PICARRO

Empowering research
with precision, reliability,
and advanced technology

Agenda

	Mercredi 23 Avril	Jeudi 24 Avril
AASQA	Corse, Atmo SUD, AirPL, Atmo BFC, Atmo Occitanie, Martinique	AURA, HDF, Atmo GE, Atmo normandie, LigAIR, Air Breizh
9h30-10:30h	• Accueil • Présentation Picarro • Exemples Applications NH_3	• Accueil • Présentation Picarro • Exemples Applications NH_3
10:30h-11h	Pause	Pause
11h-12h	• CRDS Technologie • Considération Application • Questions	• CRDS Technologie • Considération Application • Questions
12h-13h	Pause Déjeuner	Pause Déjeuner
13h-14h	Formation pratique : G / PI2103 Logicielle	Formation pratique : G / PI2103 Logicielle
14h-15h	Formation pratique: G / PI2103 « Hardware »	Formation pratique: G / PI2103 « Hardware »
15h-15h30	Pause	Pause
15h30-17h	Discussion et Question Générale	Discussion et Question Générale

Meet the Picarro EMEA team

Peter Swinkels
Associate Director, Sales EMEA

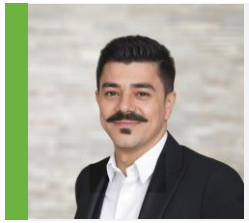
Alexandre Dembicki
Technical Sales Manager

Erik Heeren
Senior Account Manager

Magdalena Hofmann
Senior Application Scientist

Jan Woźniak
Senior Field Application Scientist

Arthur Schaeps
Manager, Customer Support



Saeid Bagheri
Technical Support Engineer

Rob van der Vleuten
Technical Support Engineer

Wei Wei
Field Service Engineer

Overview Picarro Analyzers

GHG analysis

G2301 : CO_2, CH_4, H_2O
G2311-f: CO_2, CH_4, H_2O (flux)
G2401 : CO_2, CH_4, CO, H_2O
G2401-m: CO_2, CH_4, CO, H_2O (flight)
PI5310 : N_2O, CO, H_2O
G2508 : N_2O, CO_2, CH_4, (NH_3), H_2O
G2509 : N_2O, CO_2, CH_4, NH_3, H_2O

Suitable for concentration analysis in the atmosphere. Analyzers are optimized for atmospheric concentrations.

Trace gas analyses

PI2103 : NH_3, Ammonia
PI2114 : H_2O_2, Hydrogen Peroxide
G2307 : H_2CO, Formaldehyde
SI2205 : HF, Hydrogen Fluoride
SI2108 : HCl, Hydrogen Chloride
SI2104 : H_2S, Hydrogen sulfide
PI2910/PI2920: C_2H_4O, Ethylene Oxide

Suitable for trace gas detection with a specified lower detection limit, for industrial and atmospheric use.

Isotopic analyzers

G2131-i : $\delta^{13}C$ of CO_2
G2201-i : $\delta^{13}C$ of CO_2 & $\delta^{13}C$ of CH_4
G2210-i : $\delta^{13}C$ of CH_4 & [C_2H_6]

L2130-i : $\delta^{18}O$ & $\delta^{2}H$ of H_2O
L2140-i : $\delta^{18}O$, $\delta^{17}O$, $\delta^{2}H$ & ^{17}O-excess

Suitable for field-based monitoring and laboratory application, can be used with different peripherals.

Analyzers for Hazardous Air Pollutants

Ammonia (NH_3)

Ethylene Oxide (C_2H_4O)

Formaldehyde (H_2CO)

Hydrogen Chloride (HCl)

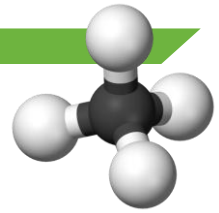
Hydrogen Fluoride (HF)

Hydrogen Sulfide (H_2S)

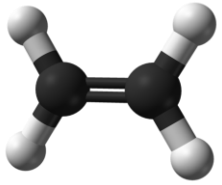
VOC measurements with BB-CRDS

- Development of Broadband CRDS for VOC
  - Analyzer capable of a scanning wide frequency range
  - Up to 40 compounds measured at the same time
  - Measurement interval < 5 sec
- 50x more sensitive than FTIR, 50x faster than GC
- Creating a large VOC library

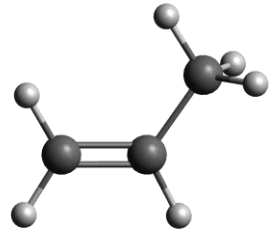
Multiple VOCs across a wide frequency range



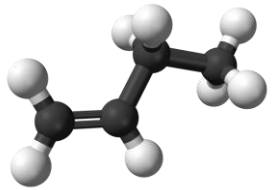
Methane: 5 atoms



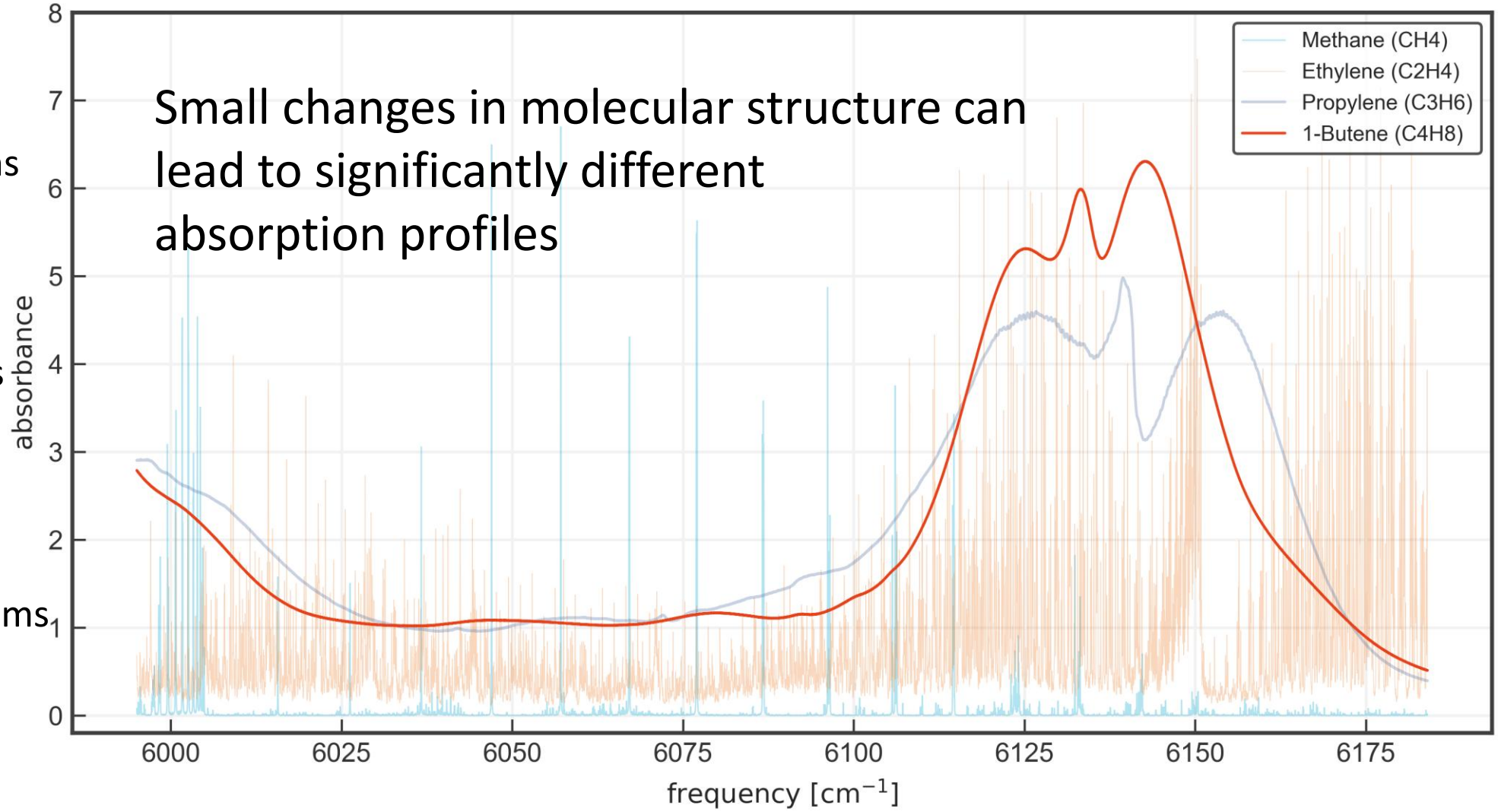
Ethylene: 6 atoms



Propylene: 9 Atoms



Butene: 12 Atoms



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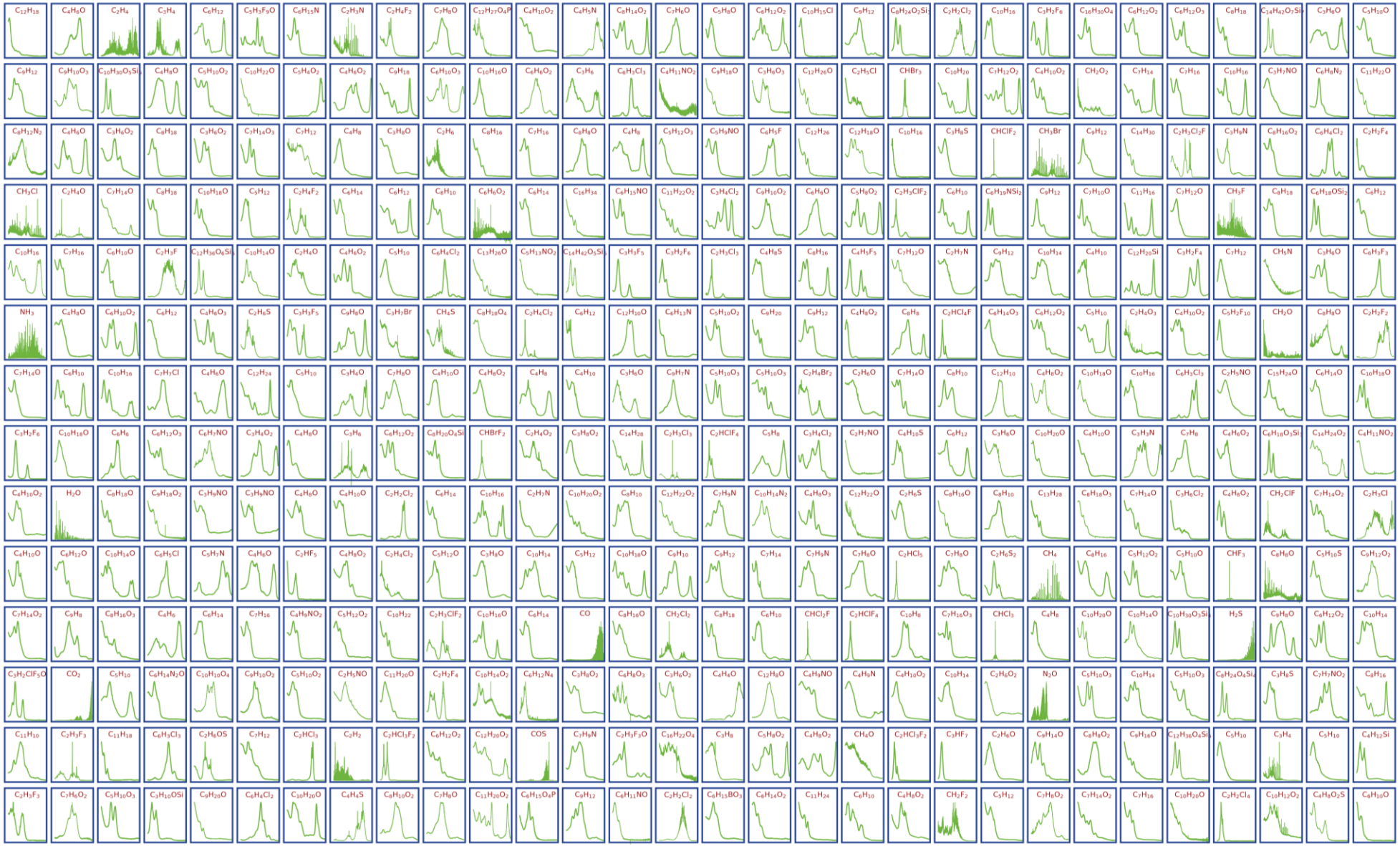
Spectral Library: **600** compounds and counting…



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Picarro's Ammonia Analyzers

Model	CO_2	CH_4	N_2O	H_2O	NH_3
G/SI/PI2103	(s)			(s)	X
G2508	X	X	X*	X	(s)
G2509	X	X	X*	X	X

X: primary measurement
s: secondary measurement
*: additional corrections for NH_3>2ppm

G2509, 5-Species Analyzer

G2509

5 species:

- CO_2 (ppb precision)
- CH_4 (ppt precision)
- N_2O (ppb precision)
- NH_3 (ppt precision)
- H_2O

- **Optimized NH_3 performance:**
  - Response time
    - Coating for sampling handling parts
    - Increased flow rate (1.3 L/min instead of 240 mL/min)
  - Accurate ammonia measurements up to 10 ppm
- **Extended CH_4 range (up to 800ppm)**
- **Surrogate gas validation**
  - Proven as ‘customized G2508’ since 2018
- **Updated water vapor correction for NH_3**
- **Added averaging intervals for N_2O**

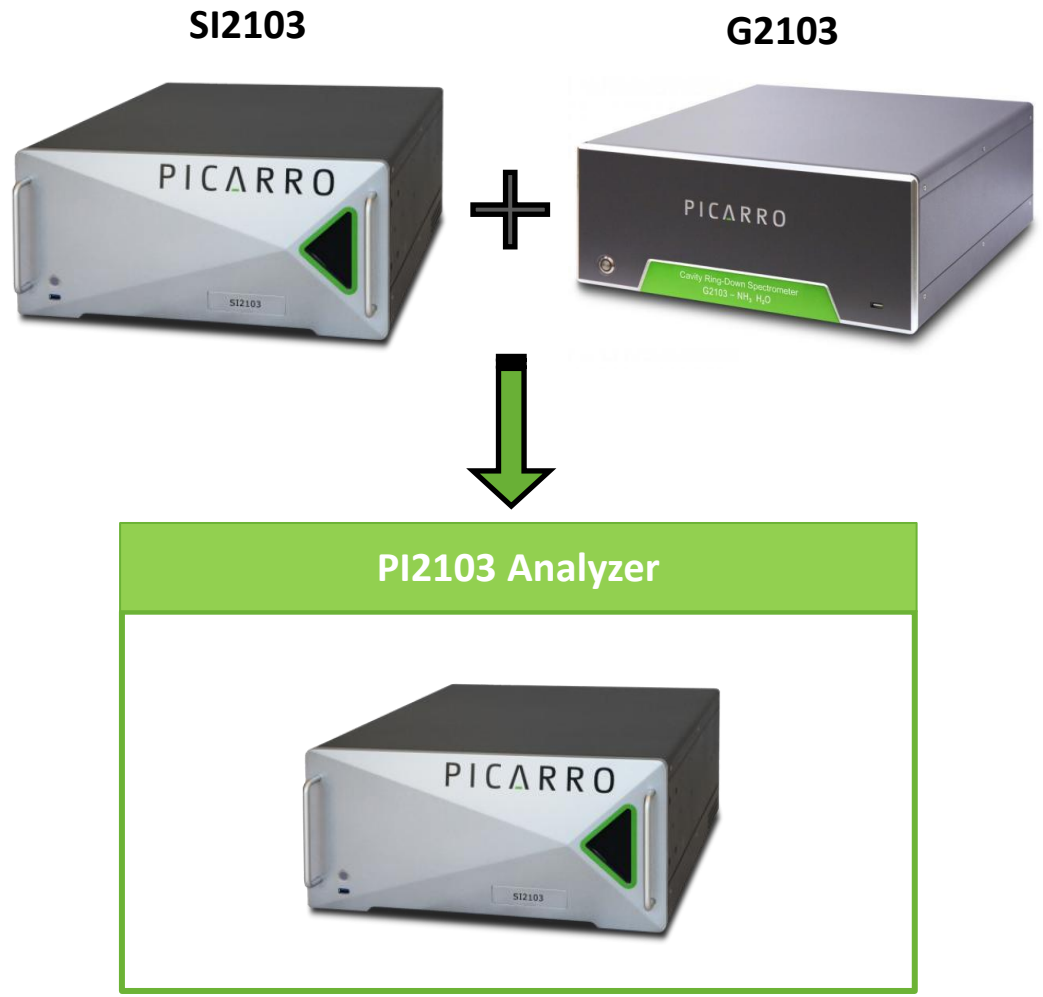
G2509, 5-Species Analyzer

G2509 Performance Specifications and Typical Performance in Air						
Specification	**N_2O**	**CH_4**	**CH_4 High Range**	**CO_2**	**NH_3**	**H_2O**
Precision Raw (1σ)	<25 ppb + 0.05% of reading **Typical = 5.0 ppb***	<10 ppb + 0.05% of reading **Typical = 0.3 ppb***	<100 ppb + 0.15% of reading **Typical = 20 ppb***	<600 ppb + 0.05% of reading **Typical = 240 ppb***	<5 ppb + 0.05% of reading **Typical = 0.16 ppb***	<500 ppm
Precision 1 min (1σ)	<10 ppb + 0.05% of reading **Typical = 1.1 ppb***	<7 ppb + 0.05% of reading **Typical = 0.1 ppb***	<40 ppb + 0.15% of reading **Typical = 7 ppb***	<300 ppb + 0.05% of reading **Typical = 74 ppb***	<3 ppb + 0.05% of reading **Typical = 0.07 ppb***	<250 ppm
Precision 5 min (1σ)	<5 ppb + 0.008% of reading **Typical = 0.6 ppb***	<5 ppb + 0.02% of reading **Typical = 0.1 ppb***	<20 ppb + 0.10% of reading **Typical = 3 ppb***	<200 ppb + 0.05% of reading **Typical = 38 ppb***	<1 ppb + 0.05% of reading **Typical = 0.04 ppb***	<100 ppm
Guaranteed Spec Range	0.3–200 ppm***	1.5–12 ppm	0–800 ppm	380–5000 ppm	0–300 ppb	0–3 %
Operating Range	0–400 ppm***	0.5–15 ppm	0–800 ppm	0.02–2 %	0–10 ppm***	0–7 %
Measurement Rate	<8 secs	<8 secs	<8 secs	<8 secs	<8 secs	<8 secs
Typical Gas Response (Rise-Fall 10-90%, 90-10%)	~8 secs	~8 secs	~8 secs	~8 secs	<2 min**	~8 secs
Report Dry Mole Fraction	Yes	Yes	Yes	Yes	Yes	N/A

G / SI / PI 2103, Single-species NH_3 analyzer

- **Superior NH_3 performance**
  - ppt precision (100 ppt, 1-σ in 100 sec*) and lower detection limit
  - Virtually no drift (less than ± 0.5 ppb/month)
  - Large concentration range (up to 50 ppm with extended range mode)
  - Short response times (<1 min for 0 – 20 ppb)
  - Surrogate gas validation of calibration

- **PI2103: Improved NH_3 analyzer**
  - Built with the best of the two existing NH_3 analyzers
  - Faster (1 Hz) measurements from G2103
  - More stable OS (Linux) and upgraded sample handling from SI2103



PI2103, Single-species NH_3 analyzer

PI2103 Performance Specifications	Typical Performance***	Specifications****
Lower Detection Limit (3σ, 300 sec)	0.03 ppb	<0.09 ppb
Zero Drift* *(peak-to-peak, 50-minute average)*	±0.04 ppb (72 hrs)	±0.15/±0.5 ppb (72 hrs/1 month)
Precision (1σ, 1 sec) **Precision** (1σ, 10 sec) **Precision** (1σ, 300 sec)	0.19 ppb 0.058 ppb 0.010 ppb	0.50 ppb + 0.1% of reading 0.17 ppb + 0.05% of reading 0.03 ppb + 0.02% of reading
Measurement Interval	1 sec	1 sec
Response Time (0–20 ppb)** *(Rise/Fall Time 10–90%/90–10%)*	<2 min	<2 min
Measurement Range	Guaranteed range 0–500 ppb Operational range 0–10 ppm Extended range 0–50 ppm (Optional)	Guaranteed range 0–500 ppb Operational range 0–10 ppm Extended range 0–50 ppm (Optional)

Main Applications for Picarro NH_3 Analyzers

G/SI/PI2103

- Ammonia monitoring at urban and rural stations
- Studying indoor air quality
- Investigating particulate matter formation
- Quantifying livestock emissions
- Quantifying vehicle emissions

G2508

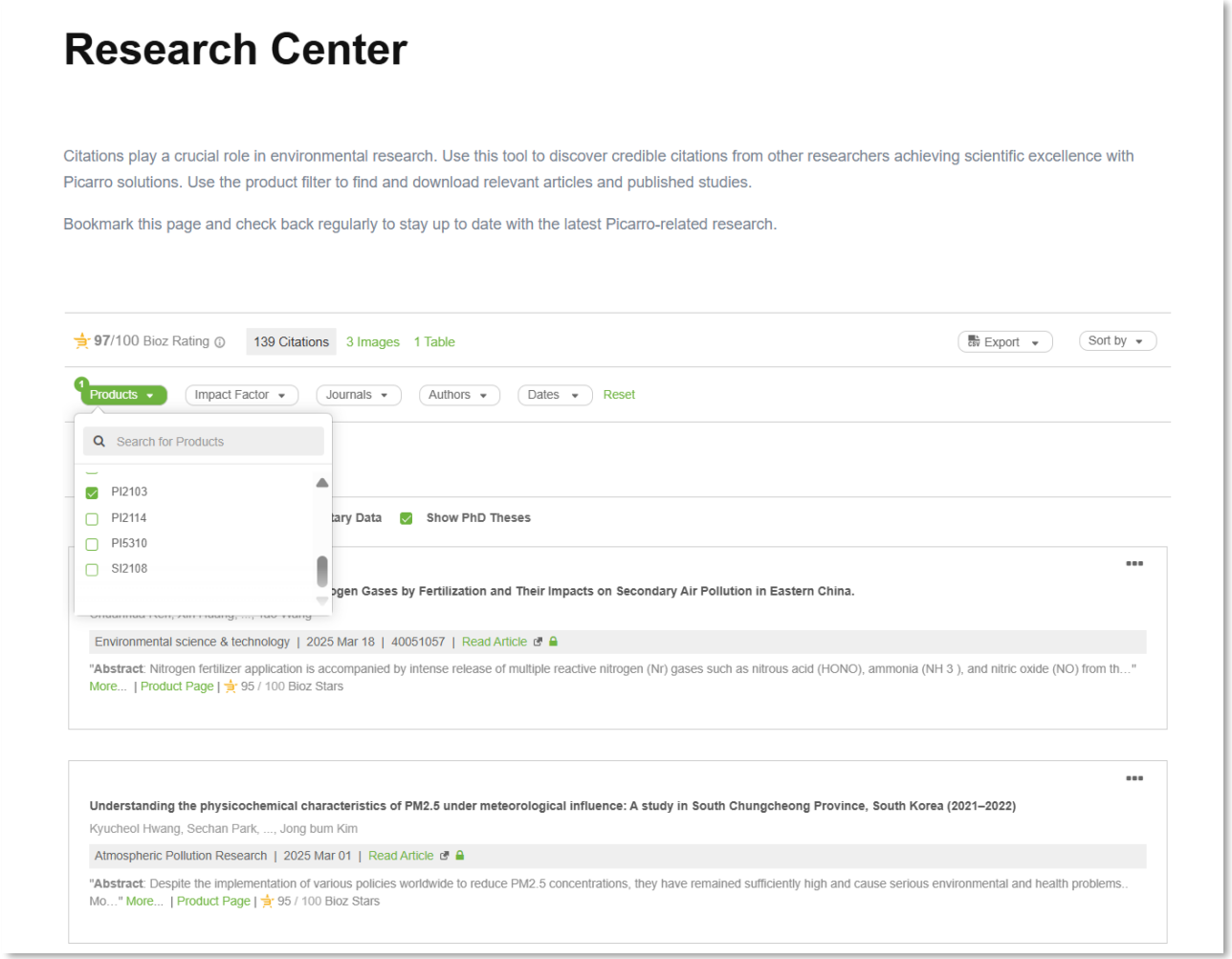
- GHG soil flux studies (recirculation)
- GHG incubation experiments (recirculation)

G2509

- Ammonia monitoring at urban stations
- Quantifying GHG and ammonia emissions of livestock
- Fertilizer studies

Picarro Research Center

- Easily discover publications that are relevant to your research: www.picarro.com/environmental/research_center



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Picarro Customer Support

- For any Technical or Application question reach out to Customer Support:
    - e-mail: support@picarro.com
    - phone: +31 85 888 1650 (international) / +1 408 962 3991 (USA)

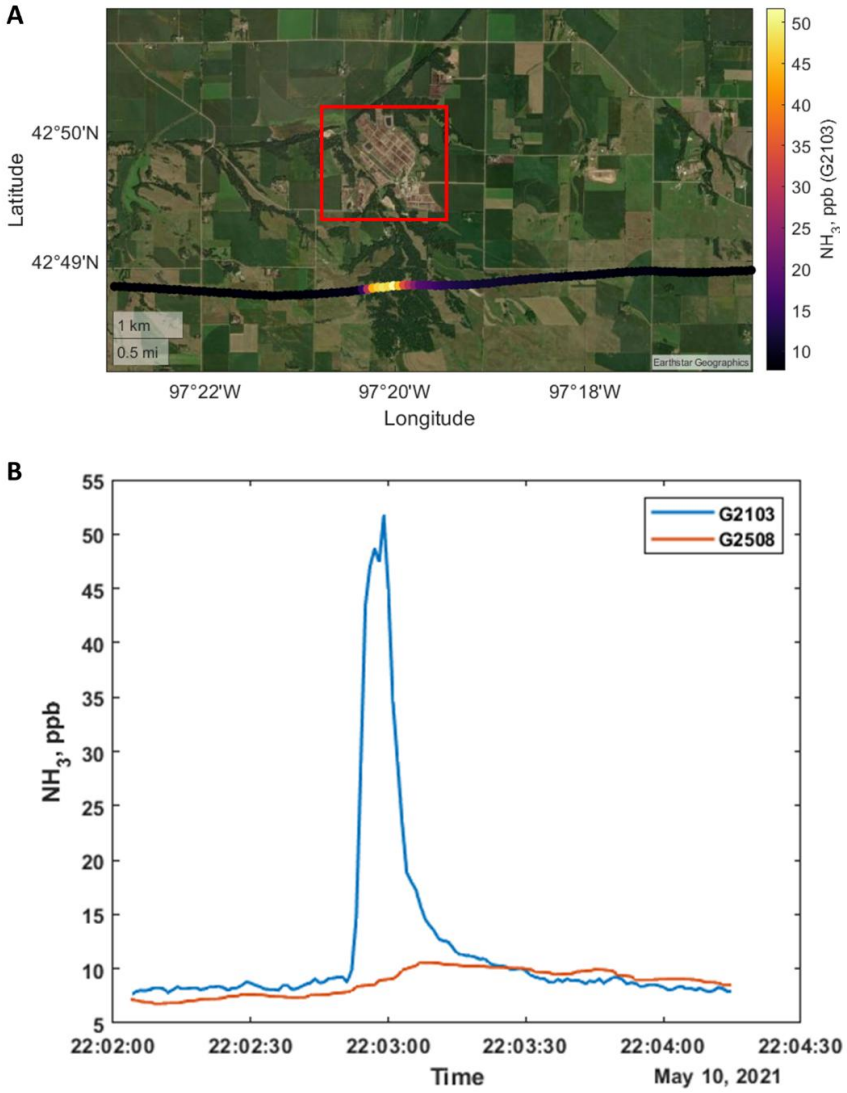
Please provide the following information:

- Serial number
- Description/overview of setup (analyzer/peripherals/experiment)
- EventLogs and Private Data from time that problem occurred
- Remote Access information (Teamviewer / Anydesk)

16

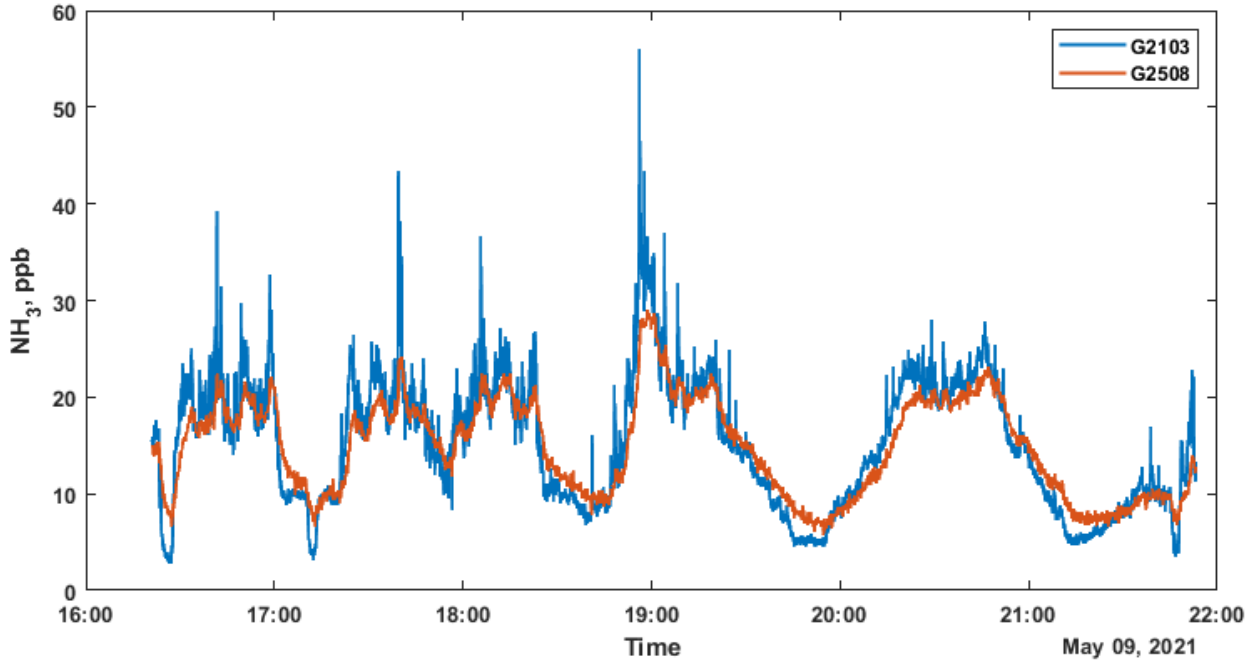
Case Studies

Use Case 1: Measuring Boundary Layer NH_3



Flight Campaign

With targeted regions included dense livestock operations, conventional row cropping, and non-developed forests.



A) G2103 data downwind of a cattle feedlot point source, with the source outlined in red. B) Time series of G2103 and G2508 measurements downwind of the same source. G2508 was interpolated to 1 hz by setting values to the most recent G2508 measurement to match the 1hz frequency of the G2103. C) Time series of NH_3 observations from G2103 and G2508

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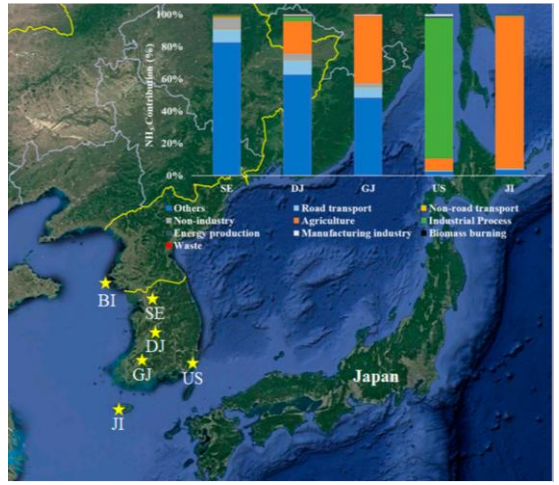
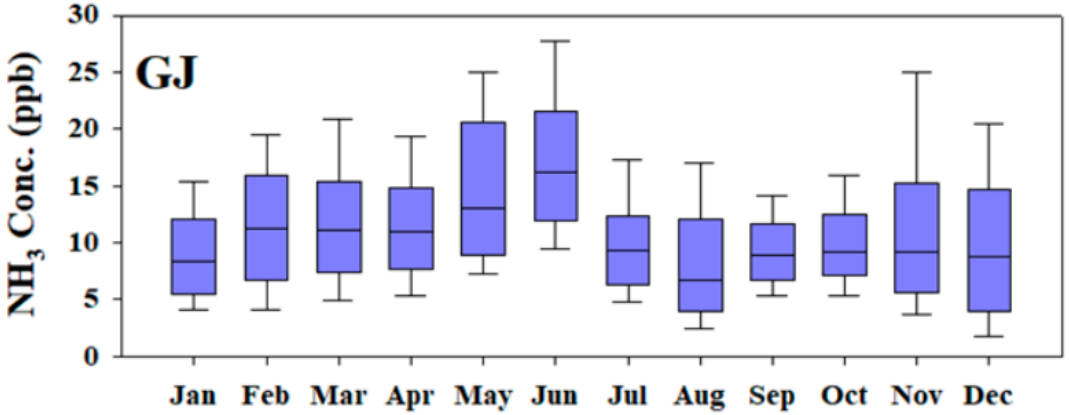
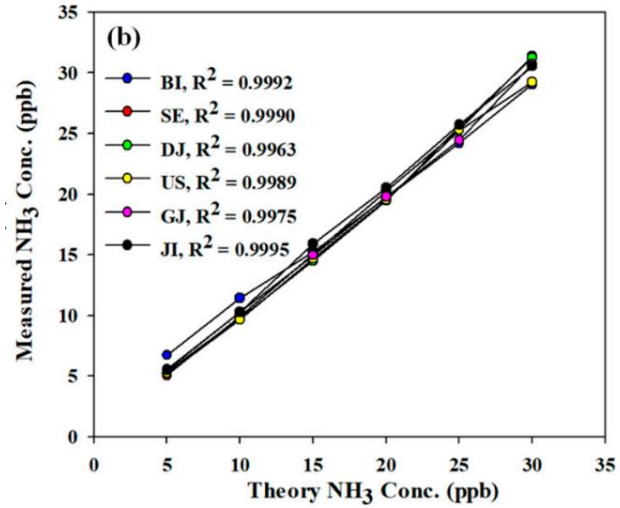
Use Case 2: Ammonia measurements in Korea

- 6 sampling sites
- Teflon tubing (short than 1.5m, heated below 40°C)
- External 47mm Teflon filter, weekly replacement
- Semi-annual calibration (dilution of 10ppm NH_3 standard gas with zero air)

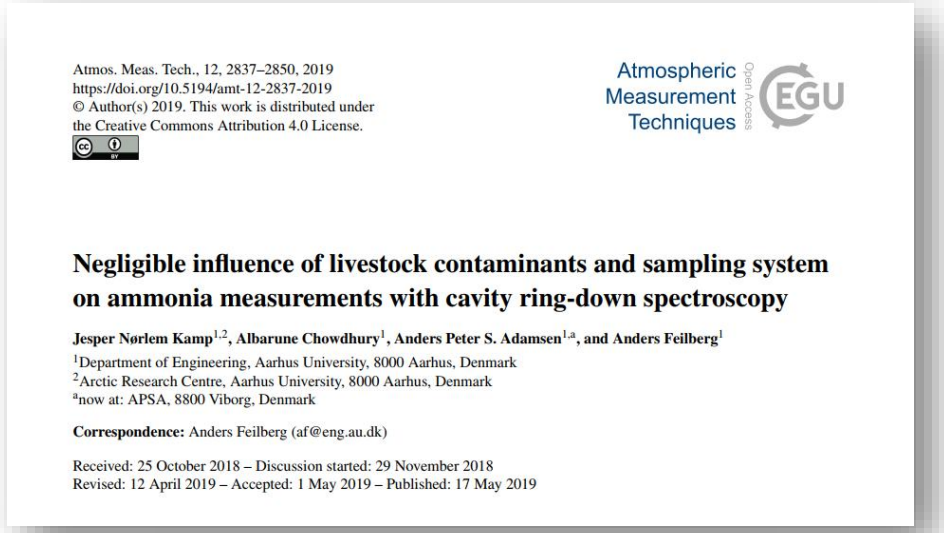






Song et al., 2024, *Distribution and Characteristics of Ammonia Concentration by Region in Korea*, Atmosphere

Use Case 3: NH_3 Measurements in a Cattle Barn (G2103)



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https://doi.org/10.5194/amt-12-2837-2019

Atmospheric Measurement Techniques
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EGU

Negligible influence of livestock contaminants and sampling system on ammonia measurements with cavity ring-down spectroscopy

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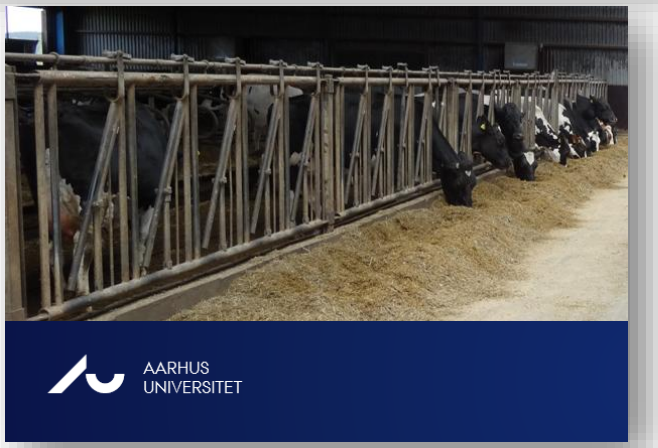
Revised: 12 April 2019 – Accepted: 1 May 2019 – Published: 17 May 2019

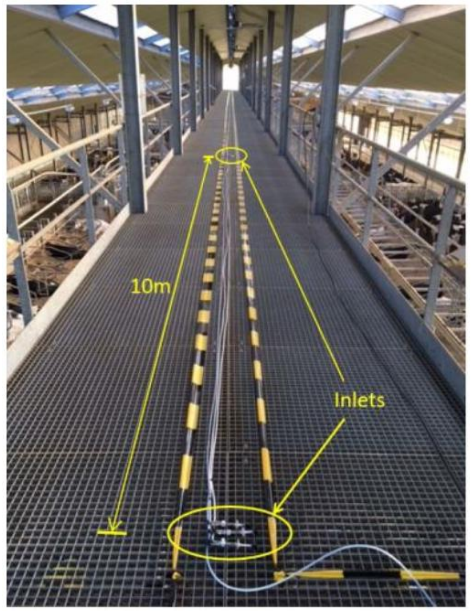


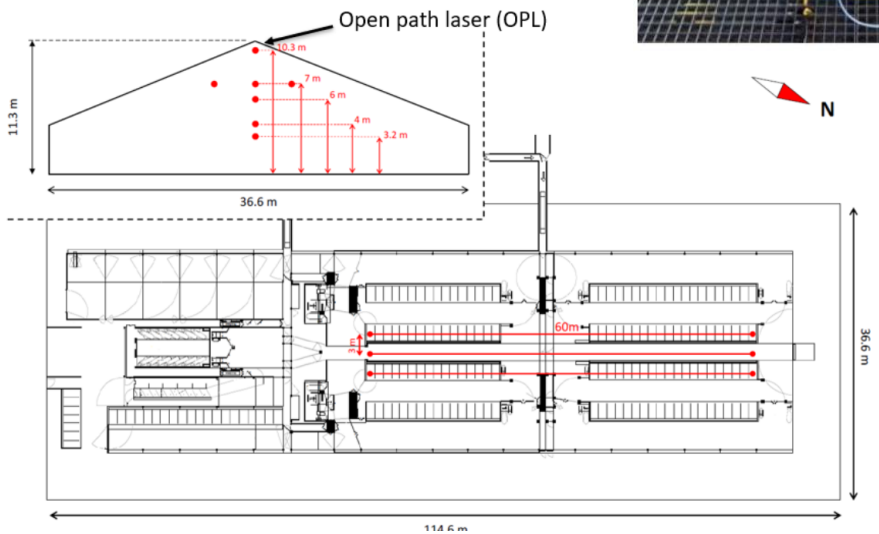
Source: Photo credit Aarhus University, Denmark

Key findings

- Excellent linearity
- No significant H_2O, CO_2, CH_4 and VOC interferences on NH_3 data
- Negligible effect of particulate filter
- CRDS analyzer provides fast, precise and accurate observations of NH_3 in cattle barns
- Good response time

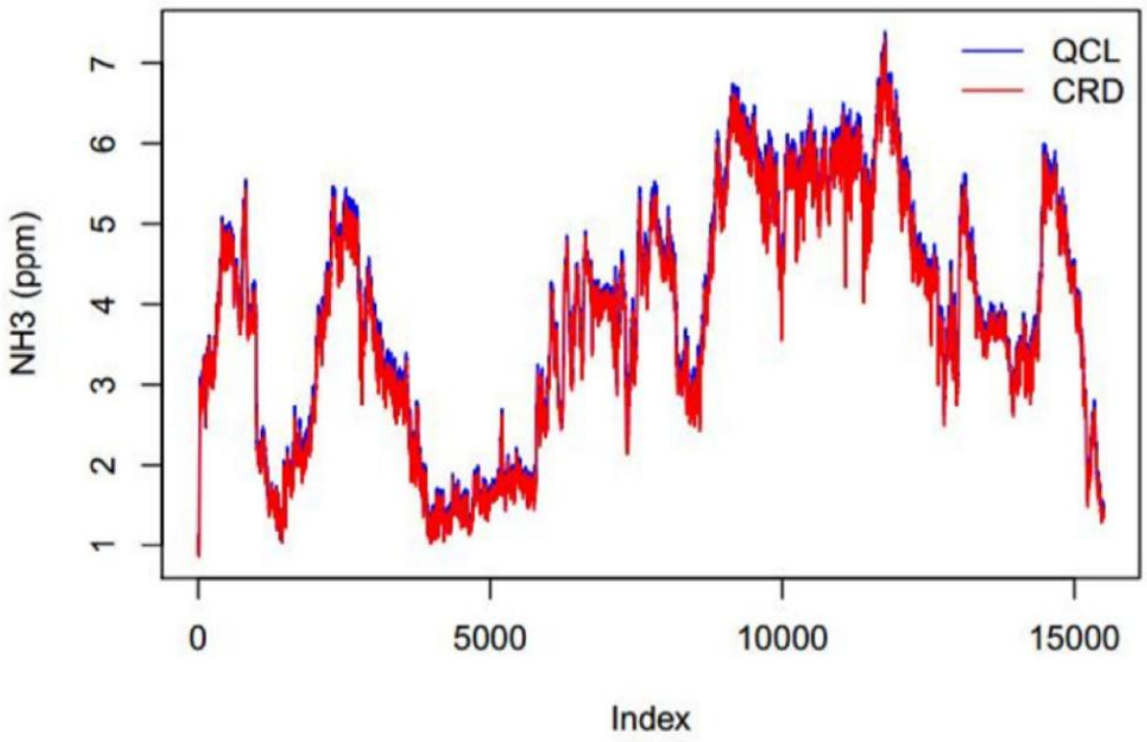
Use Case 4: NH_3 & GHG Measurements in a Dairy Barn

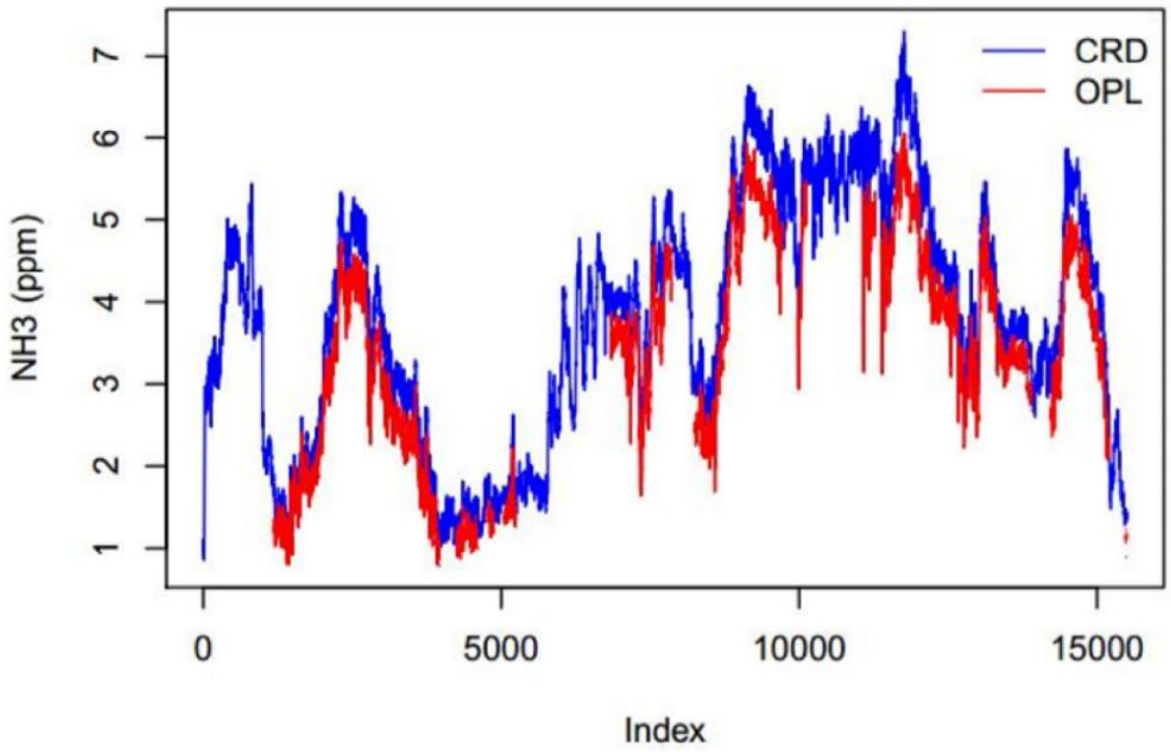




- Investigating ammonia abatement techniques for livestock (Flemish research Institute for Agriculture, Fisheries and Food (ILVO) in Belgium)
- G2509 analyzer optimized for ammonia measurements (Teflon sample handling parts, increased flow rate of about 1.3L/min)
- Performance comparison between G2509, an open-path tunable diode laser (OPL) and a closed-path quantum cascade laser (QCL)
- The air was measured at multiple inlets inside the dairy barn

Use Case 4: NH_3 & GHG Measurements in a Dairy Barn





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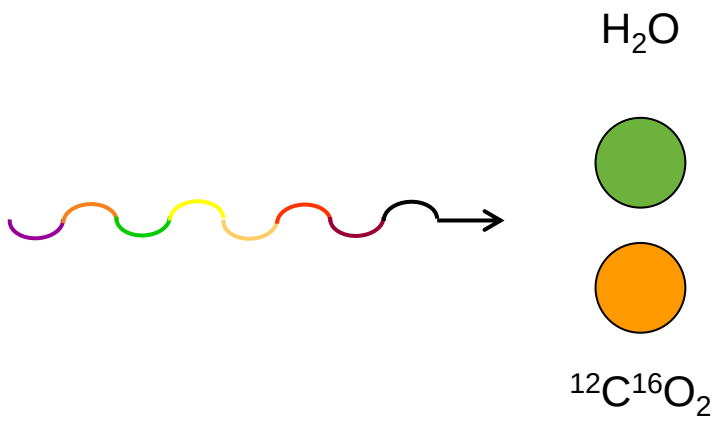
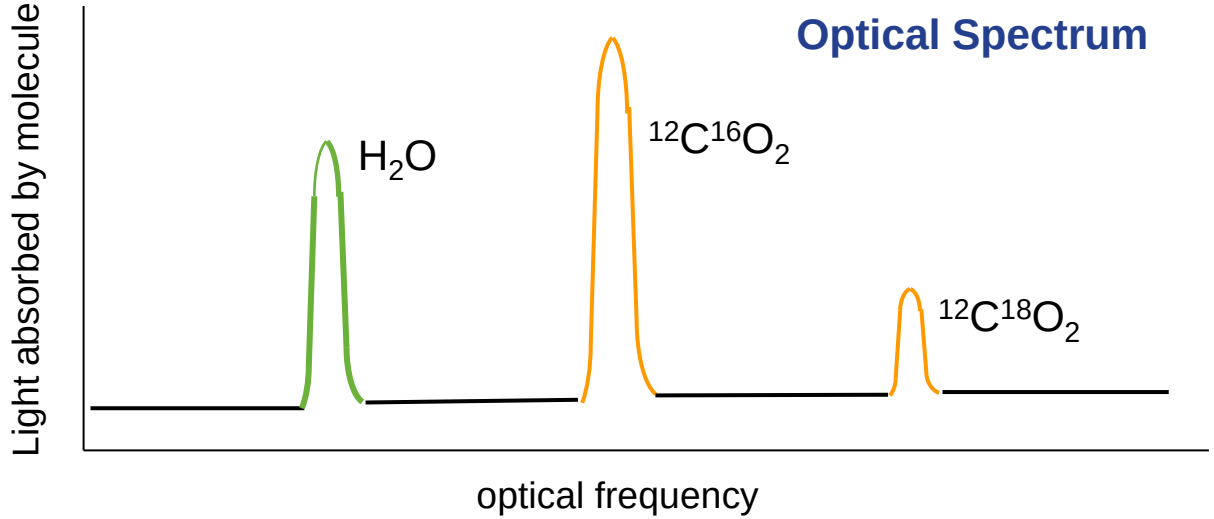
CRDS Theory

Resonant Optical Spectroscopy

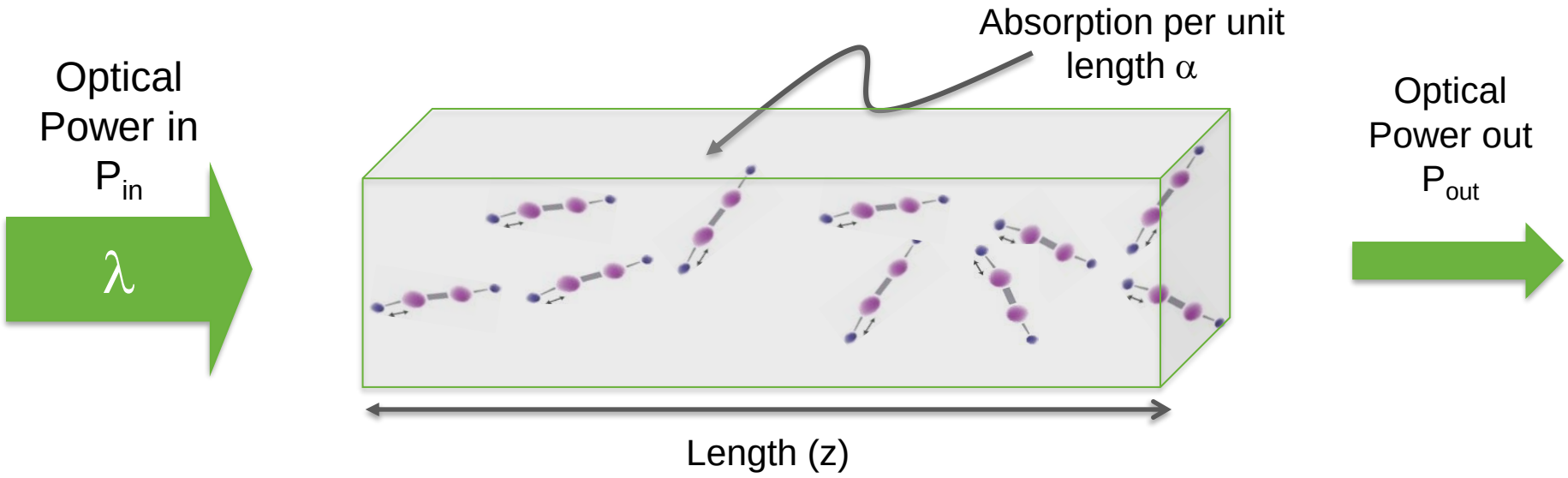




Each type of molecule has a unique optical absorption

1. Molecules absorb at optical frequencies where they resonate mechanically
2. A spectrum is measured by changing the frequency of light passing through a sample and measuring the amount of light absorbed
3. A spectrum of a given species of molecule usually consists of a number of absorption features
4. By measuring an isolated absorption feature of a species, its concentration can be determined

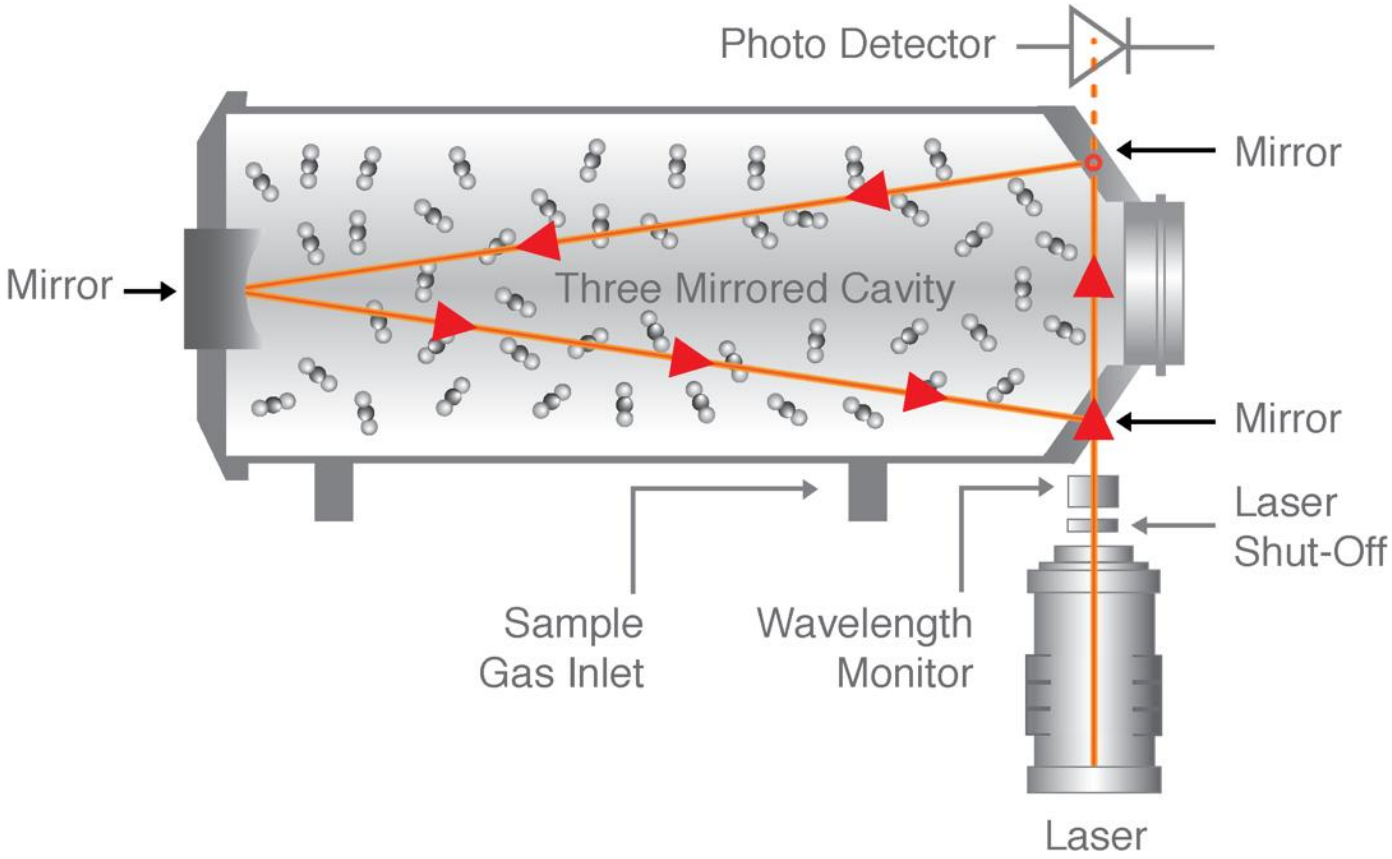
Beer-Lambert Law for Optical Absorption



$$P_{out} = P_{in} e^{-(\alpha_{molecule} + \alpha_{everything\ else})z}$$

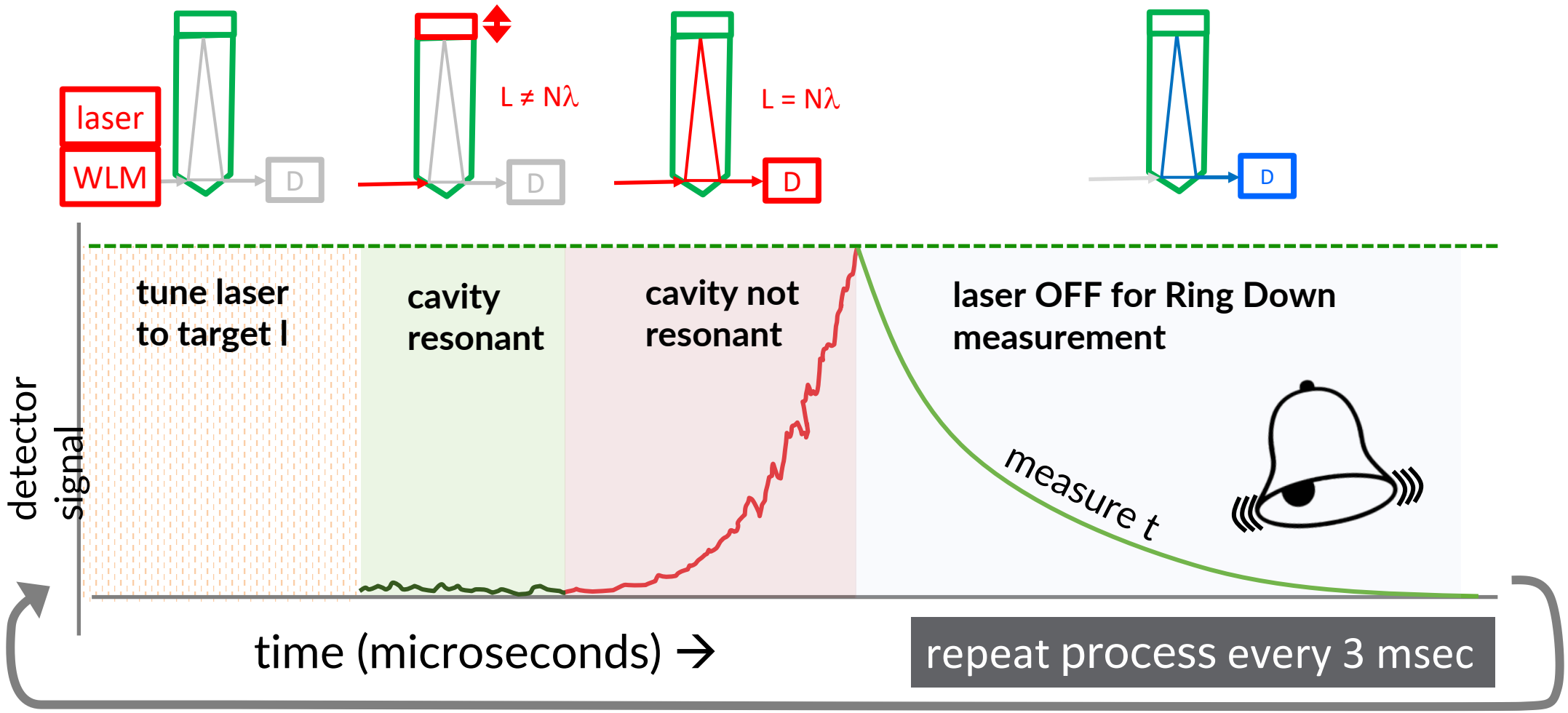
- **Maximize $\alpha_{molecule}$:** Pick λ where the target molecule absorbs strongly
- **Minimize $\alpha_{everything\ else}$:** Pick λ where all the other molecules don't absorb, and take care so that there is no loss of signal in your optics
- **Maximize z:** Get the longest path length you possibly can

CRDS: Time, not Absorbance



- CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration of (and sometimes isotopes of) H_2O, CO_2, CH_4, N_2O, CH_2O, NH_3, etc.
- Measure decay rate, rather than absolute absorbance
- Small 3-mirrored cavity ~ 35 cc
- Long effective path-length (> 10 km)
- Time-based measurement
- Laser is switched on and off, and scanned across wavelengths

CRDS: Principle of Operation



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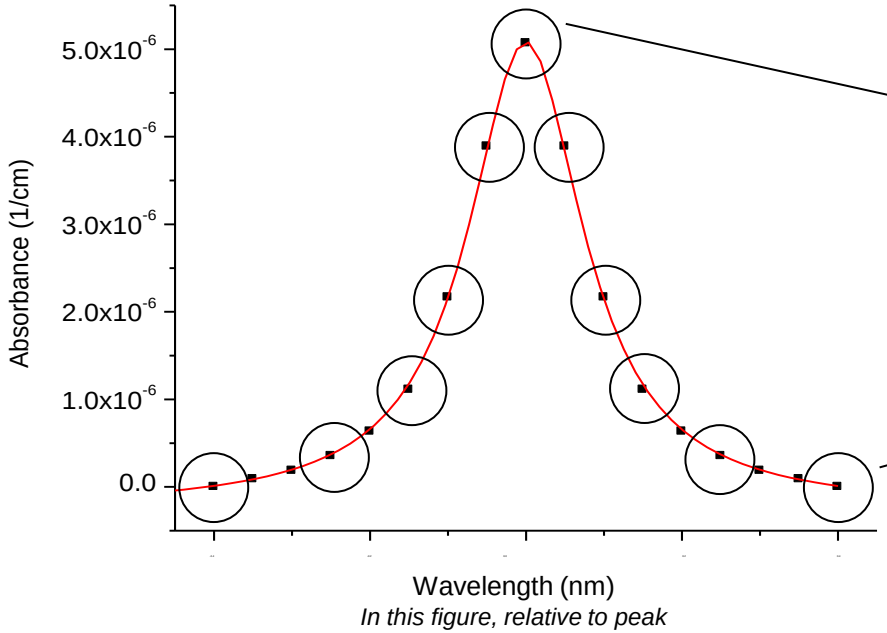
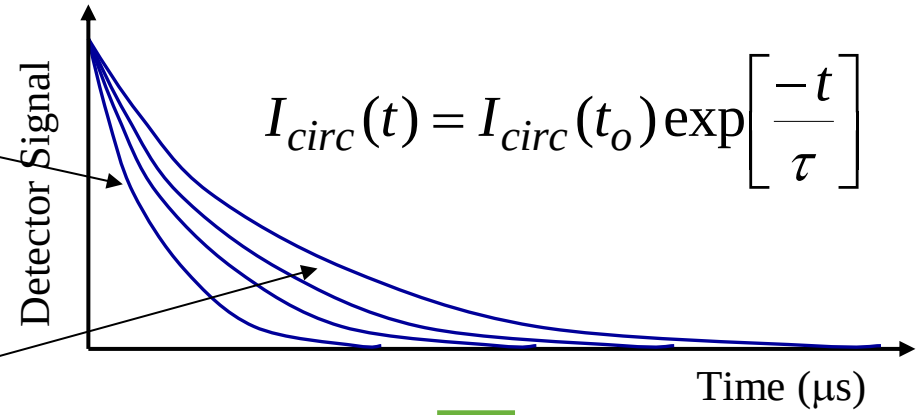
Turning Ring-Down Times into Concentrations

1. Select wavelength using λ-monitor



2. Measure decay time using CRDS



$$I_{circ}(t) = I_{circ}(t_o)\exp\left[\frac{-t}{\tau}\right]$$

3. Calculate loss (a)

$$\alpha = {}^{1}/_{c\tau}$$

I = light intensity in cavity
c = speed of light
t = cavity ring-down time
a = cavity loss per unit length (ppm/cm)

Repeat

Gas concentration is proportional to the area under the curve, given constant T and P

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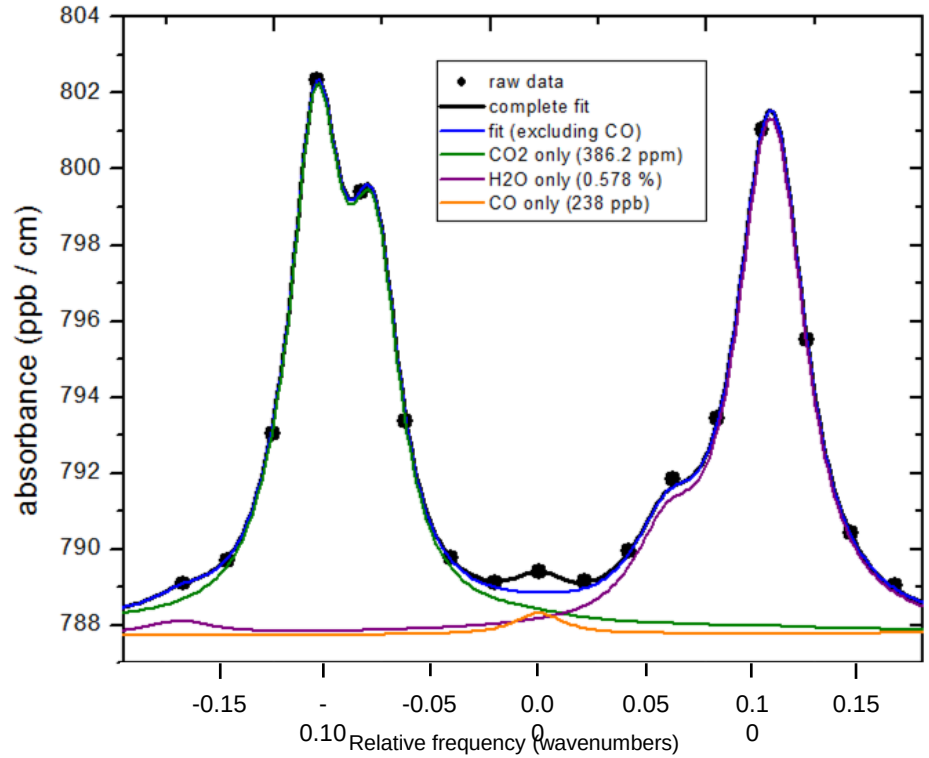
Generating Stable Spectrograms

1. A high-quality **absorption measurement**
   - CRDS delivers a precise and accurate measurement of the optical loss

2. A clean stable **frequency axis**
   - An accurate and precise tool for determining the laser wavelength

3. Precise **temperature control**
   - Engineered control loops

4. Precise **pressure control**
   - Engineered control loops



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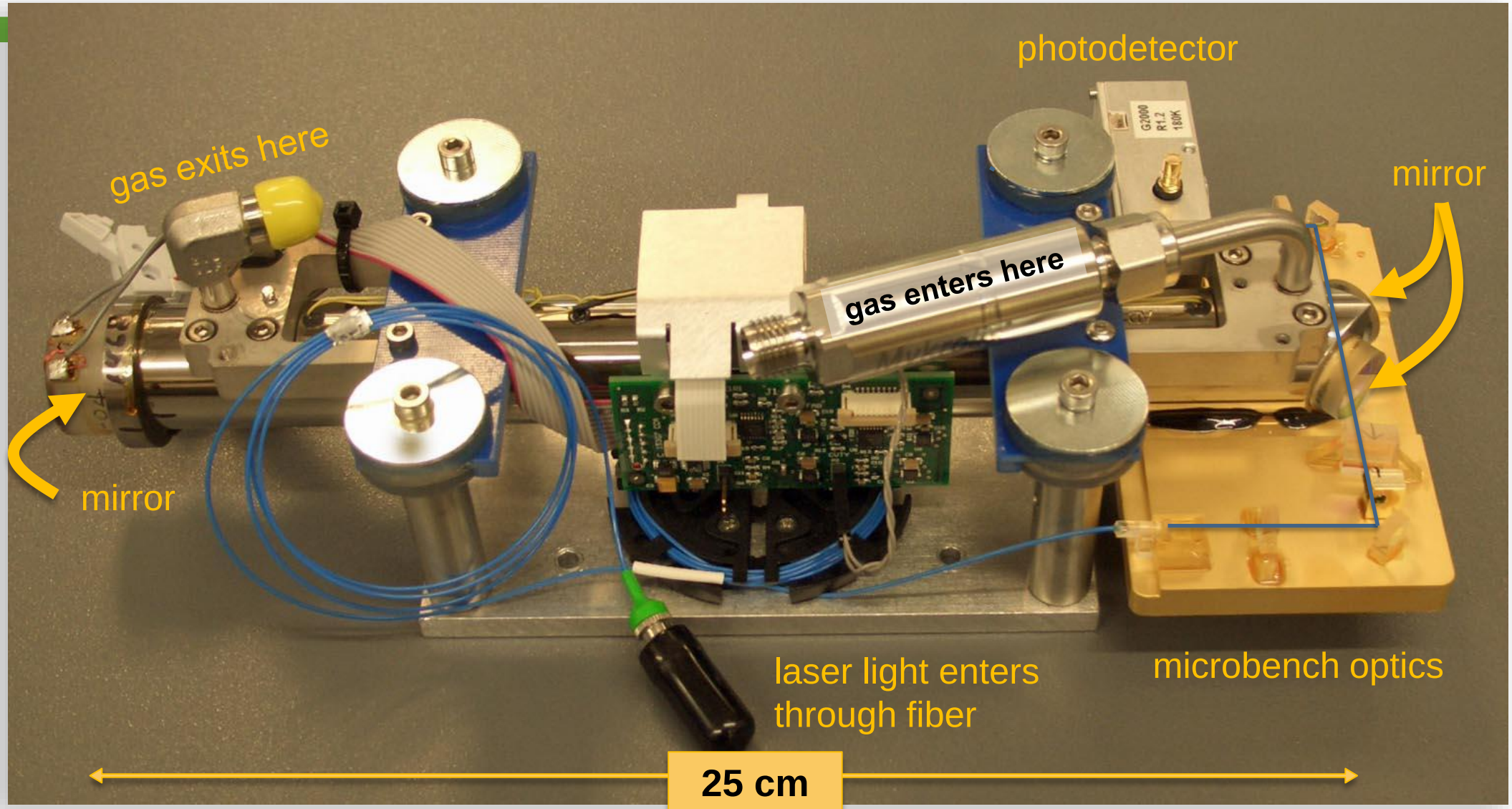
Nuts and Bolts



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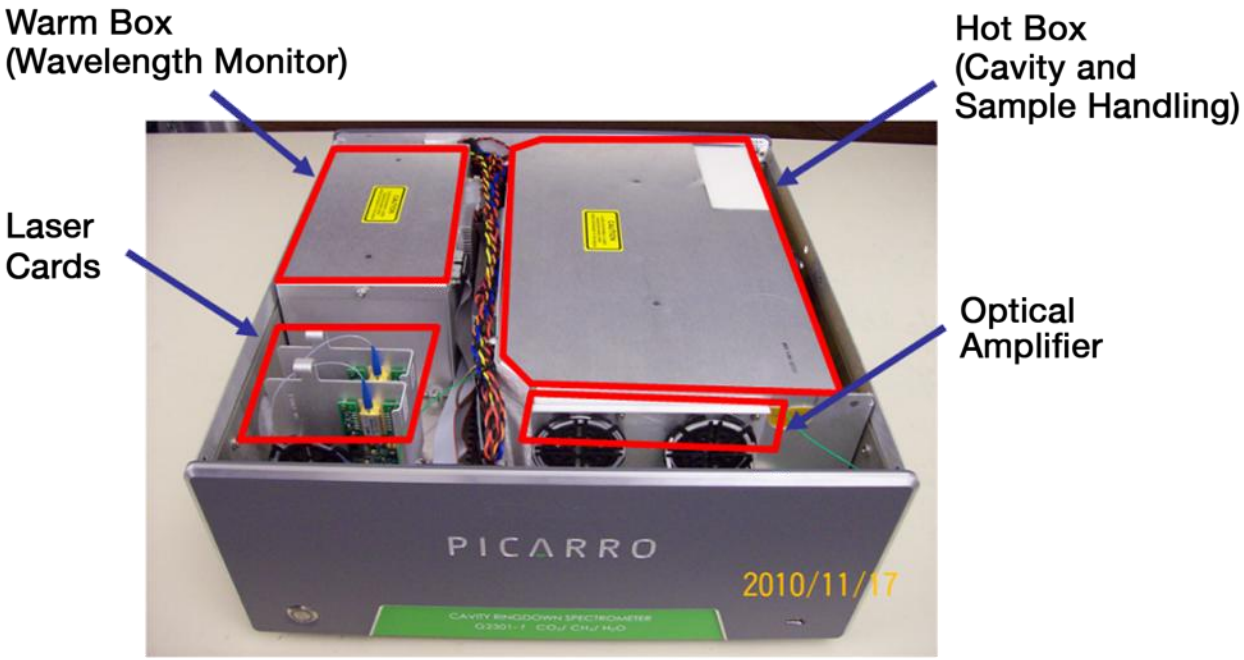
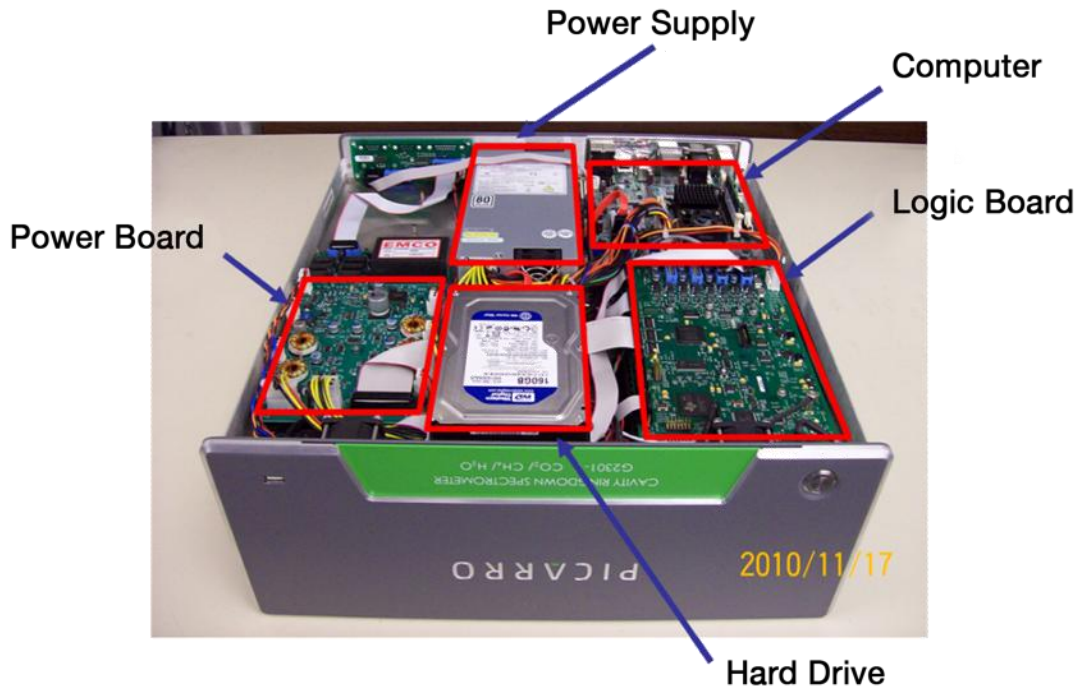
Inside the Box

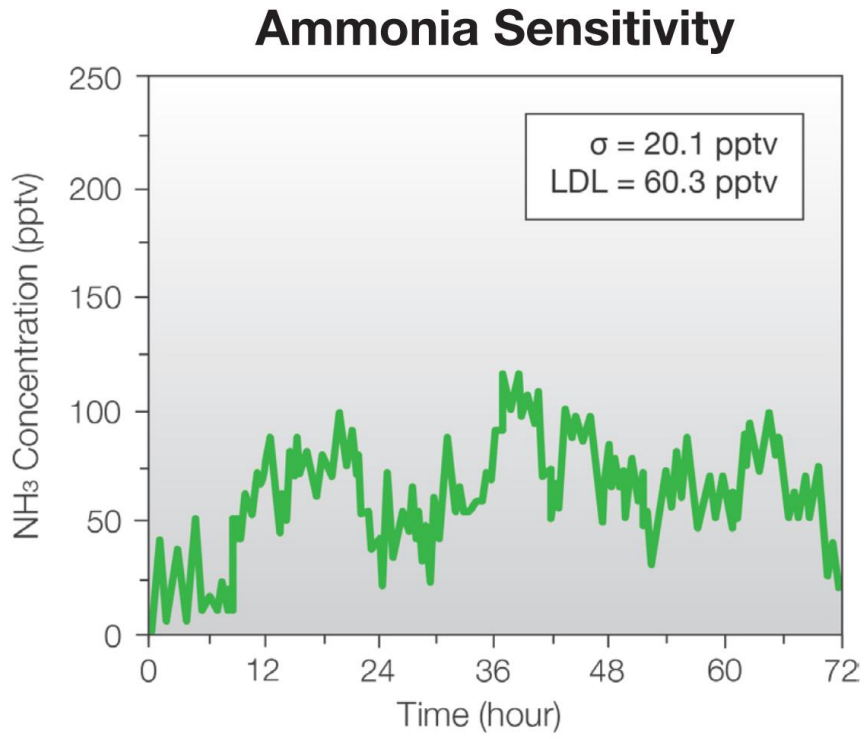




Application Considerations

Surrogate Gas Validation (PI2103/G2509)

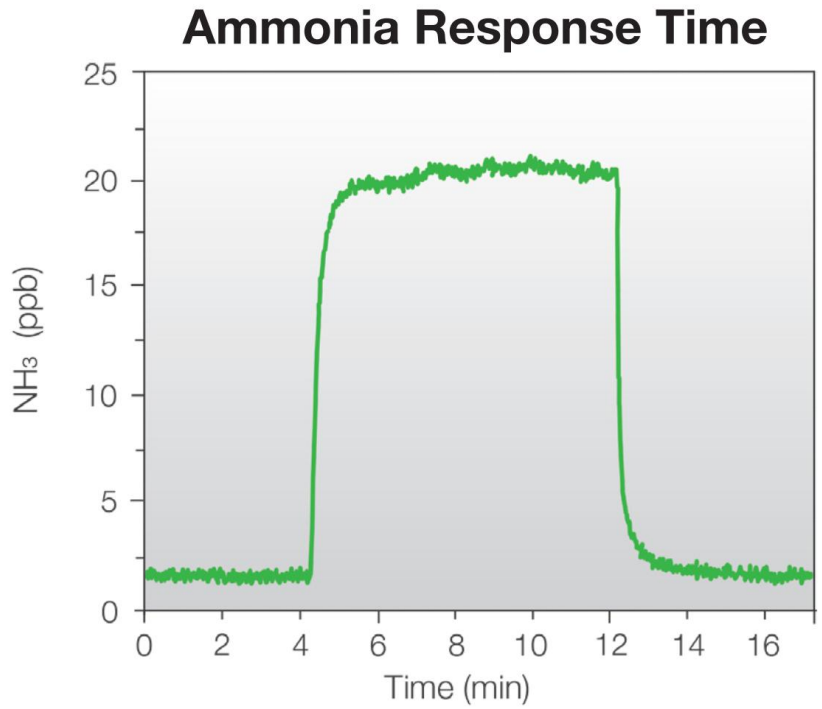
- Wavelength monitor constantly corrects drift (water vapor is measured as reference line)
- Surrogate gas validation (monthly to yearly)
  - Carbon dioxide acts as surrogate gas: non-reactive, easily commercially available, adsorption spectrum adjacent to ammonia
  - Avoids common accuracy issues of ammonia calibration standards (adsorption and stability)
  - Verify zero-drift with zero-air measurement (Phosphoric Acid Impregnated Charcoal (PAIAC) as NH_3 scrubber)
- Surrogate Gas Validation Tech Document



Typical noise zero drift of the PI2103 analyzer over 72 hours.

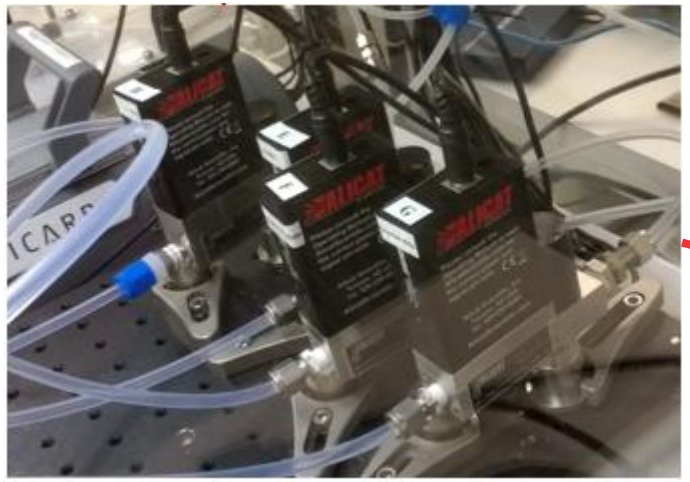
Analyzer Response Time

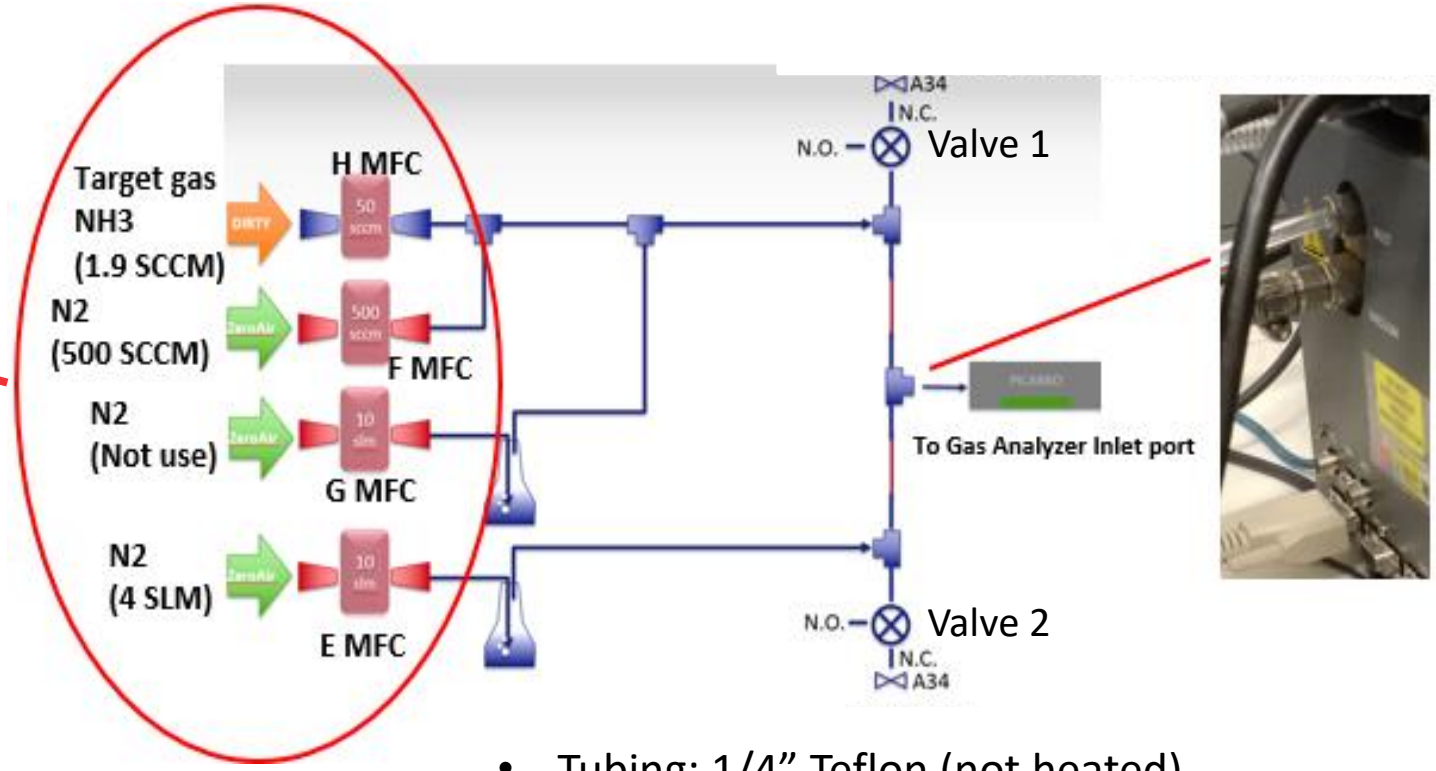
- Minimizing dead volumes
  - –Compact measurement cavity of 30mL
- Use of material with low adsorption of NH_3
  - –Teflon/PTFE for tubing and connectors
  - –Coatings for stainless steel components
- Increased flow rate (>1.5L/min)
- Response time (0-20ppb), 10-90%, 90%-10 rise/fall time: <2min
- Every analyzer is tested to guarantee the specified response time



Typical response time for a 10-90% and 90-10% 20 ppb ammonia challenge

Response time testing at Picarro

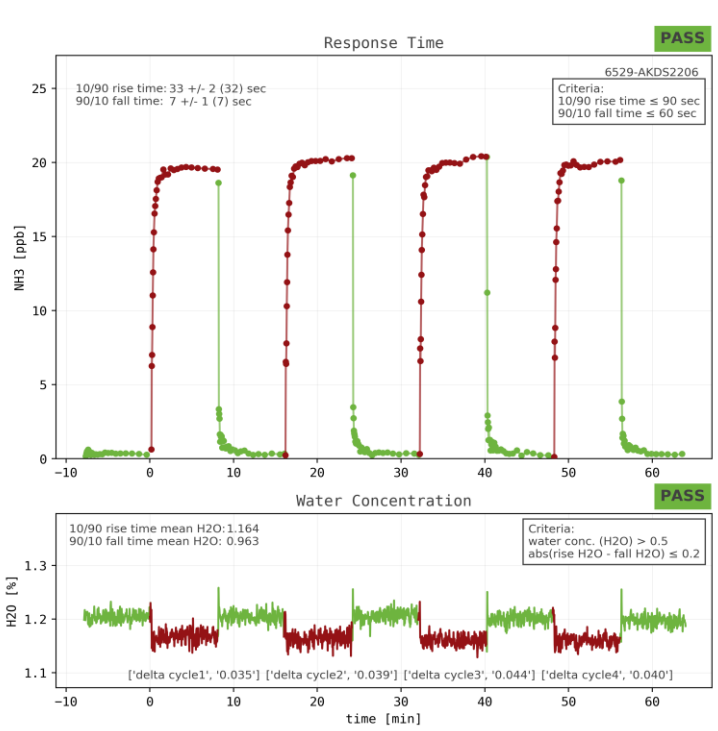




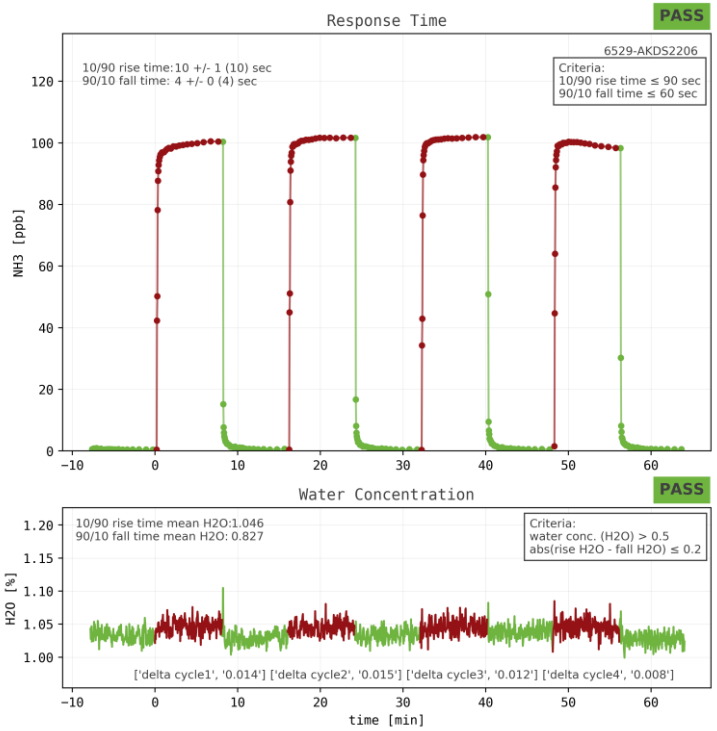
- Tubing: 1/4” Teflon (not heated)
- Abs. humidity: 1%

The sample gas is never in contact with the three-way valves (metal surfaces)!

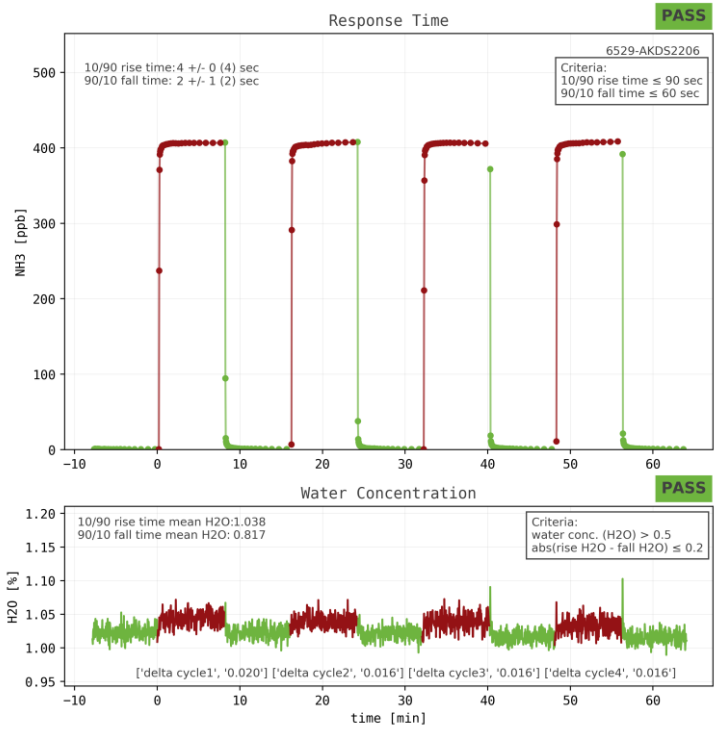
PI/G2103 response time in humid air (1% H_2O)



20 ppb



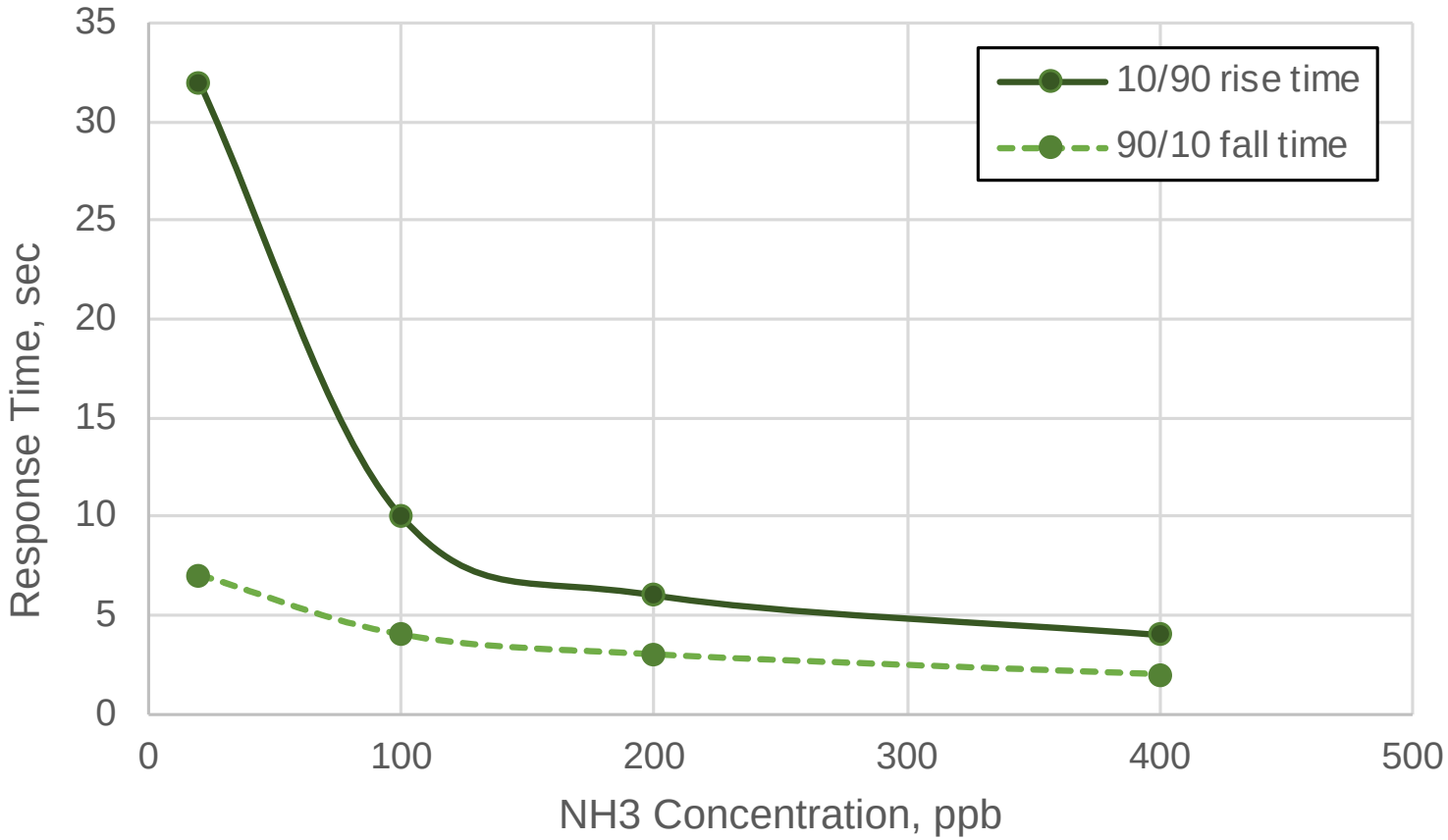
100 ppb



400 ppb

PICARRO

PI/G2103 response time in humid air (1% H_2O)



The 10 to 90% response time depends on the NH_3 concentration:

The higher the NH_3 concentration, the faster the response time.

Sample Gas Handling for Ammonia Measurements

- Use appropriate material: PTFE (Teflon), PFA, Silconert 2000 coated, PFTE coated
- Keep inlet tubing as short as possible
- Consider heating sample line tube to ~45°C
- An additional assist pump may be required when working with long tubing
- Note: Ammonia dissolves in condensed water!

Field Deployment

- Transportation
  - –Horizontal position
- Protection against harsh weather conditions
  - –Shelter for instrument, e.g., enclosures
- Battery: Deep cycle battery
- External filter recommended
  - –Recommended pore size and frequency of filter replacement varies for applications

UGT ClimBox

Hands-On Training

Topics: Software

- GUI
- User data vs. private data
  - Instrument Status
  - Outlet valve for troubleshooting
- Data file viewer
- Setup Tool
- Quick introduction to Controller
- Connecting Picarro 16-port manifold or other valve systems
- Analyzer shutdown options

Topics: Inside the Analyzer

- Opening the Box
- Maintenance (Video tutorials: https://www.picarro.com/environmental/environmental-video-tutorials)
  - Filter replacement
  - Fan replacement
  - Replacing Pump diaphragms
- Resetting cables

Consumables G2103/PI2103

Part number hardware	Short description	Frequency
C0360	Drierite	Before shutdown under high humidity levels
-	External particulate filter (3µm)	Depends on particulate load, often every 1-4 week replacement for ambient monitoring
S1021, S3174	Particulate filter (0.45µm) (Teflon for NH_3, HF, and HCl).	After 12 months, (if higher dust load every 3 to 6 months)
S2068	Complete fan kit	Expected after 3 to 5 years
S2009	External vacuum Rebuild Kit	Expected after ~15’000 hours (approx. 2 years cont. running)

PICARRO

For more information, please visit www.picarro.com

or email info@picarro.com