SEMTECH LASAR GAS ANALYZERS

Combining

Feedback Absorption Spectroscopy,

Amplified Resonance

and

Low Pressure Sampling

for the

Measurement of Nitrogen-Containing Compounds

in

Automotive Emissions

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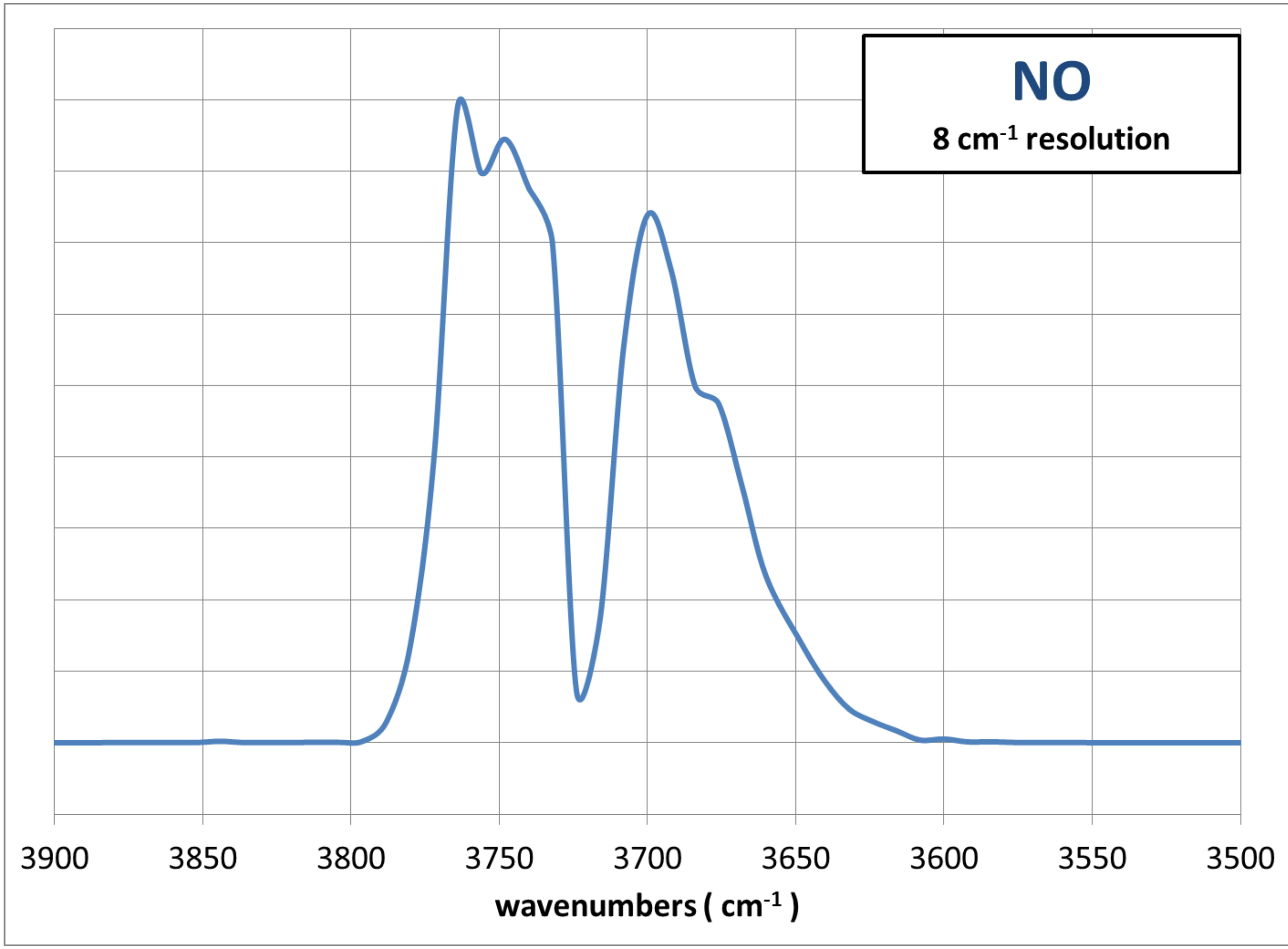
www.sensors-inc.com

TABLE OF CONTENTS

- ✓ Proposed Solution for N_2O measurement.
- ✓ Proposed Solution for NH_3 measurement.

PROBLEM: INTERFERENCES



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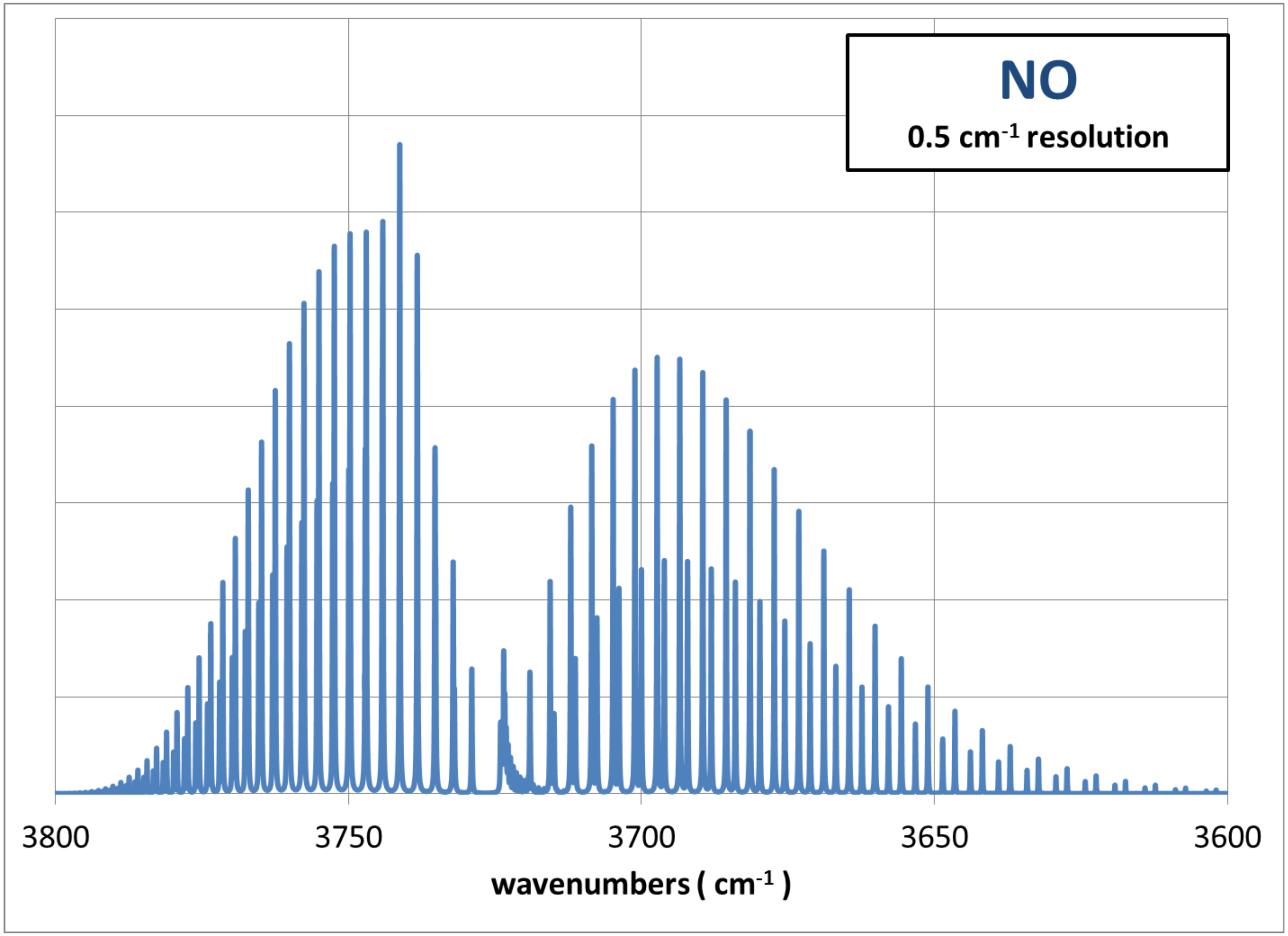

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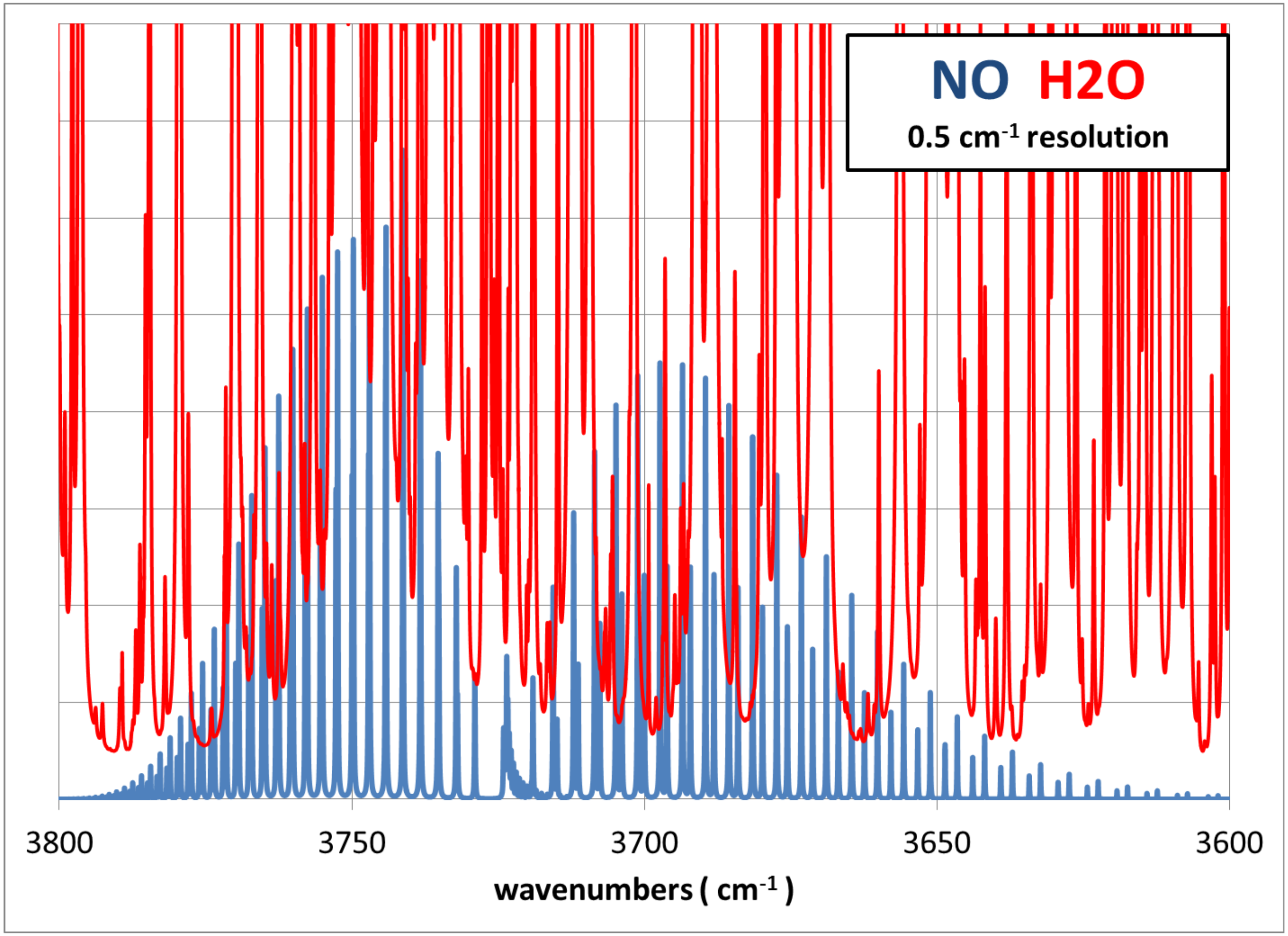

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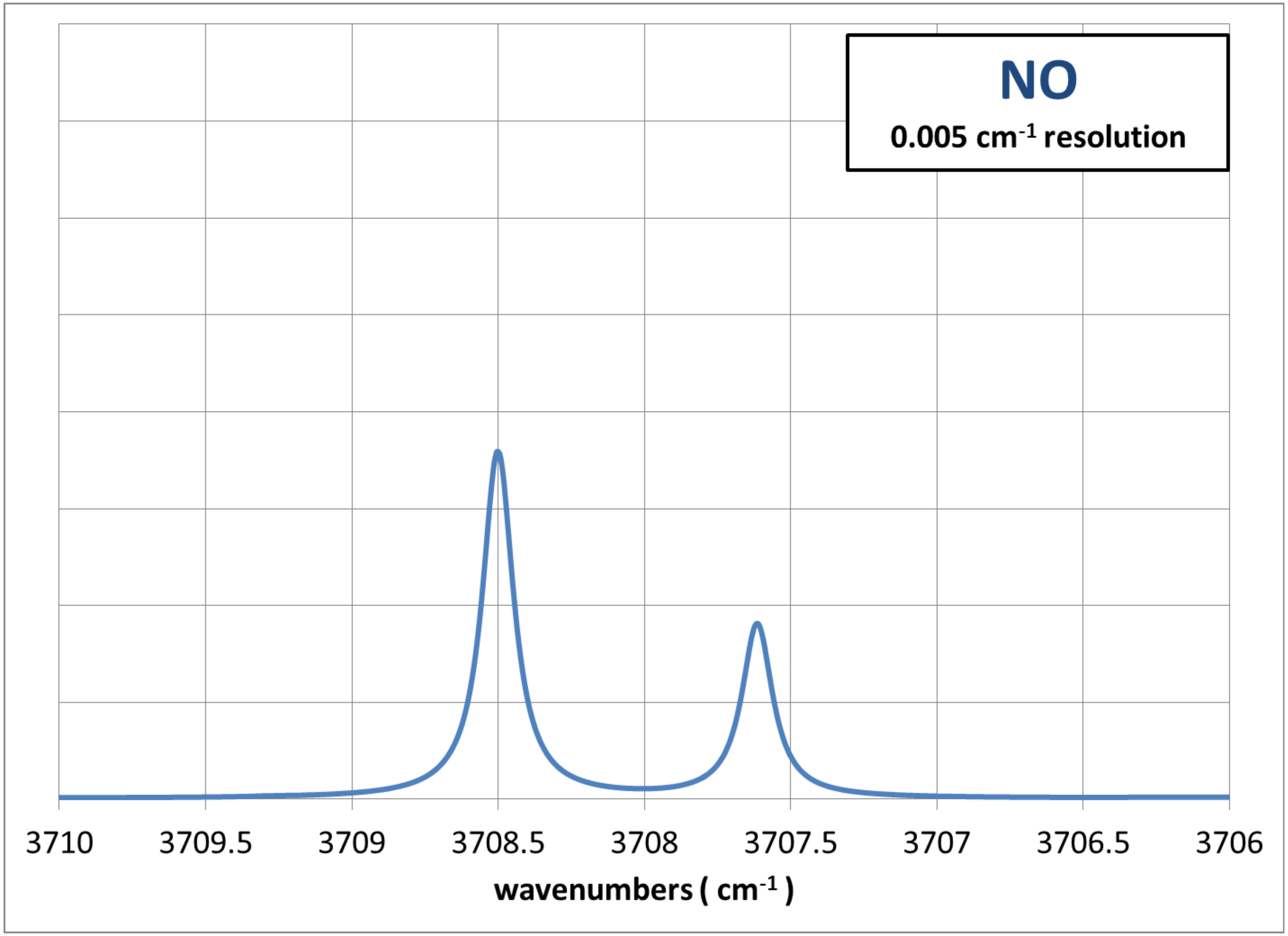

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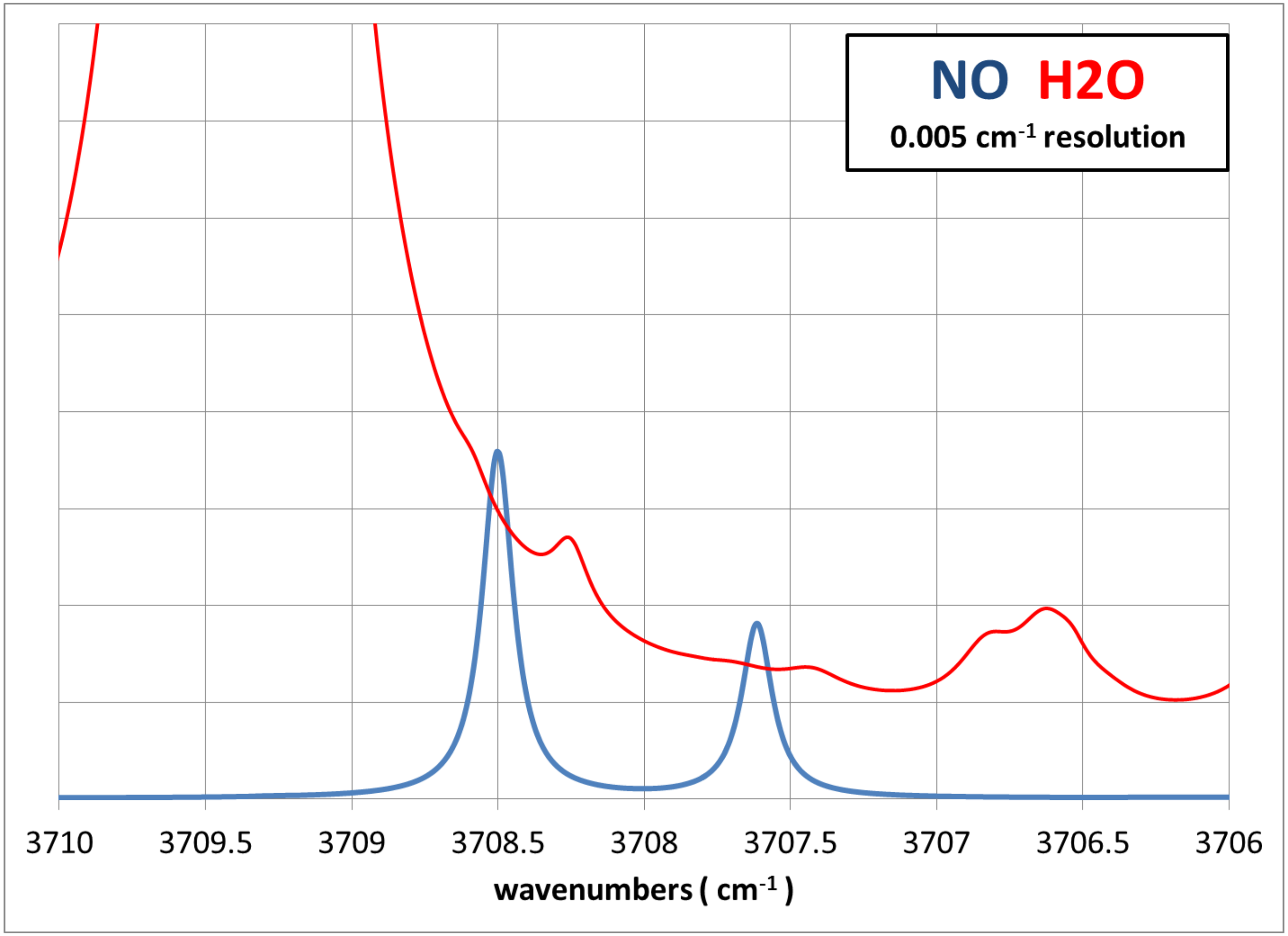

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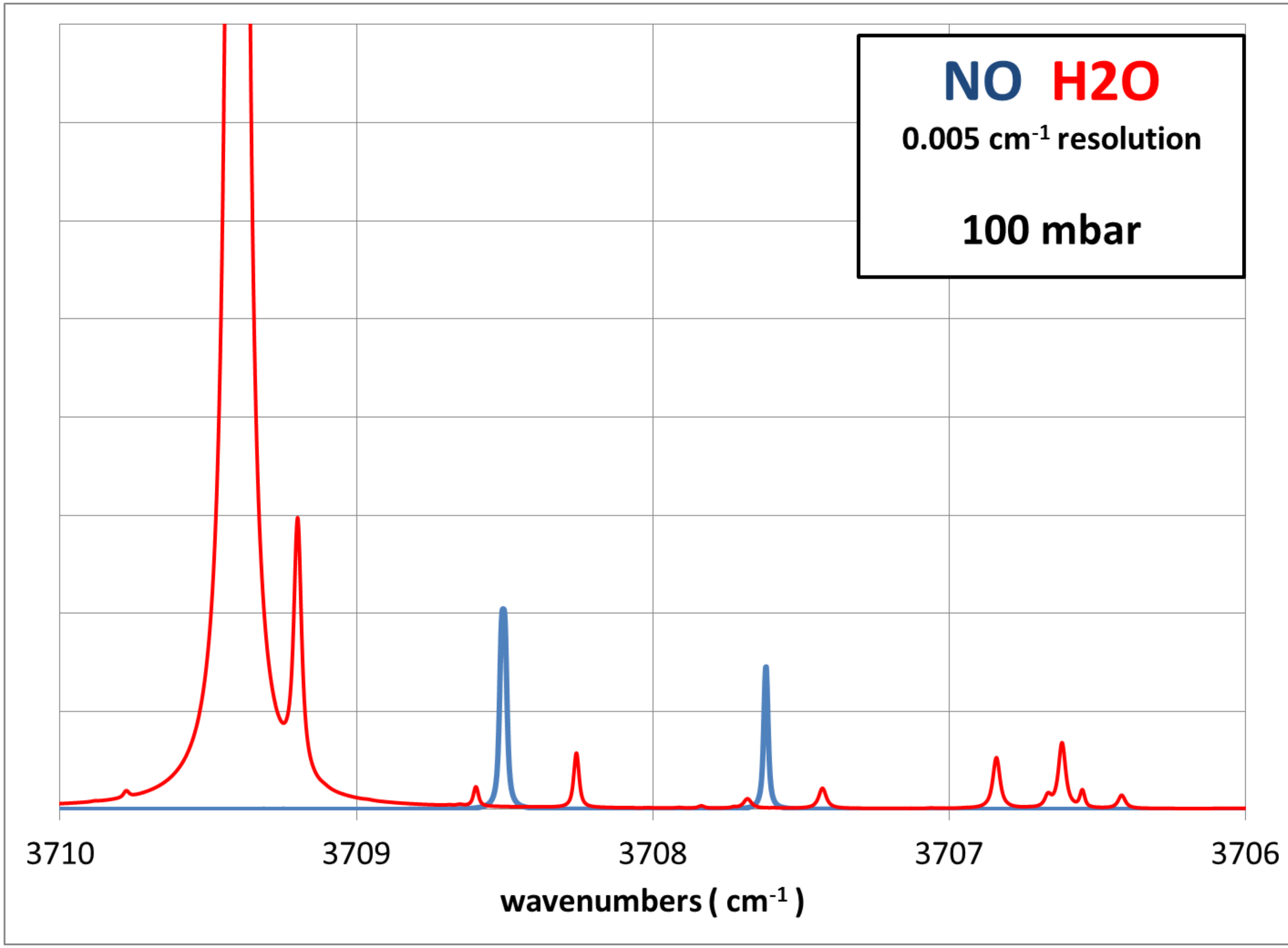

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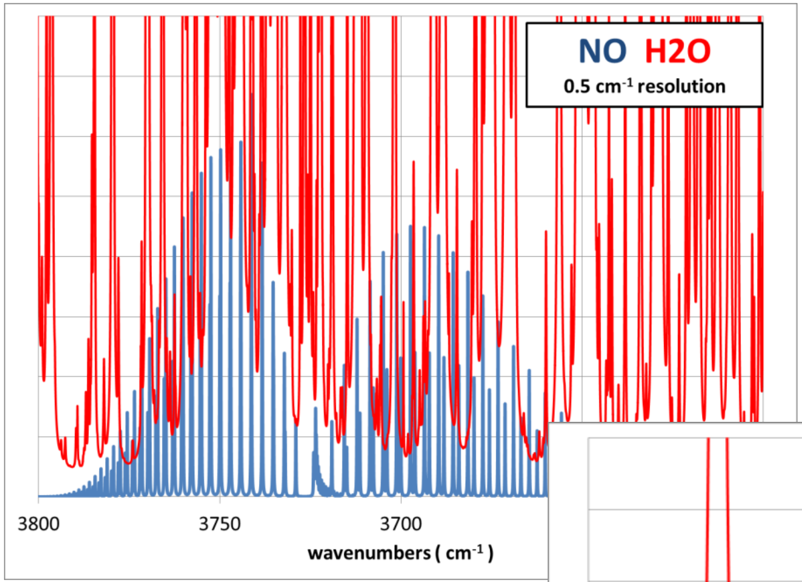
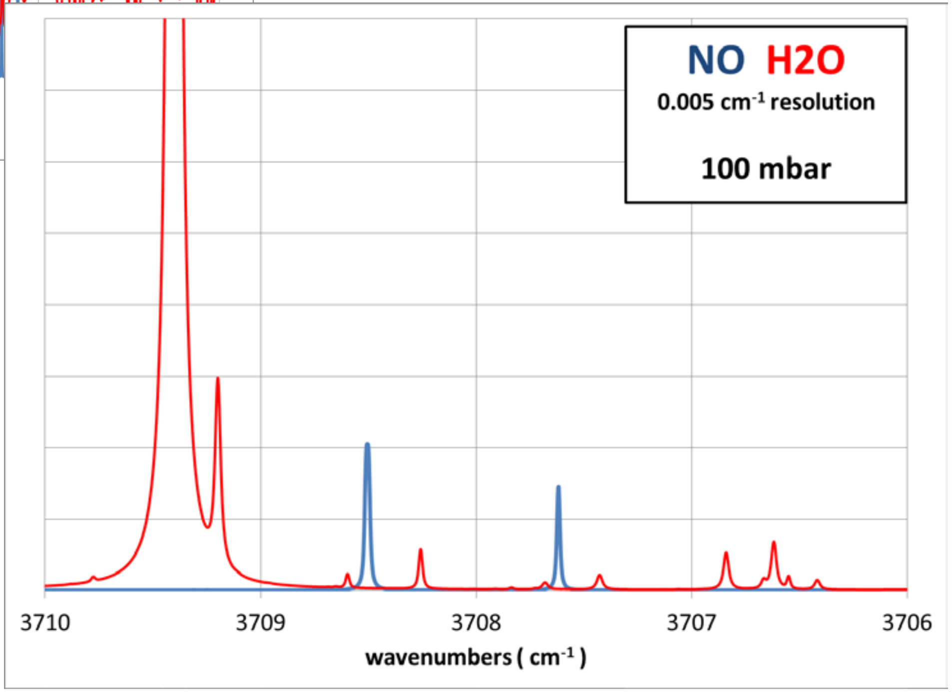


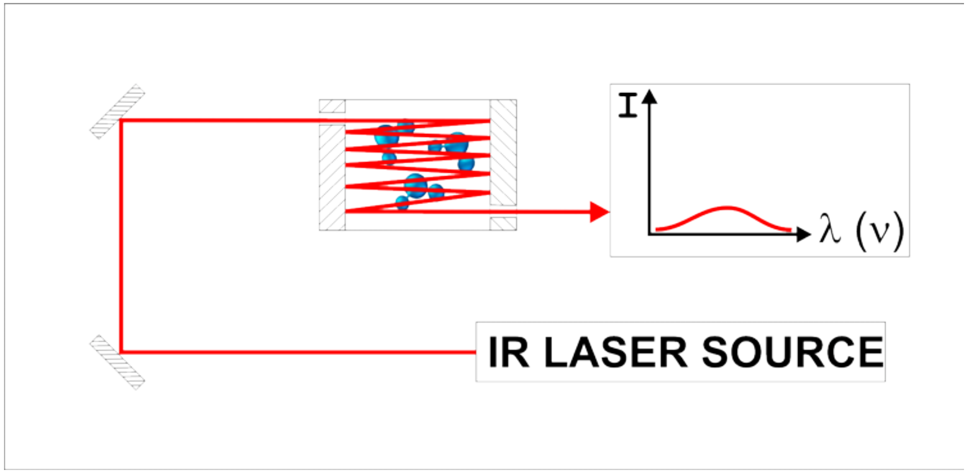
SOLUTION:

0.005 cm^{-1} Resolution

Low Absolute Pressure



PROBLEM: SENSITIVITY



SOLUTION 1:

Increase Signal

Standard Multipass Gas Cell
Mirror Reflectivity ~ 0.985

$$C = A / \ell . \varepsilon$$

Traditional Design:

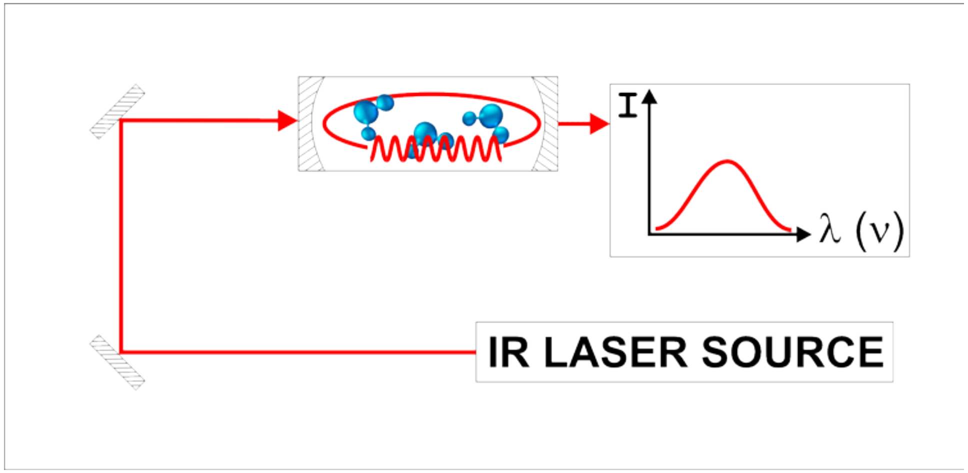
Multipass Gas Cell

Pathlength = ℓ_1 = 1 – 10 m

PROBLEM: SENSITIVITY

SOLUTION 1:

Increase Signal



Resonant Cavity Gas Cell
Mirror Reflectivity ~ 0.995 to 0.9995

$$C = A / \ell . \varepsilon$$

Sensitivity Improvement

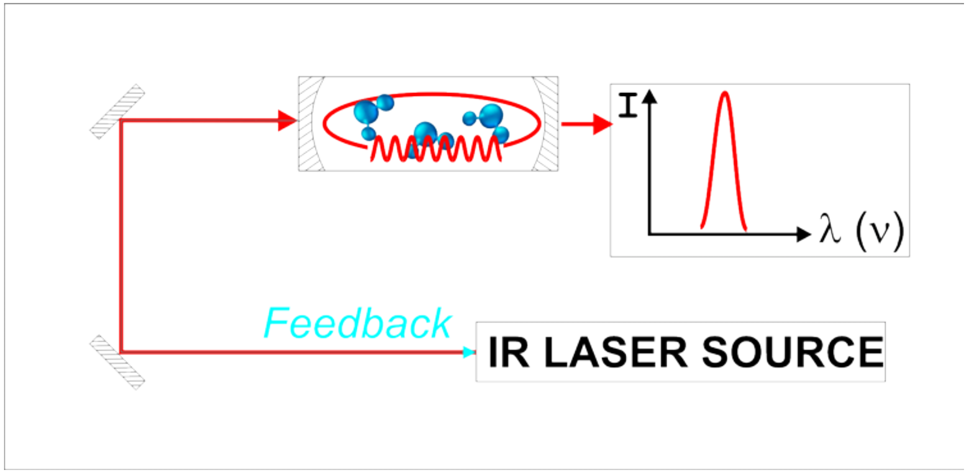
ℓ_2 / ℓ_1 = 1,000 X

<u>LASAR Design:</u>

Resonant Cavity Gas Cell

Pathlength = ℓ_2 = 1 – 20 km

PROBLEM: SENSITIVITY



SOLUTION 2:

Reduce Noise

Feedback enables increase of laser purity:

- Reduced Noise
  (single scan noise = 4.10^{-10} A.U.)
- Increased Signal Intensity
  (10X increase compared to laser alone)
- Improved Instrumental Response Linearity
  (4 orders of magnitude)

PROBLEM: SENSITIVITY

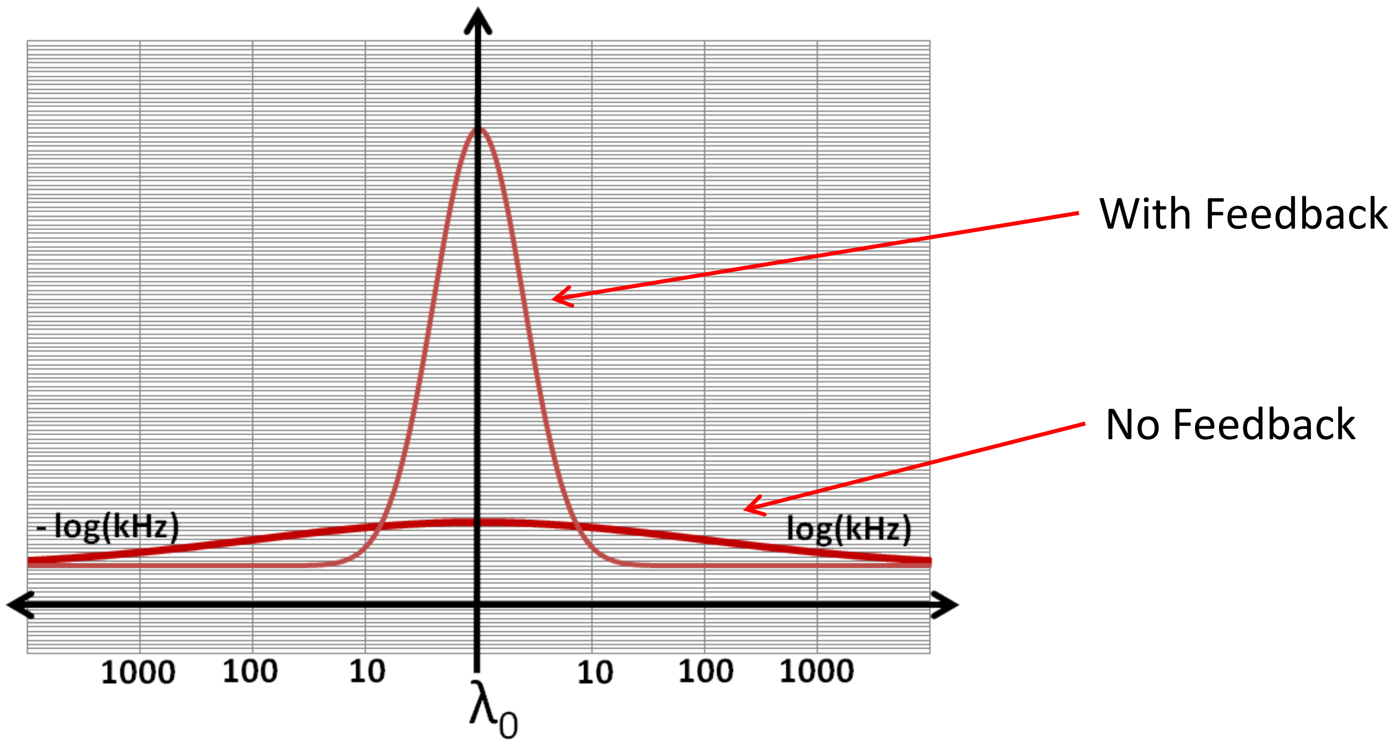
SOLUTION 2:

Reduce Noise

Laser output **with** feedback and **with** mode locking

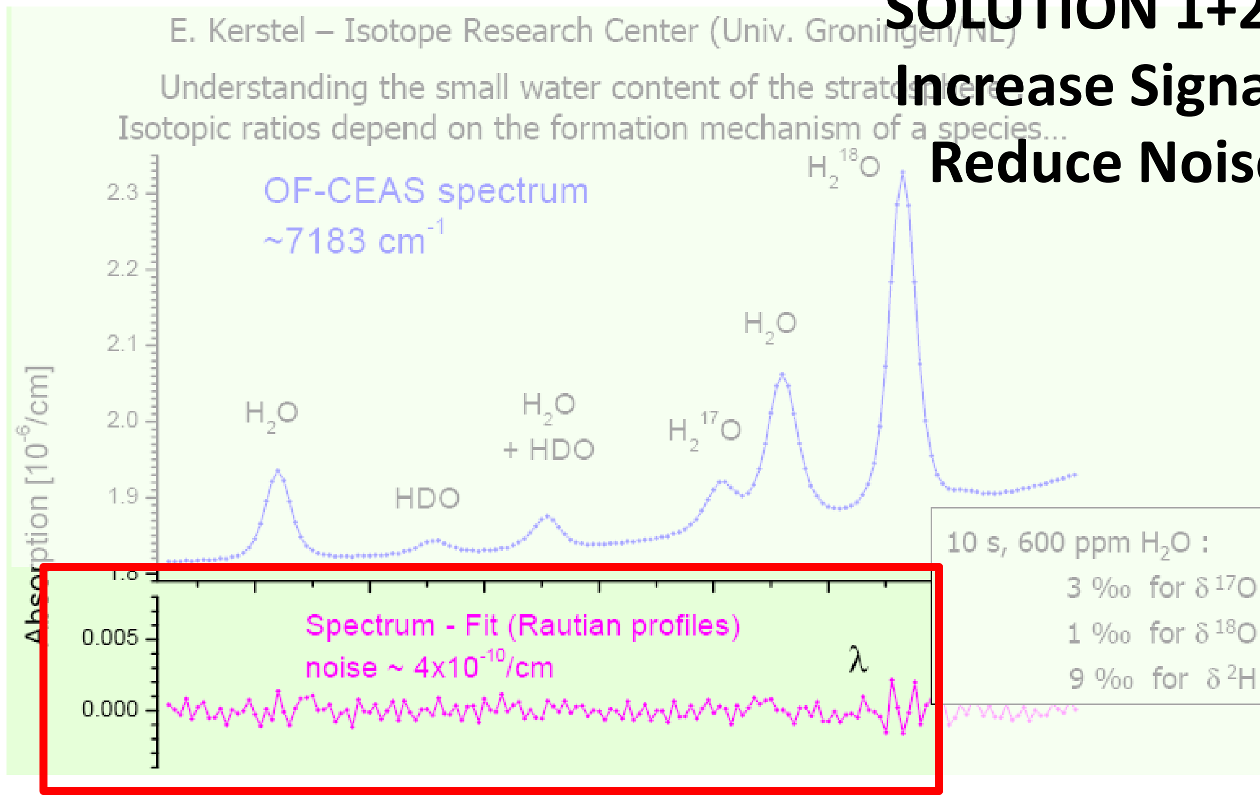
➪ **10 kHz bandwidth** (100X improvement)

➪ **10X signal intensity increase**



PROBLEM: SENSITIVITY

SOLUTION 1+2:
Increase Signal
Reduce Noise

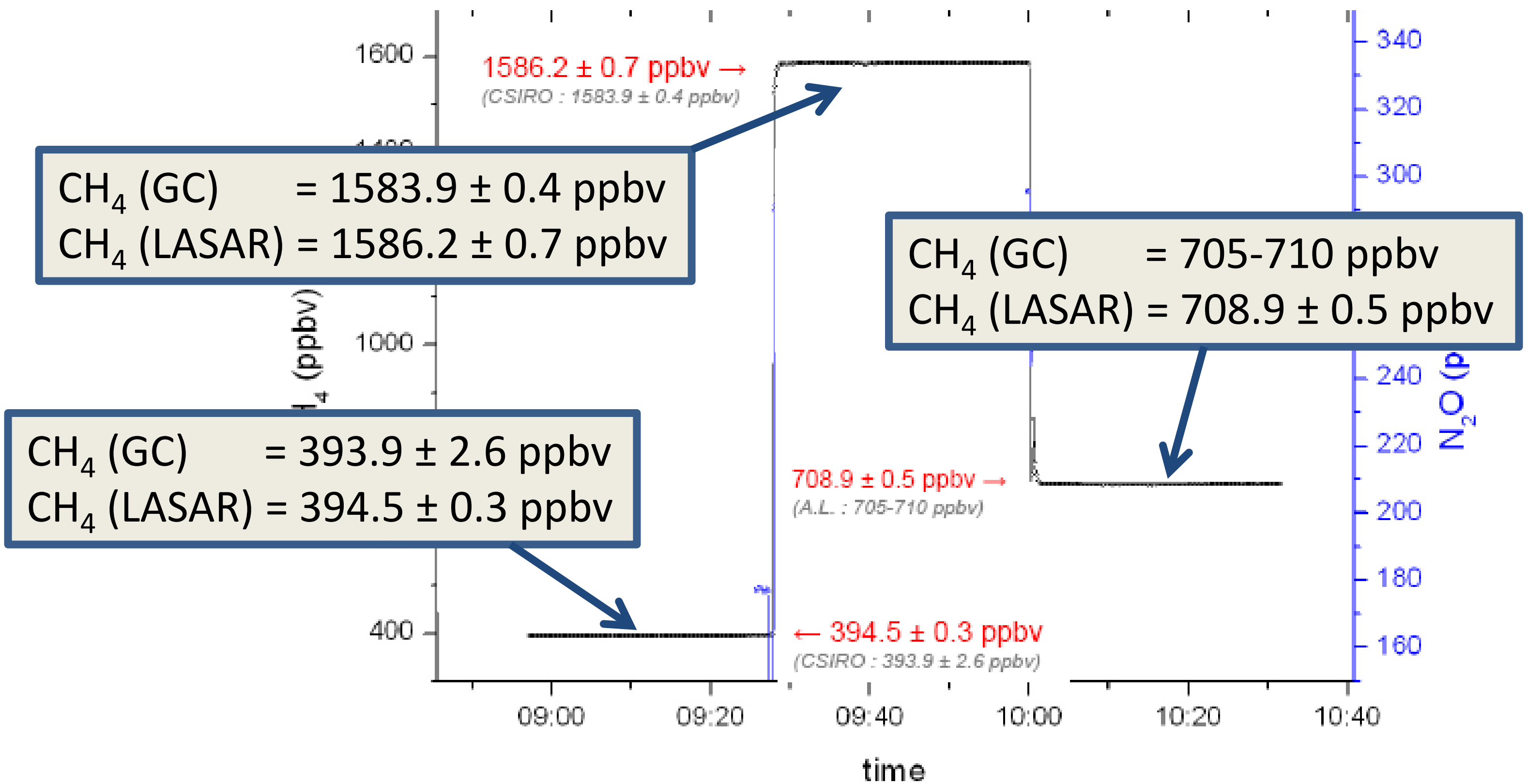


Experimental determination of spectrometer p2p noise

Kerstel E.R.T., Inannone R.Q., Chenevier M, Kassi S., Host H.J., Romanini D. “A Water Isotope (2H, 17O, 18O) Spectrometer Based on Optical Feedback Cavity-Enhanced Absorption for In-Situ Airborne Applications.” 2006, Appl. Phys. B., 85, pp. 397-406.

PROBLEM: SENSITIVITY

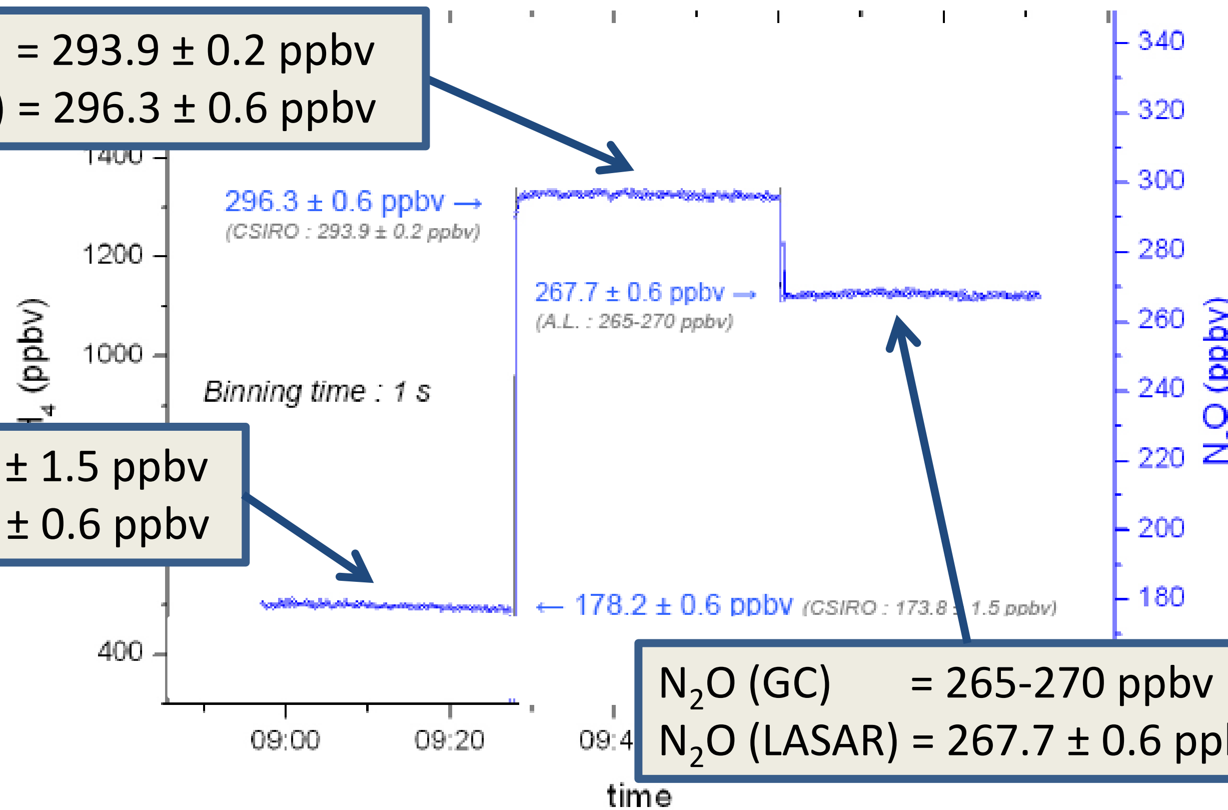
SOLUTIONS 1 + 2:
Increase Signal + Reduce Noise



SOLUTIONS 1 + 2:
Increase Signal + Reduce Noise

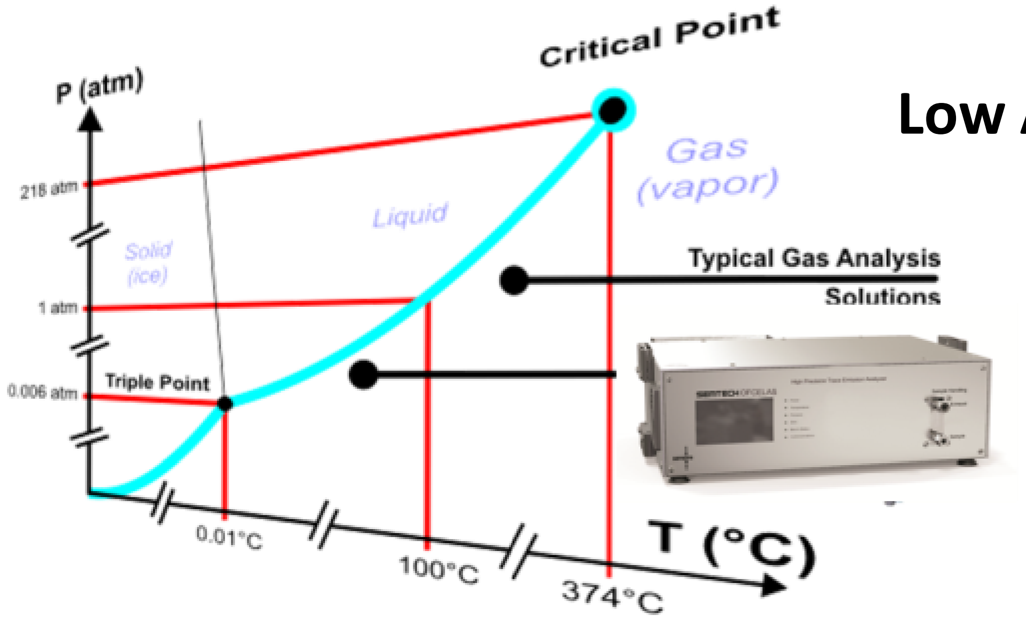
N_2O (GC) = 293.9 ± 0.2 ppbv
N_2O (LASAR) = 296.3 ± 0.6 ppbv

N_2O (GC) = 173.8 ± 1.5 ppbv
N_2O (LASAR) = 178.2 ± 0.6 ppbv



N_2O (GC) = 265-270 ppbv
N_2O (LASAR) = 267.7 ± 0.6 ppbv

PROBLEM: SAMPLING ACCURACY



SOLUTION:
Low Absolute Pressure In Sampling Line

$H_2O_{(g)}$ % vol.	Dew Point T°C @ 50 mbar
10 % vol.	- 2.73°C (27.1F)
20 % vol.	+ 6.96°C (44.5F)
30 % vol.	+13.01°C (55.4F)

No Sample Conditioning

No H2O Removal

No risk of removing H2O soluble molecules

PROBLEM: SAMPLING ACCURACY

Problem:

Sample

sample →

Chemical Reactions

$[NH_3] = x$

$[NH_3] = y$ (>< x)

Arrhenius equation gives the dependence of the rate constant *k* of chemical reactions on the temperature *T*

Reaction Coef. Rate
a.k.a. Rate Constant

Reaction activation energy

Temperature

$$k(T) = Z\rho . e^{Ea/RT}$$

Collision frequency

Steric factor

Gas constant

PROBLEM: SAMPLING ACCURACY

Problem: Sample **sample** → **Chemical Reactions**

[NH_3] = *x* **[NH_3] = *y* (>< *x*)**

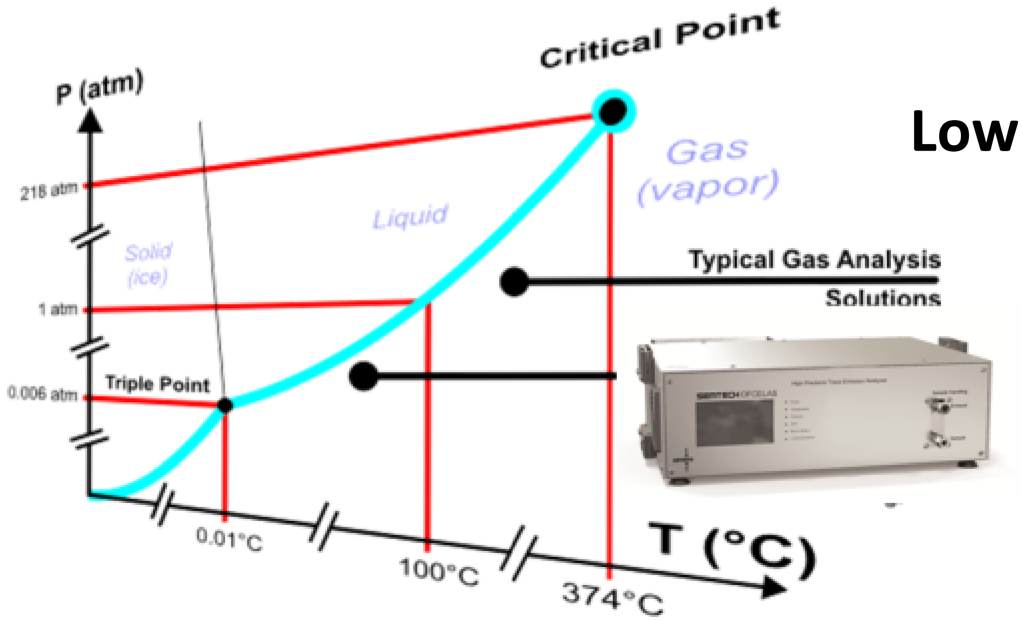
Detailing the collision frequency Z in Arrhenius equation gives the dependence of the rate constant *k* on concentration (N_A)

Collision frequency — Number of molecules / volume — Reaction cross section

$$Z = N_A \sigma_{AB} \cdot (8 k_B T / \pi \mu_{AB})^{1/2}$$

Boltzmann's constant — Temperature — Reduced mass of the reactants (A and B)

PROBLEM: SAMPLING ACCURACY

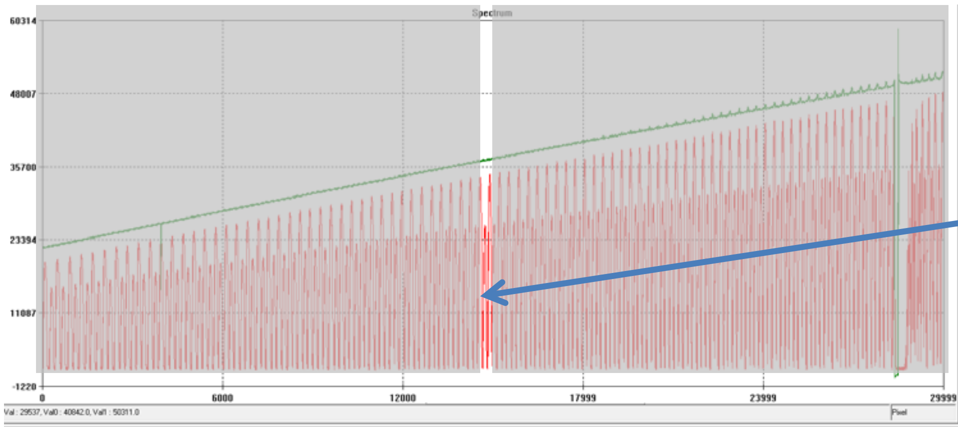


SOLUTION:
Low Absolute Pressure
In Sampling Line

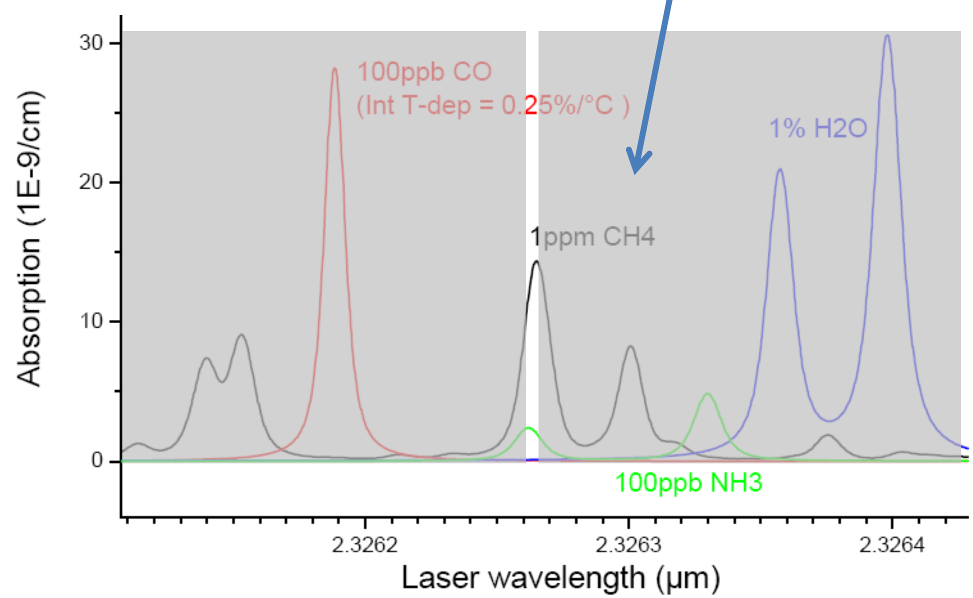
No Sample Conditioning Errors

Reduced Chemical Reactions in Sampling Line

PROBLEM: MULTIGAS CAPABILITIES

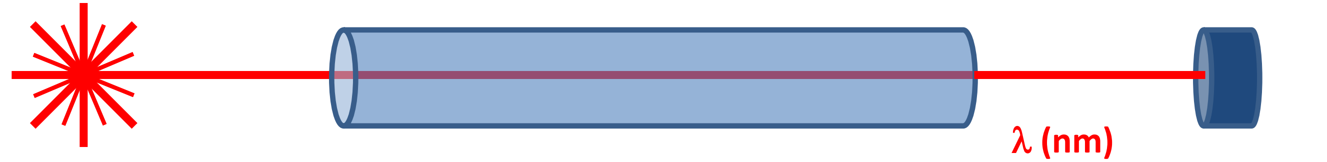


Spectral Range Observed
With DFB Laser and
Resonant Cavity

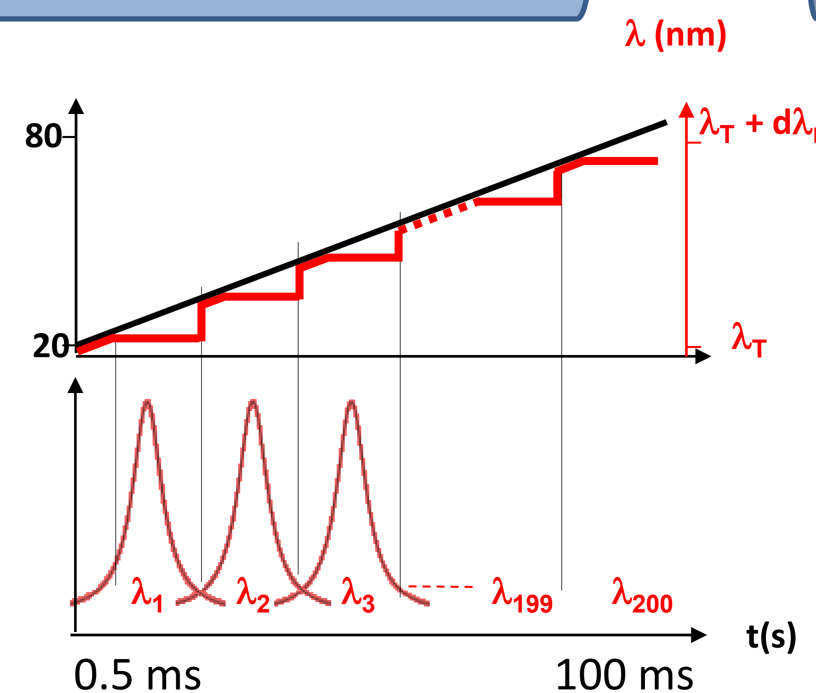


PROBLEM: MULTIGAS CAPABILITIES

SOLUTION:
Scanning Laser

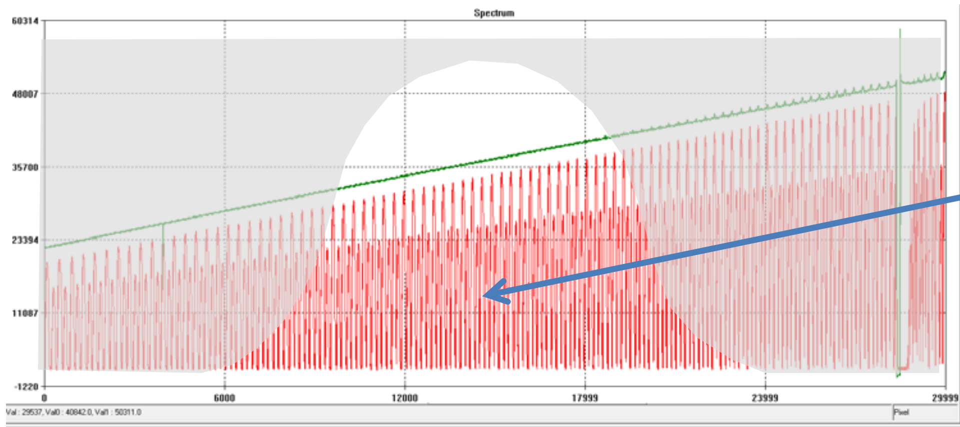


Scanning
200 Wavelengths
Every 100 MilliSec.

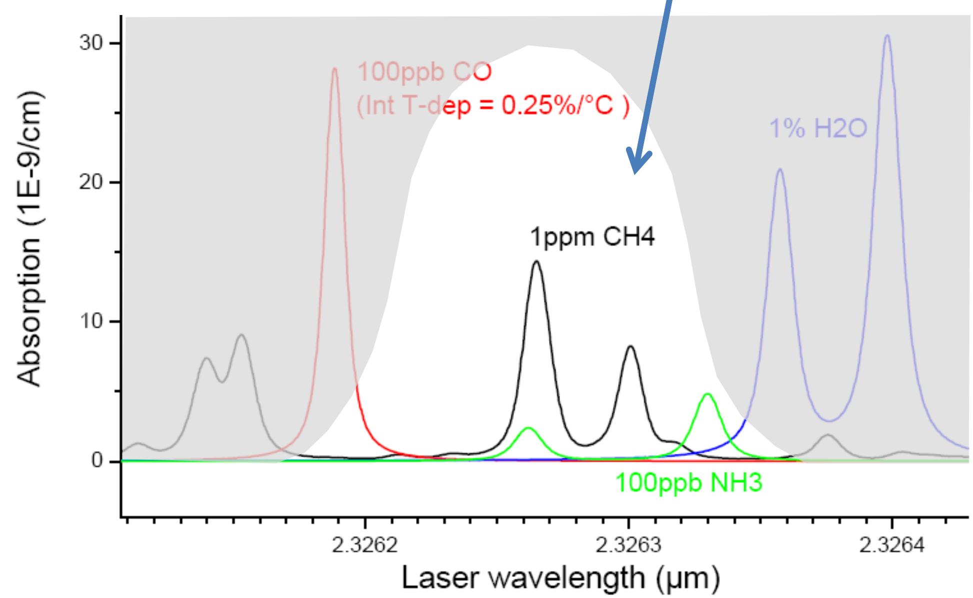


PROBLEM: MULTIGAS CAPABILITIES

SOLUTION:
Scanning Laser

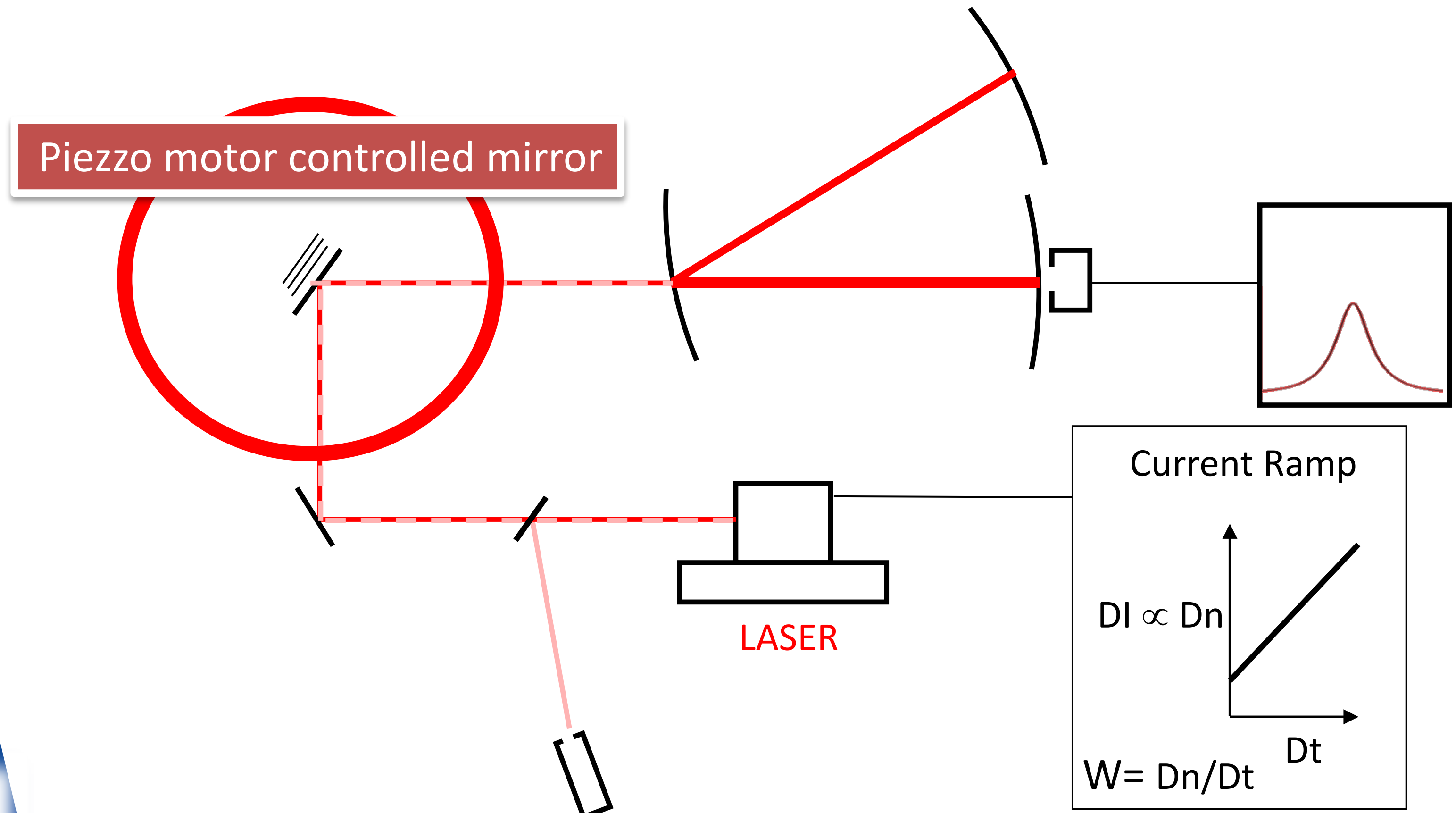


Spectral Range Observed
With Scanning DFB Laser
And Resonant Cavity



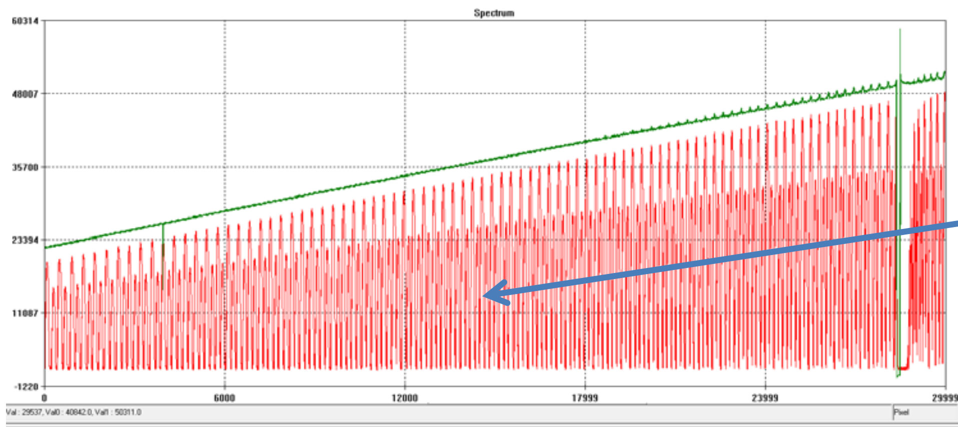
PROBLEM: MULTIGAS CAPABILITIES

SOLUTION:
Phase Modulated
Feedback Scanning Laser

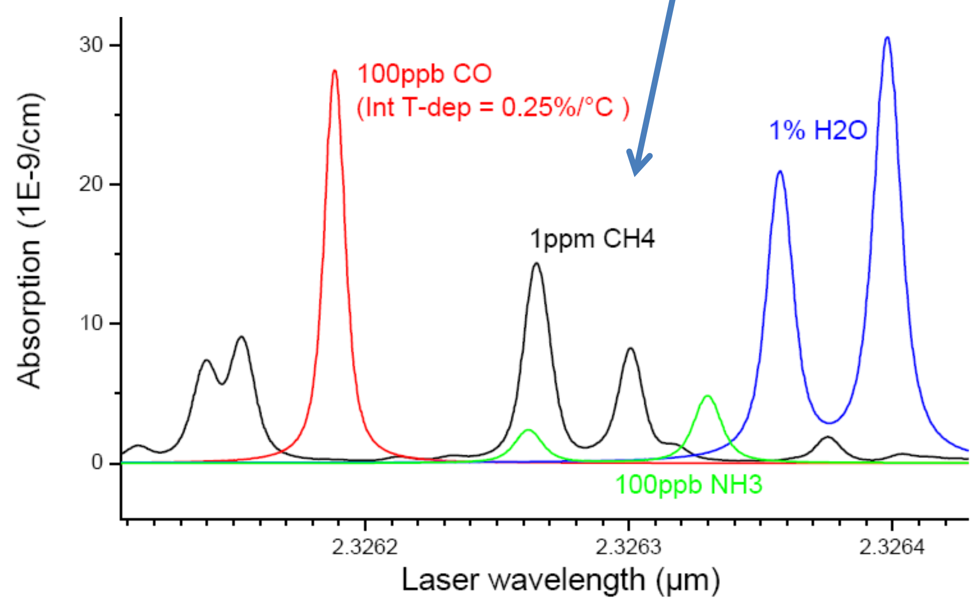


PROBLEM: MULTIGAS CAPABILITIES

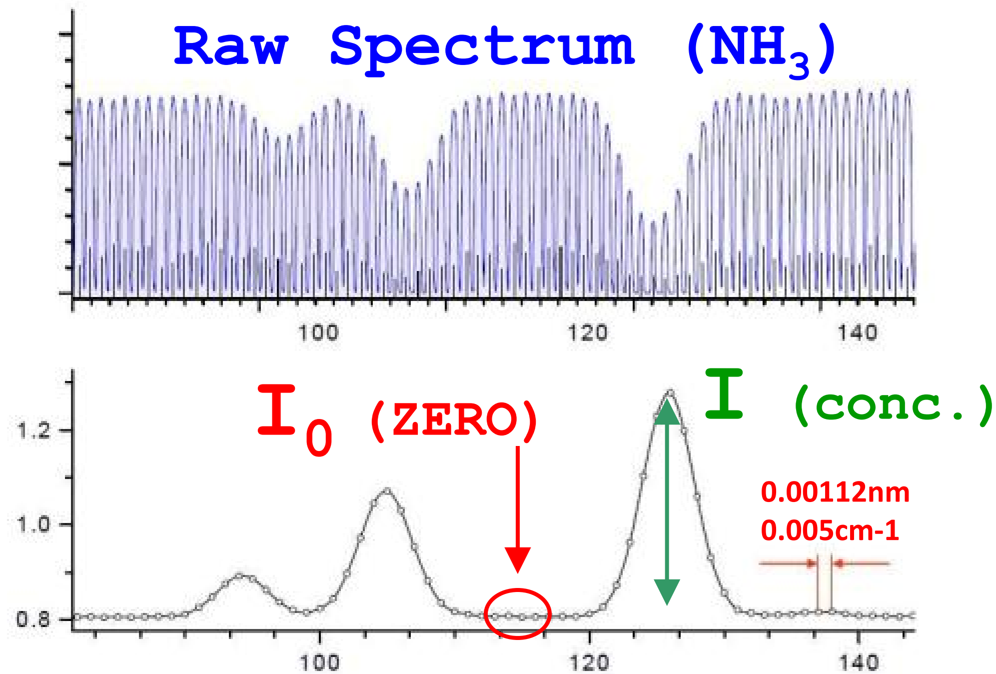
SOLUTION: Phase Modulated Feedback Scanning Laser



Spectral Range Observed
With Scanning
Phase modulated
Feedback DFB Laser
And Resonant Cavity



SOLUTION: Phase Modulated Feedback Scanning Laser



$$\text{Abs.} = I - I_0$$

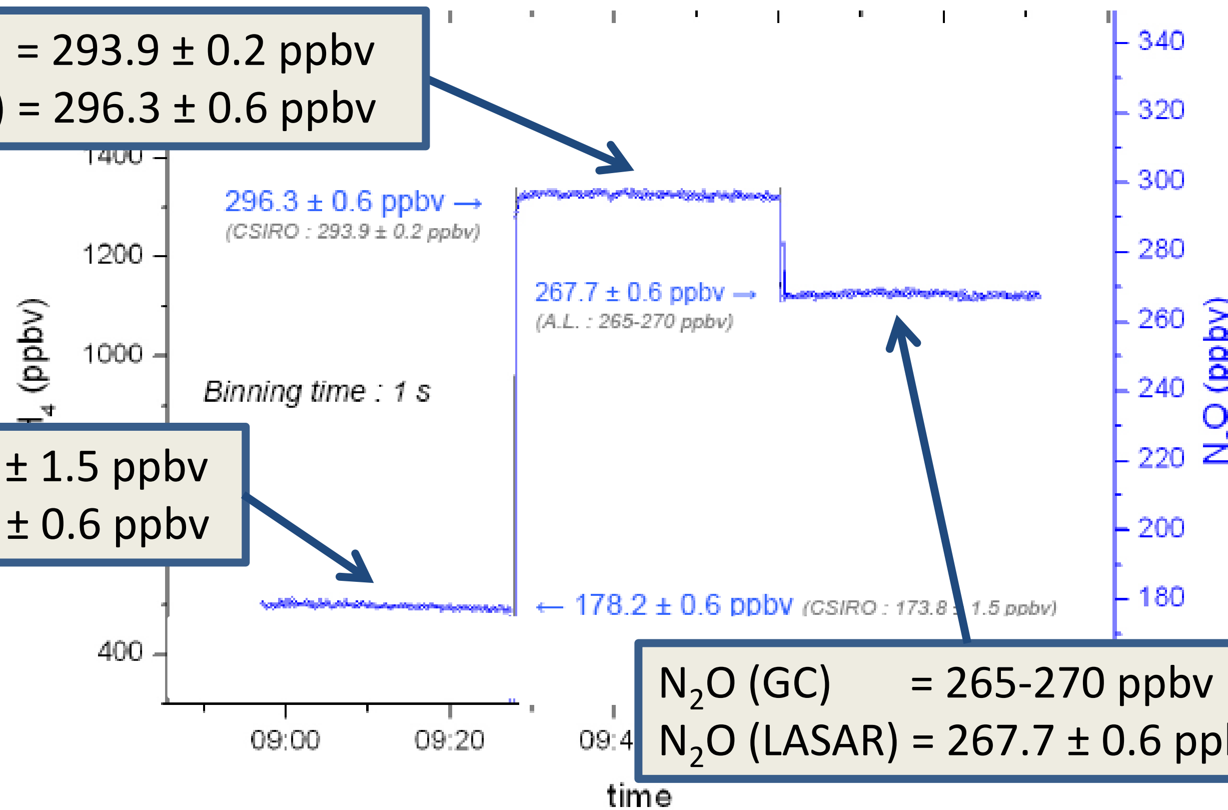
Added Benefit:

AUTO-ZERO (SELF-REFERENCING) EVERY 100 msec.

PROPOSED SOLUTION FOR N2O MEASUREMENT

Accuracy

N_2O (GC) = 293.9 ± 0.2 ppbv
N_2O (LASAR) = 296.3 ± 0.6 ppbv

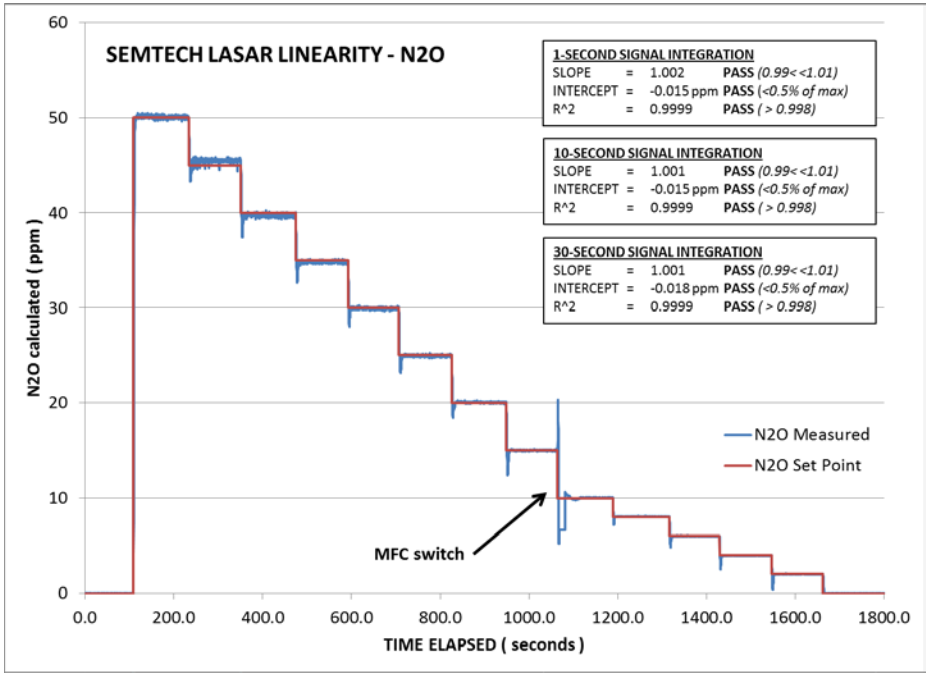


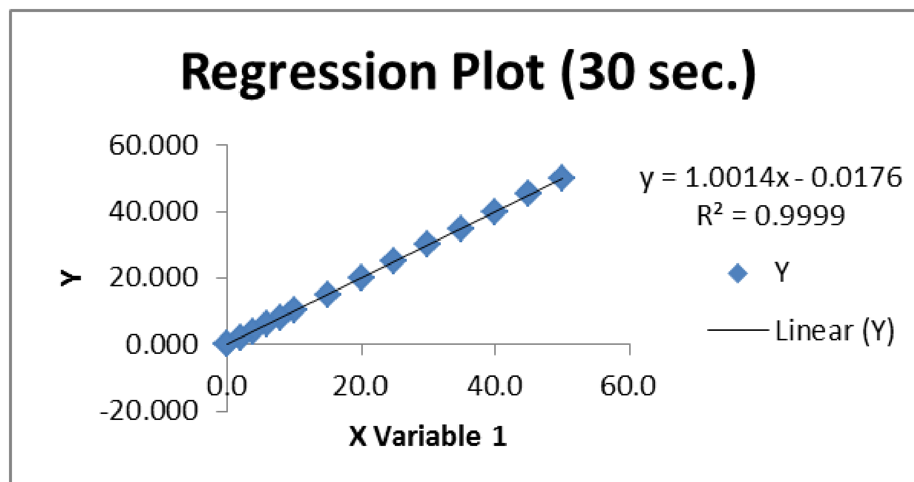
N_2O (GC) = 173.8 ± 1.5 ppbv
N_2O (LASAR) = 178.2 ± 0.6 ppbv

N_2O (GC) = 265-270 ppbv
N_2O (LASAR) = 267.7 ± 0.6 ppbv

PROPOSED SOLUTION FOR N_2O MEASUREMENT

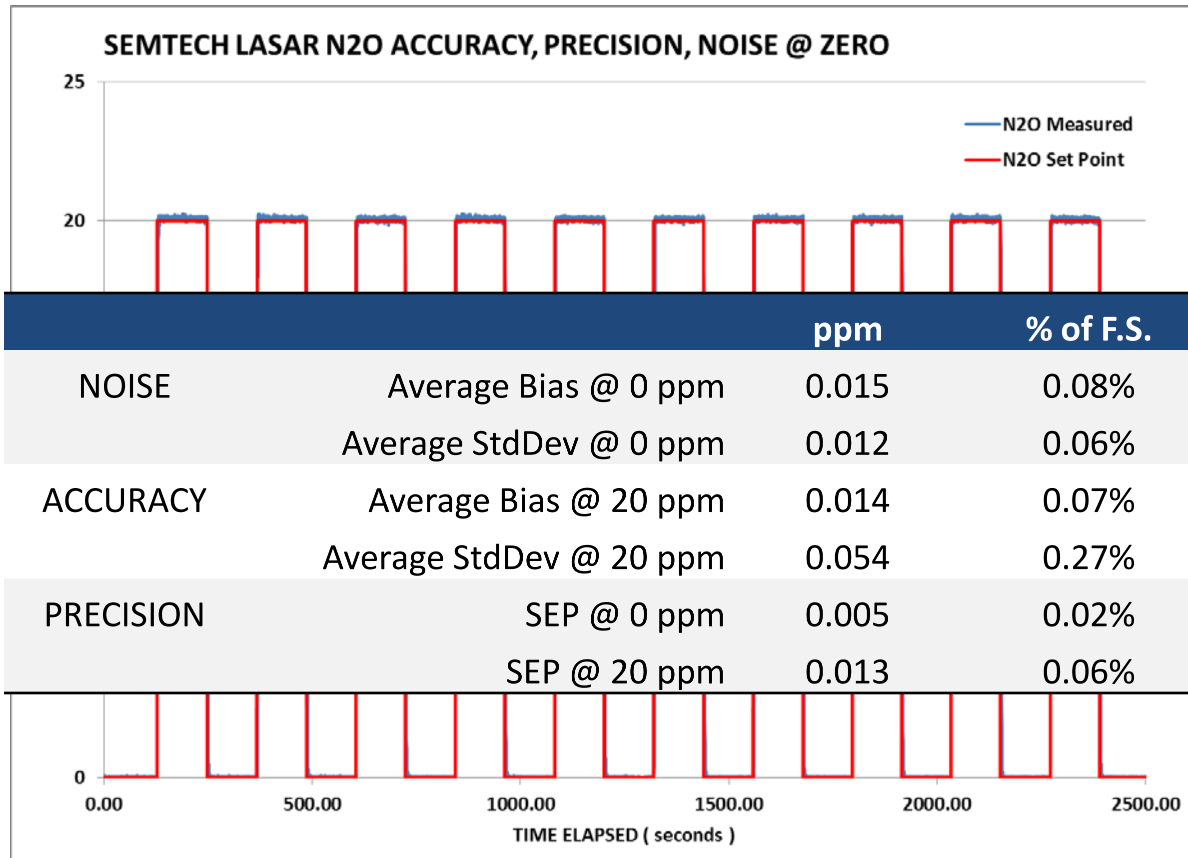
N_2O Linearity





PROPOSED SOLUTION FOR N_2O MEASUREMENT

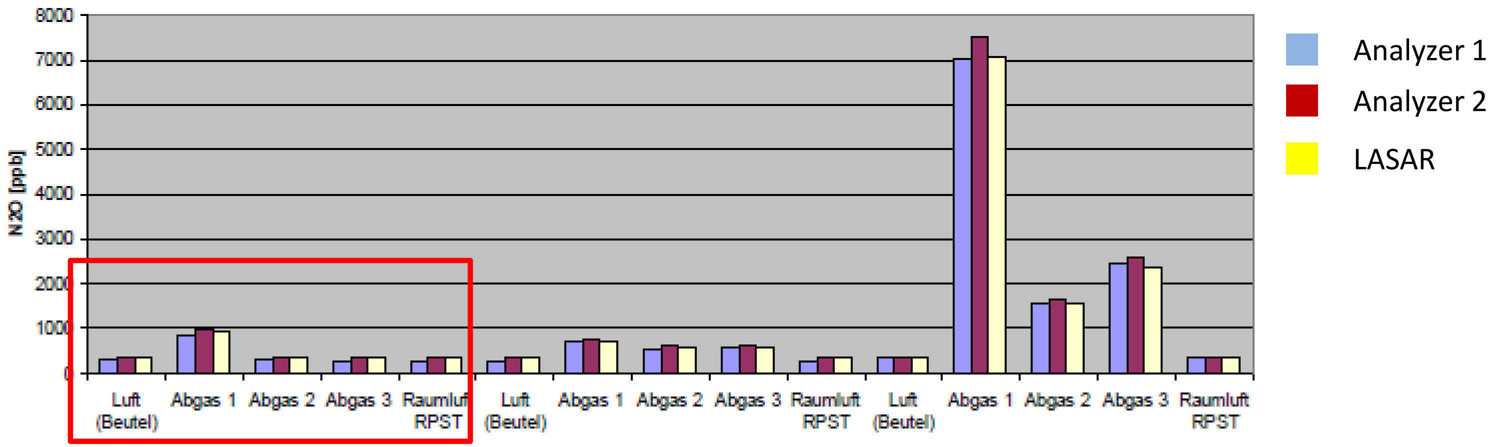
N_2O Precision Accuracy Noise @ Zero



		ppm	% of F.S.
NOISE	Average Bias @ 0 ppm	0.015	0.08%
	Average StdDev @ 0 ppm	0.012	0.06%
ACCURACY	Average Bias @ 20 ppm	0.014	0.07%
	Average StdDev @ 20 ppm	0.054	0.27%
PRECISION	SEP @ 0 ppm	0.005	0.02%
	SEP @ 20 ppm	0.013	0.06%

PROPOSED SOLUTION FOR N_2O MEASUREMENT

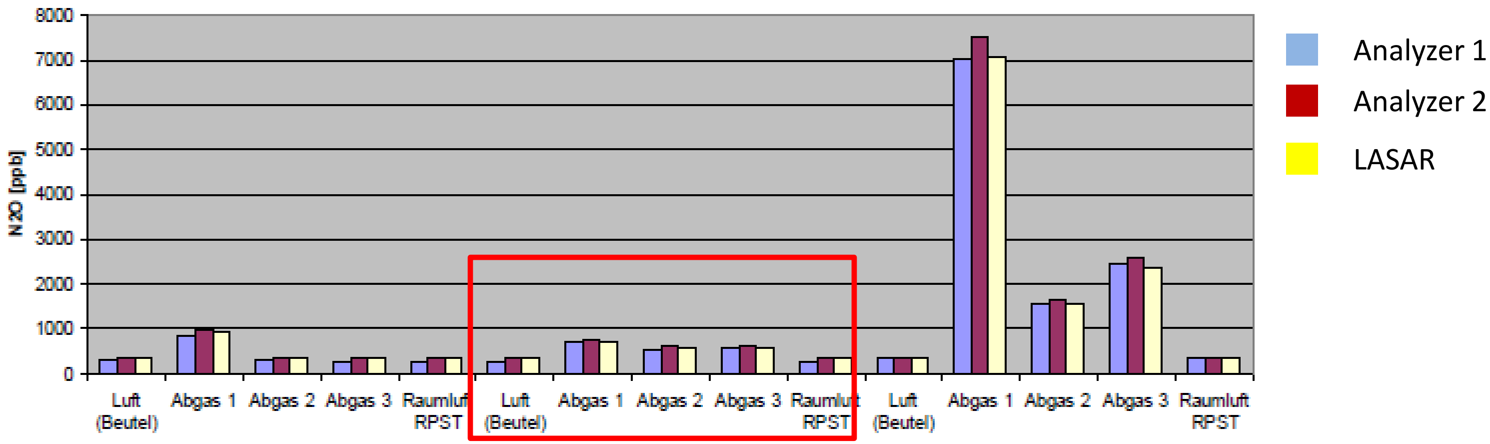
N_2O Reproducibility / Stability



	Analyzer 1 N2O [ppb]	Analyzer 2 N2O [ppb]	SEMTECH LASAR N2O [ppb]
Luft (Beutel)	300	370	340
Abgas 1	820	970	940
Abgas 2	300	350	330
Abgas 3	290	345	330
Raumluft RPST	250	370	330
Average	275	370	335
Std Dev.	35	0	7
Expected	330	330	330

PROPOSED SOLUTION FOR N_2O MEASUREMENT

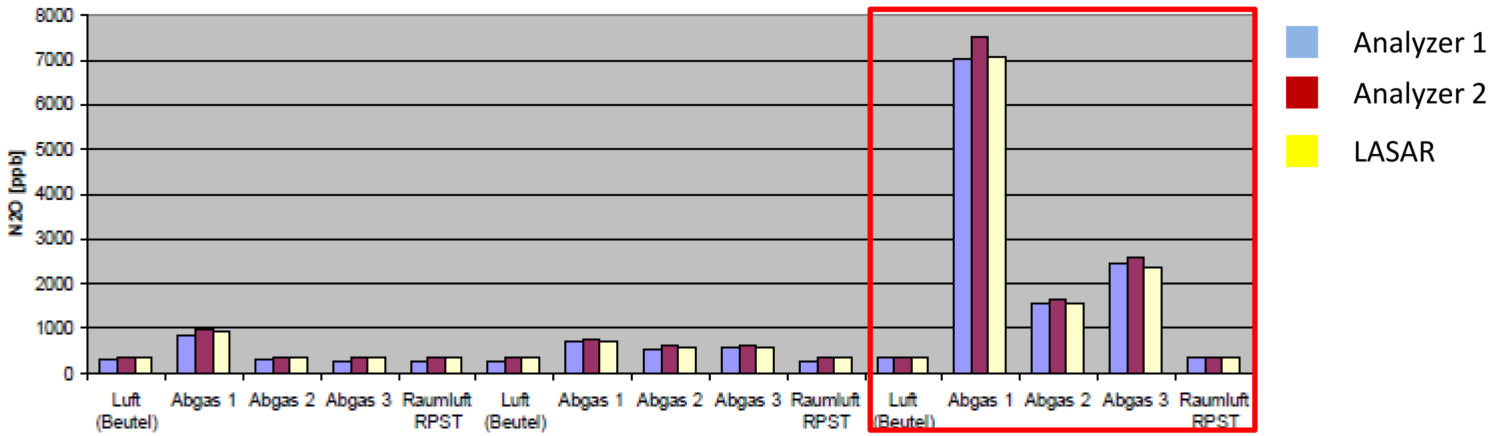
N_2O Reproducibility / Stability



	Analyzer 1 N2O [ppb]	Analyzer 2 N2O [ppb]	SEMTECH LASAR N2O [ppb]
Luft (Beutel)	290	380	350
Abgas 1	690	765	720
Abgas 2	550	620	570
Abgas 3	570	650	590
Raumluft RPST	260	365	350
Average	275	373	350
Std Dev.	21	11	0
Expected	330	330	330

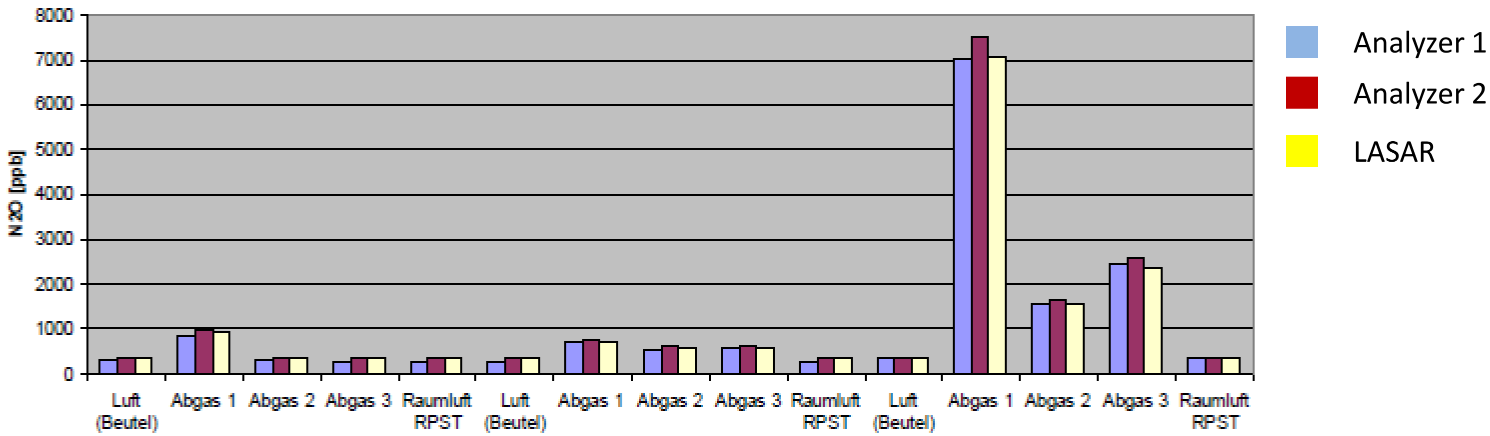
PROPOSED SOLUTION FOR N_2O MEASUREMENT

N_2O Reproducibility / Stability



	Analyzer 1 N2O [ppb]	Analyzer 2 N2O [ppb]	SEMTECH LASAR N2O [ppb]
Luft (Beutel)	350	360	330
Abgas 1	7010	7520	7080
Abgas 2	1570	1660	1560
Abgas 3	2440	2560	2350
Raumluft RPST	330	370	330
Average	340	365	330
Std Dev.	14	7	0
Expected	330	330	330

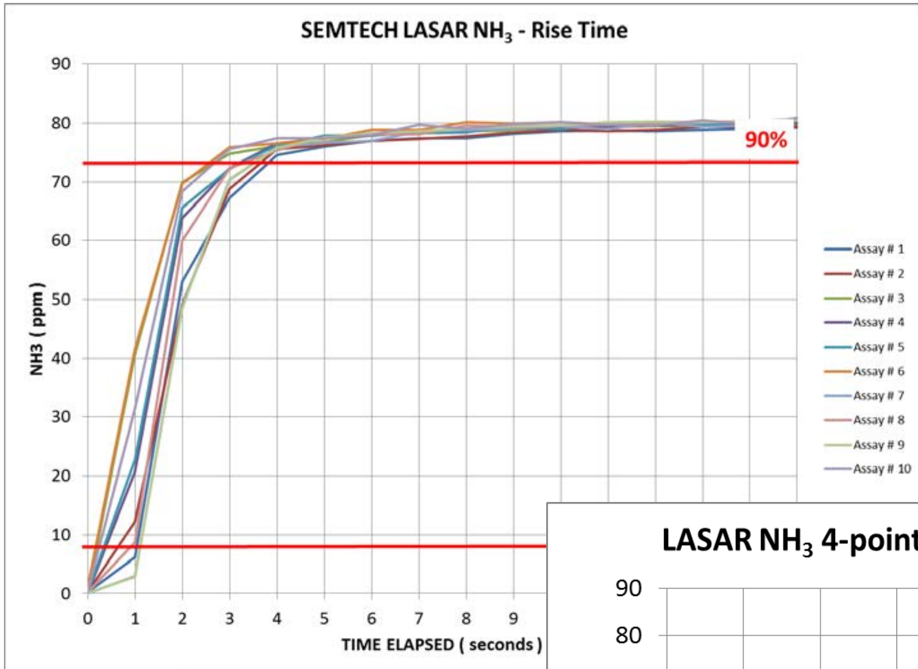
N_2O Reproducibility / Stability



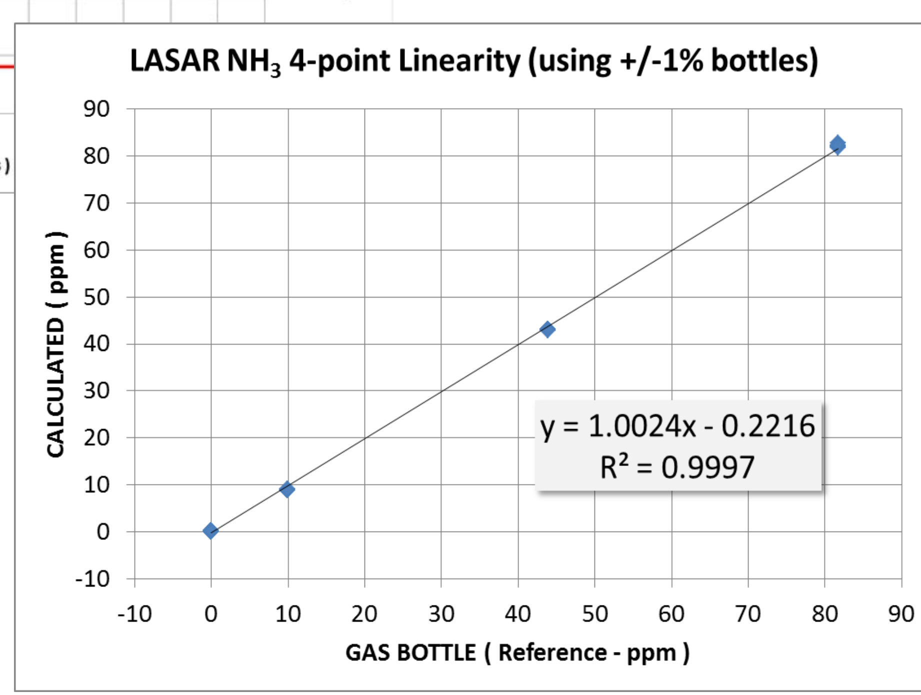
	Analyzer 1 N2O [ppb]	Analyzer 2 N2O [ppb]	SEMTECH LASAR N2O [ppb]
Average	297	369	338
Std. Dev.	39	7	10
Expected	330	330	330

PROPOSED SOLUTION FOR NH_3 MEASUREMENT

NH_3 Rise Time

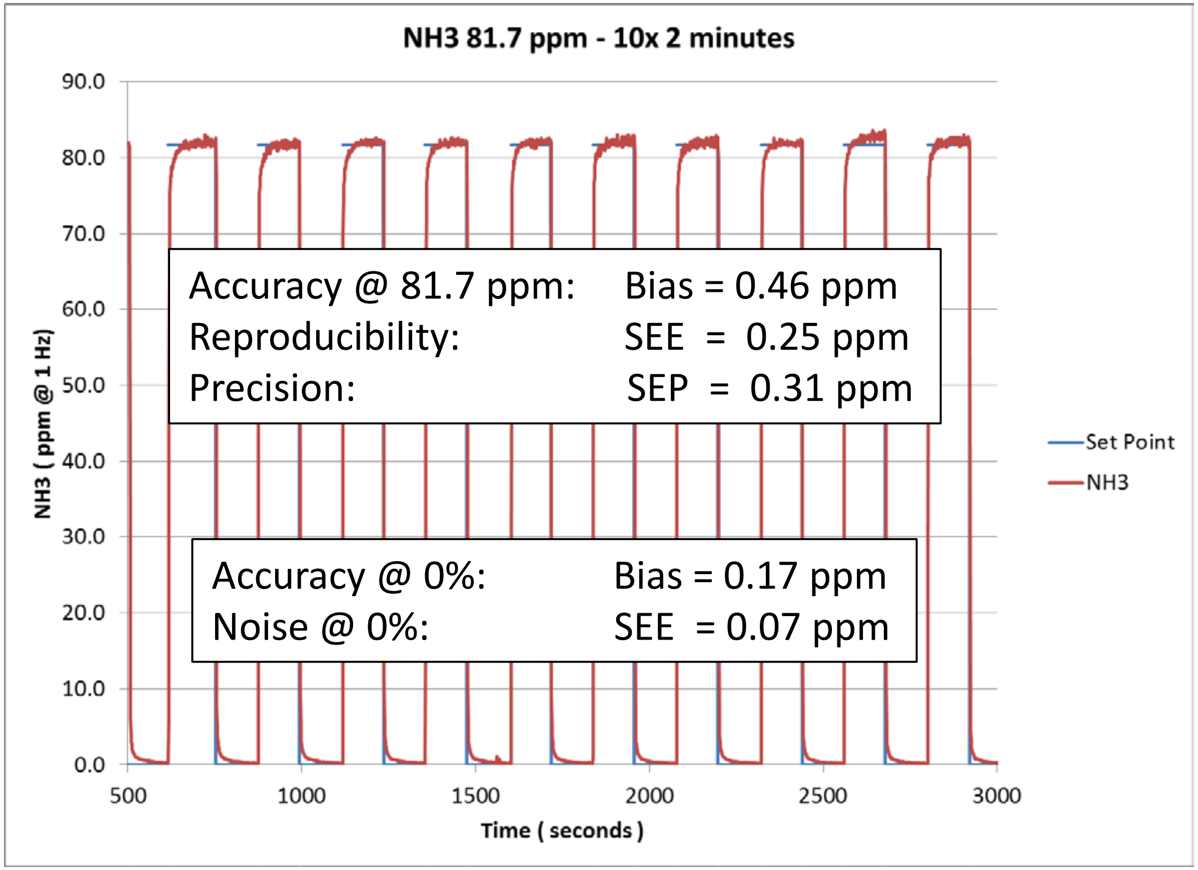


NH_3 Linearity



PROPOSED SOLUTION FOR NH_3 MEASUREMENT

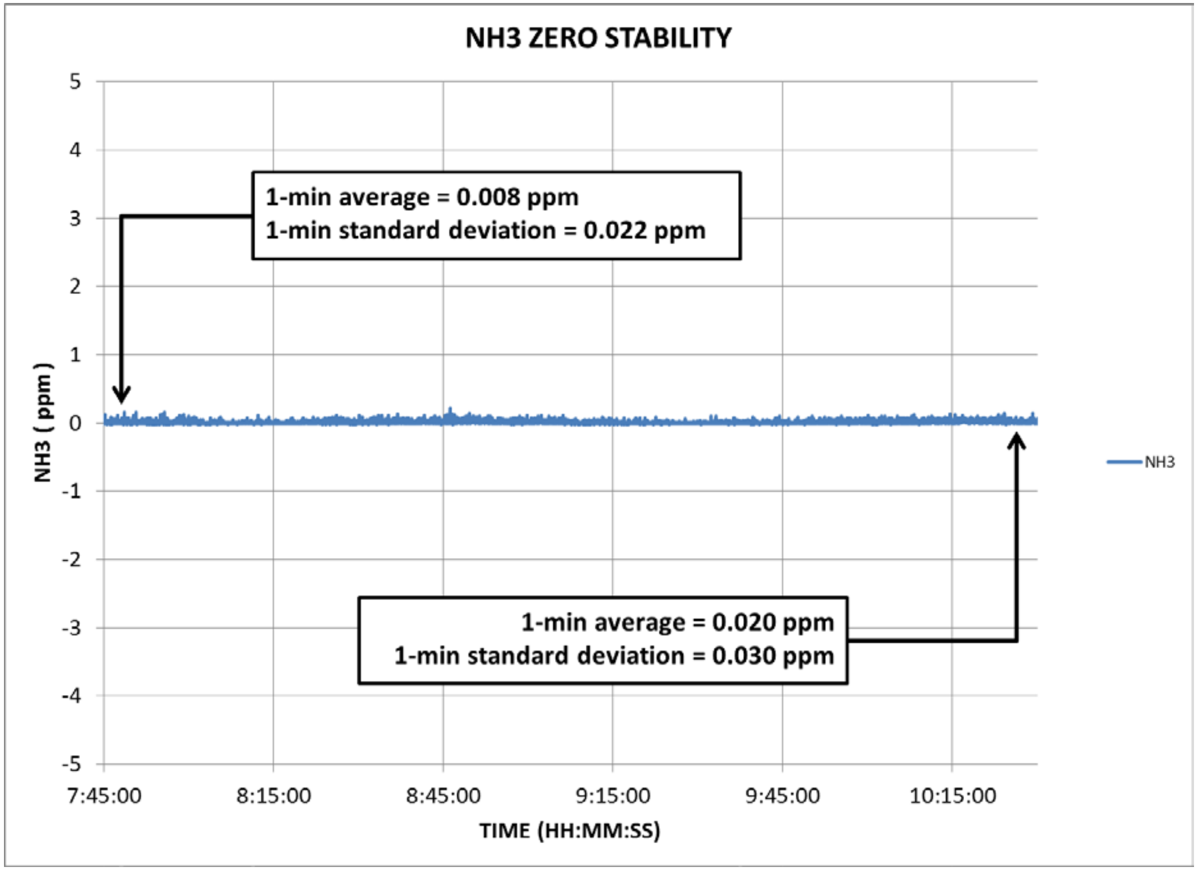
NH_3 Precision
(0-1000 ppm calibration)



PROPOSED SOLUTION FOR NH_3 MEASUREMENT

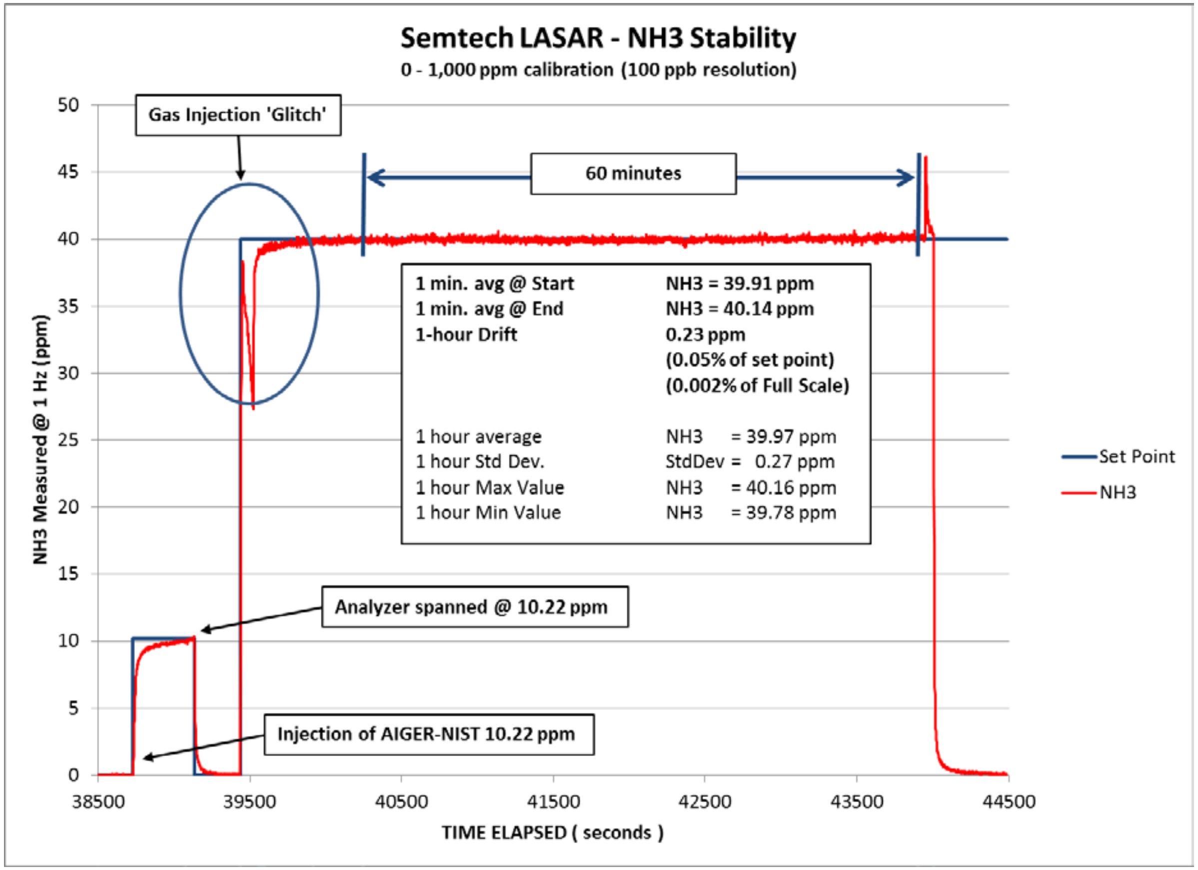
NH_3 Zero Drift

(0-1000 ppm calibration)



PROPOSED SOLUTION FOR NH_3 MEASUREMENT

NH_3 Span Drift
(0-1000 ppm calibration)



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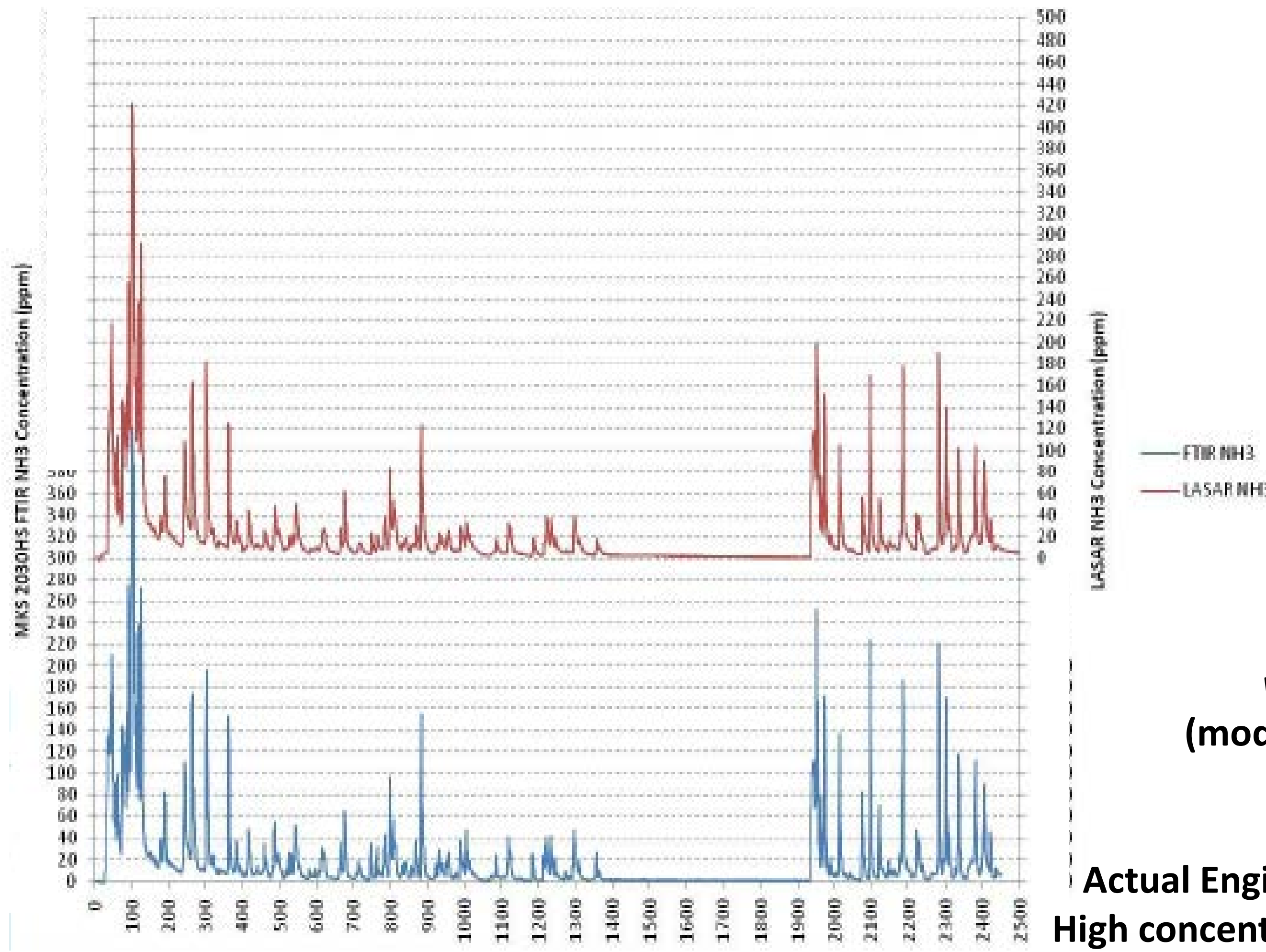
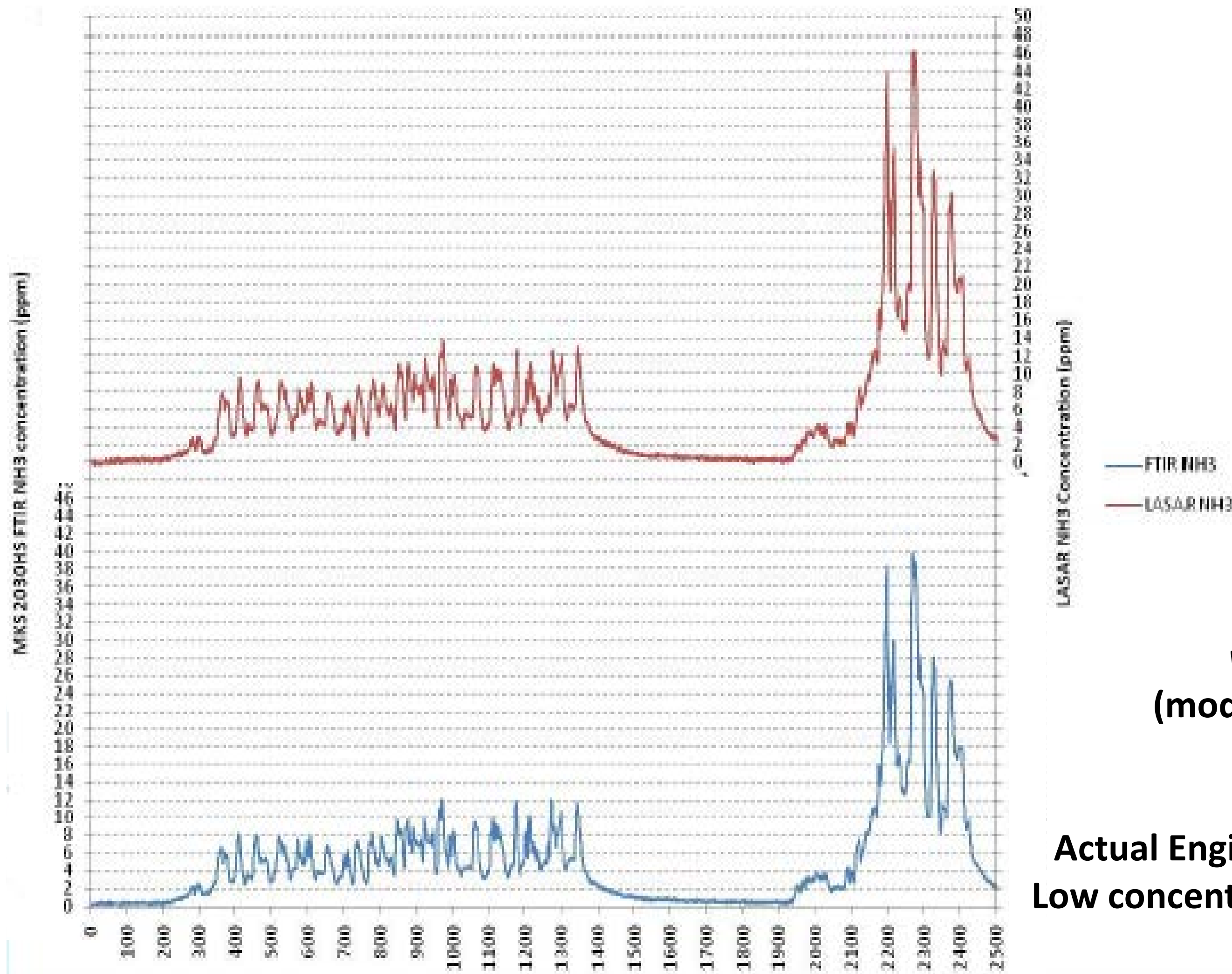


LASAR
***vs.* FTIR**
(modal raw)

NH_3
Actual Engine Test
High concentrations

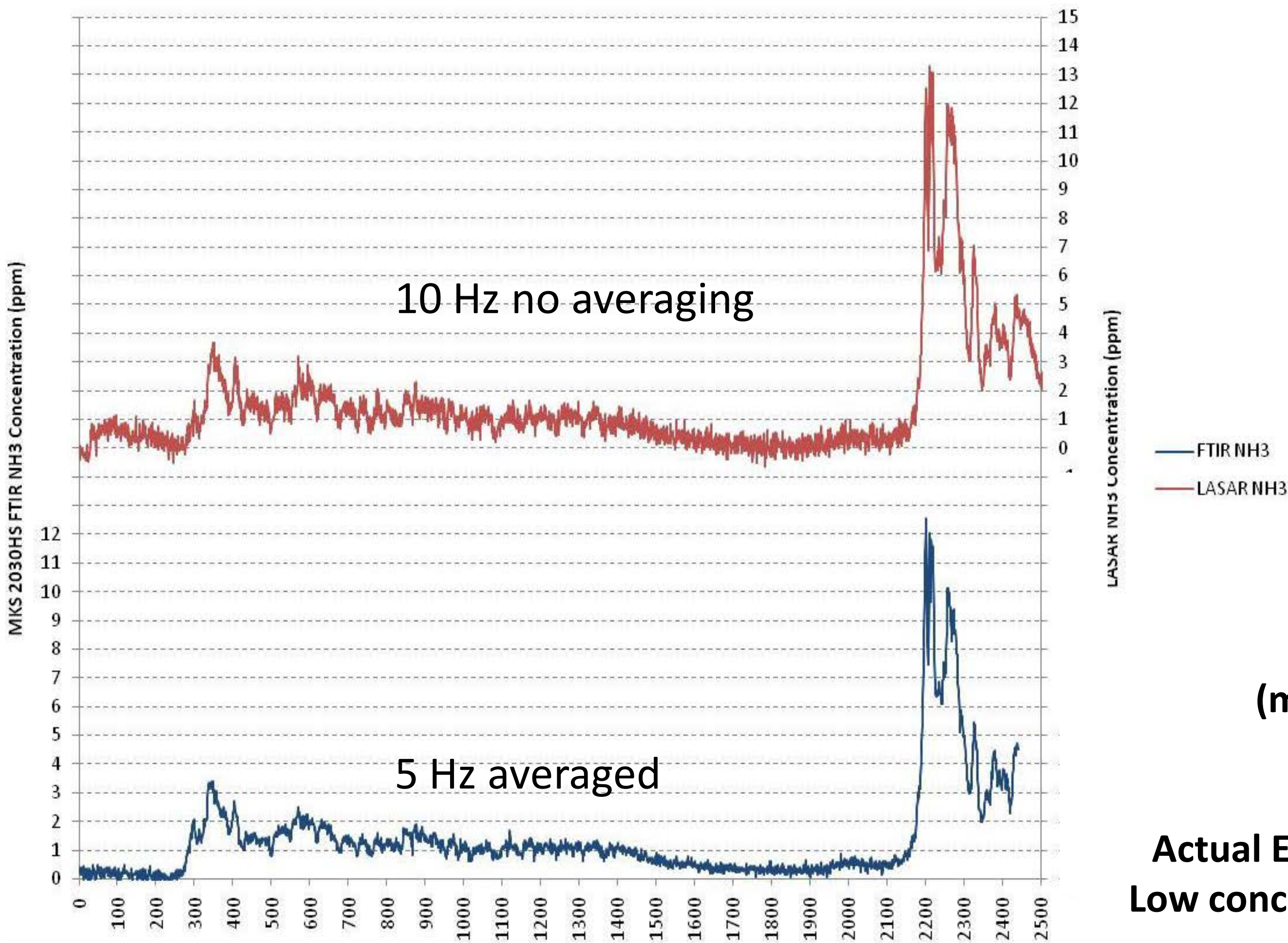
PROPOSED SOLUTION FOR NH_3 MEASUREMENT



LASAR
***vs*. FTIR**
(modal raw)

NH_3
Actual Engine Test
Low concentrations

PROPOSED SOLUTION FOR NH_3 MEASUREMENT



LASAR
***vs.* FTIR**
(modal raw)

NH_3
Actual Engine Test
Low concentrations

CONCLUSIONS

Spectroscopic Interferences

- 0.005 cm-1 resolution
- Low Pressure Spectroscopy

Spectroscopic Sensitivity

- Increase signal (pathlength)
- Reduce Noise (optical feedback)

Sampling Accuracy

- No sample conditioning errors
- Reduced chemical reactions rates in sampling line.

Multiple Gases

- Scanning laser with phase modulation for extended wavelength range.

CONCLUSIONS

N_2O Measurement

- Linearity
- Accuracy
- Precision
- Reproducibility / Stability

NH_3 measurement

- Fast rise time
- Linearity
- Accuracy
- Precision
- Reproducibility
- Zero and Span Drift
- Matching FTIR (time domain)