instead specify explicitly what modification/correction is needed eg. “Remove last 2 minutes of remark”. An example of a typical excel with lab annotations:

	A	B	C	D	E	F	G
1	yearmonthday	sample	remark	inyecciones	obs		
21	20241113	S4-CA-P2-14	S4-CA-P2-14_1	3	ok		
22	20241113	S4-CA-P2-15	S4-CA-P2-15_1	4	descartar antes de 12:05:55		
23	20241113	S4-CA-P2-16	S4-CA-P2-16_1	3	ok		
24	20241113	S4-CA-P2-17	S4-CA-P2-17_1	3	ok		
25	20241113	S4-CA-P2-18	S4-CA-P2-18_1	3	ok		
26	20241113	S4-CA-P2-19	S4-CA-P2-19_1	3	ok		
27	20241113	S4-CA-P2-20	S4-CA-P2-20_1	3	ok		
28	20241113	6ppm-3	6ppm-3_1	4	ok		
29	20241113	aire-3	aire-3_1	3	Añadir remark: 12:52:40-12:56:40		
30	20241113	S4-CA-P2-21	S4-CA-P2-21_1	3	ok		
31	20241113	S4-CA-P2-22	S4-CA-P2-22_1	3	ok		
32	20241113	S4-CA-P2-23	S4-CA-P2-23_1	3	ok		
33	20241113	S4-CA-P2-24	S4-CA-P2-24_1	3	ok		
34	20241113	S4-CA-P2-25	S4-CA-P2-25_1	4	ok		
35	20241113	S4-CA-P2-26	S4-CA-P2-26_1	3	ok		
36	20241113	lab-2_baseline	lab-2_baseline	-	baseline lab 13:20-13:22		
37	20241113	S4-CA-P2-27	S4-CA-P2-27_1	3	ok		
38	20241113	S4-CA-P2-28	S4-CA-P2-28_1	4	ok		
39	20241113	S4-CA-P2-29	S4-CA-P2-29_1	3	ok		
40	20241113	S4-CA-P2-30	S4-CA-P2-30_1	3	ok		
41	20241113	6ppm-4	6ppm-4_1	3	ok		
42	20241113	aire-4	aire-4_1	3	ok		

7. Record lab-N2O baseline for ~2 minutes once it has reached a stable concentration. Use remark "**lab_baseline**". If using TG10 + TG20, make sure to use an extension tube to take "ambient" air from outside the lab (avoids highly variable CO_2 from user respiration). While you are measuring the baseline, fill 5-8 exetainers with the same air (taking it next to the inlet tube) and save them for later. (the CO2 in the lab is too inconsistent and variable to be used for the baseline and "aire" exetainers).

8. Carefully and slowly, open the air supply from the cylinder and increase the flow with the regulator until the N2O baseline drops and stabilizes (with the air cylinder open with enough flow, N2O baseline should be stable between -4 and -5 ppb, negative baseline). Air should be flowing out of the vent tube a bit (you should be able to feel it with your finger in front, without blocking the vent). Make sure that the N2O baseline is stable for 1-2 minutes.

9. Record Synthetic air N2O baseline for a couple of minutes with the remark "**loop_baseline**".

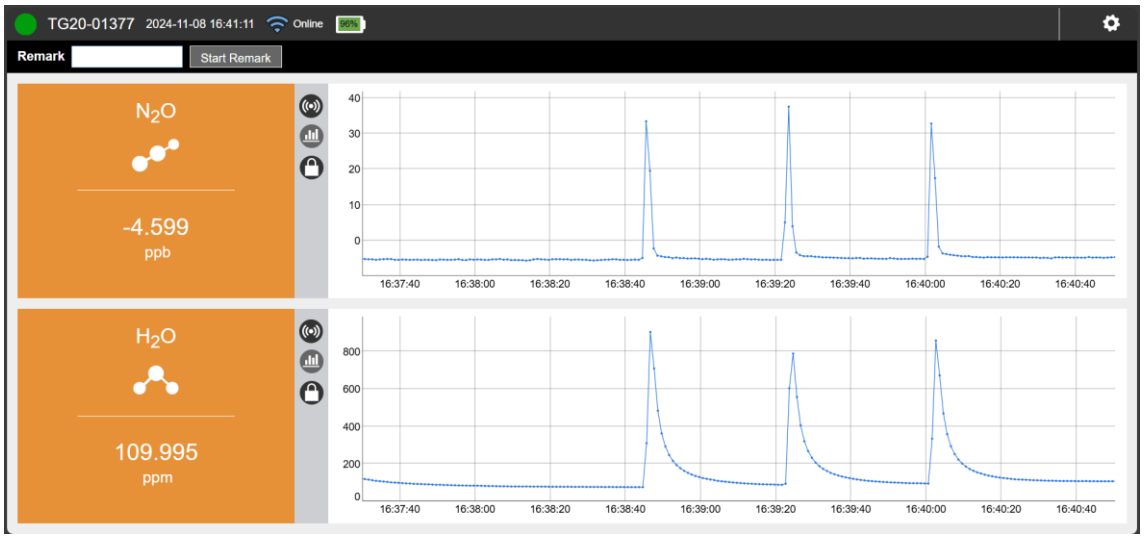
Screenshot of LiCOR app showing drop of N2O baseline after connection to Air cylinder

Injecting samples

10. General sequence for samples and standards: To ensure the quality of the data, injections of the Certified standard mix (6ppm N_2O, 15ppm CH_4, 3000ppm CO_2) and laboratory air as an internal standard (~340 ppb N_2O, measured in **lab_baseline** each day) will be used. Both "standards" are sampled from pre-evacuated exetainers filled to ~25ml with the gas (same treatment as true samples). The 6ppm standard corresponds to that of the standard cylinder, the "air" standard is collected into exetainers while acquiring the lab baseline (to know what concentration they are, internal standard).
    These standards will be injected (with 3 replicates) at the beginning and end of the session, plus every 10-15 samples. The typical remarks of a general day will be:
    - **"lab_baseline"** (continuous measurement)
    - **"loop_baseline"** (continuous measurement)
    - "**6ppm-1_1"** (3 injections of 1 ml)
    - **"aire-1_1"** (3 injections of 1 ml)
    - **Samples 1 to 10** (3 injections of 1ml each)
    - "**6ppm-2_1"** (3 injections of 1 ml)
    - **"aire-2_1"** (3 injections of 1 ml)
    - **Samples 11 to 20** (3 injections of 1ml each)
    - "**6ppm-3_1"** (3 injections of 1 ml)
    - **"aire-3_1"** (3 injections of 1 ml)

11. For every sample we follow these steps:
    a. Go to the "remark" window in the top-left corner and write the sample-code (without underscores!!) and volume injected (in ml) separated by an underscore (e.g. "S3-CA-A2-15_1", "S1-DU-R2-21_1", "S4-CU-A2-2_0.8").
    

    b. Once you are ready to do the first injection click on "START REMARK" and wait 10 seconds before injecting.
    c. Inject your sample *n* times, allowing for at least 10 seconds between injections. At least 3 consecutive injections are recommended. To ensure homogeneous concentration in every injection, flush the syringe using the 3-way stopcock 3 times with 0.2ml of sample before each injection (this allows the "dead volume" of ~0.2ml in the stopcock and needle to be equilibrated with the exetainer N2O concentration). Allow 5-10 seconds between the filling of syringe and the injection, the **stopcock should be open** to allow the excess pressure of the syringe to equilibrate to atmospheric pressure.



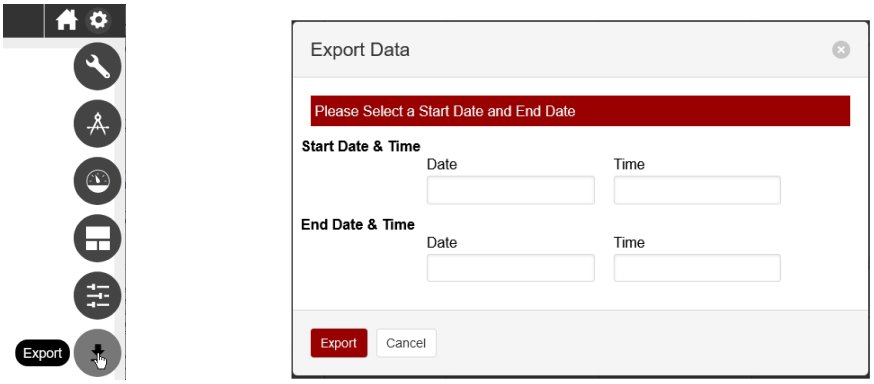
Example of 3 consecutive injections with 10s interval of baseline in between them.

d. When finished with the sample injection, allow 10 seconds of baseline and click “END REMARK”.

Note: *During the analysis, make sure that the baseline is stable, if it increases, make sure that the air supply is enough by checking the flow-meter (increase regulator pressure and/or flow-meter valve if needed). Close the air supply from the regulator when taking breaks of more than 10-15 minutes to save air. Allow the baseline to return to normal before injecting the next sample.*

Export and shutdown

12. When you finish for the day, download the data from the Li-COR. In the top-right corner of the application, Go to **Options > Export**, specify a date-time range, and click **Export**. Dates are displayed as YYYY-MM-DD. Time options are given in a 24-hour clock (00:00 through 24:00). The exported data will be downloaded in a text file of ".data" extension. You may be prompted with a security message, allow the download to your laptop. We should download the data daily and, in any case, one text-file per injection session should be stored (i.e. if you forgot to export the data of a previous day, make sure to export only 1 day per ".data" file)



Screenshots of export menu.

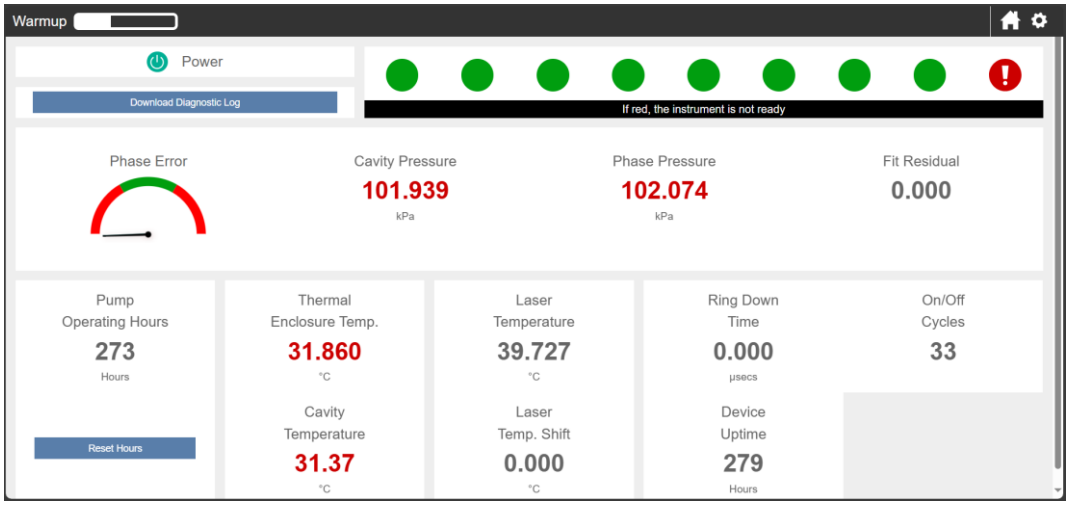
13. Close the air supply by turning the regulator counterclockwise. Disconnect the air supply tubing from the Licor (putting the nut back to avoid losing the bushing and ferrule). Write down the final pressure of the cylinder in the Air log sheet and then close the cylinder main valve.

Note: *make sure to notify when Air in cylinder is running low (<60bar), so we can order a new one in time.*

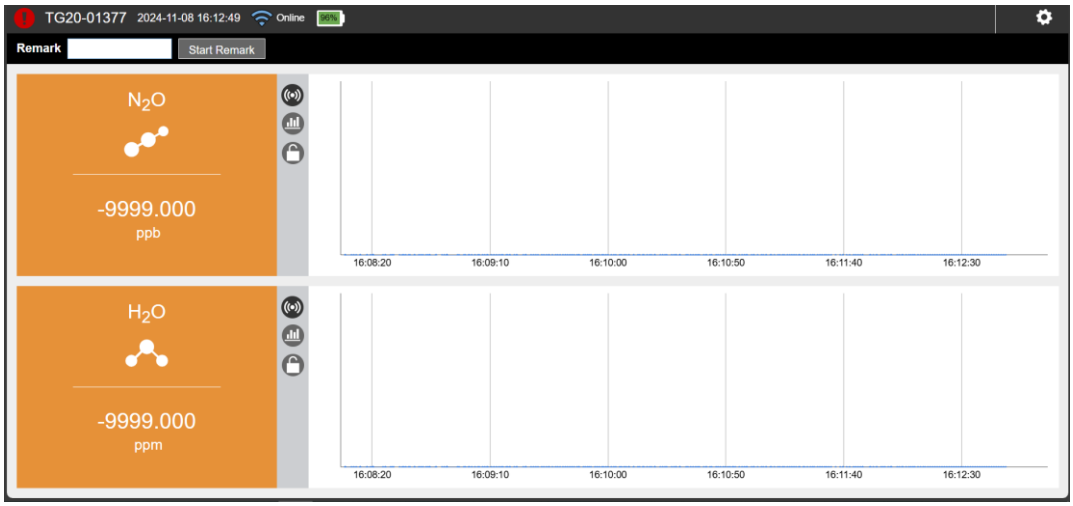
14. Power off the Li-COR from the web-browser (within the **Options > Diagnostics** tab). Wait until it shuts down.

Extra screenshots:

Diagnostic tab during warmup cycle:



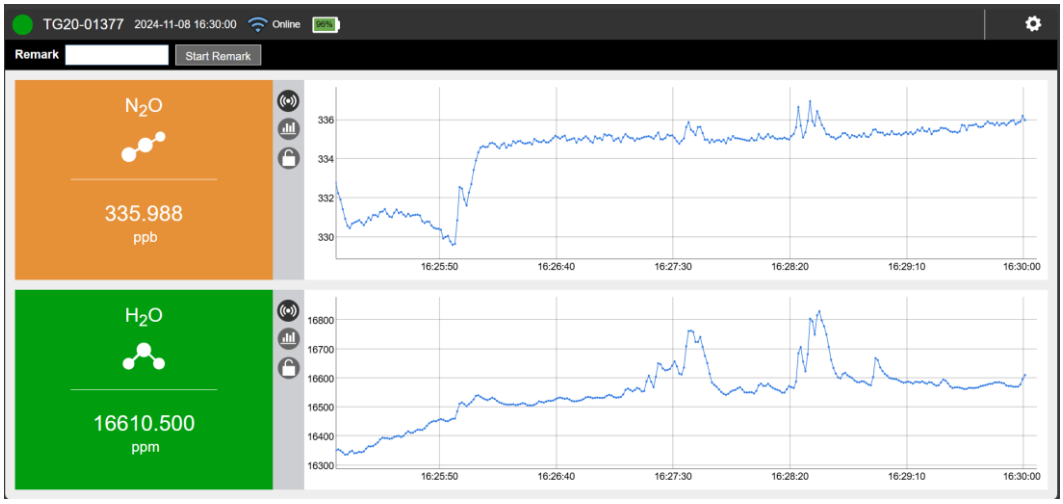
Pump starts but no measurements yet:



Licor starts to record concentration data:

Licor finishes warmup cycle, all green lights, status ready and stabilization of baseline:

Before opening Air cylinder:



Drop in baseline after Cylinder is open