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Calibration strategies for cavity ring-down spectroscopy

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HIGHGAS Stakeholder Workshop
November 14th, 2014

Greenhouse Gas instruments

Greenhouse Gas Analyzer CO_2, CH_4, H_2O
The World's Gold Standard

CO, CO_2, CH_4 and H_2O
Precisely One Instrument

CRDS Analyzer CO_2 CH_4 H_2O Measurements in Air
Model G2301

The world's highest precision analyzer for the top three greenhouse gases

- Global #1 in precision and accuracy, and portability
- The lowest guaranteed drift of any instrument
- Unique water correction feature automatically reports dry mol fraction
- Innovative software featuring intuitive user interface & customization tools
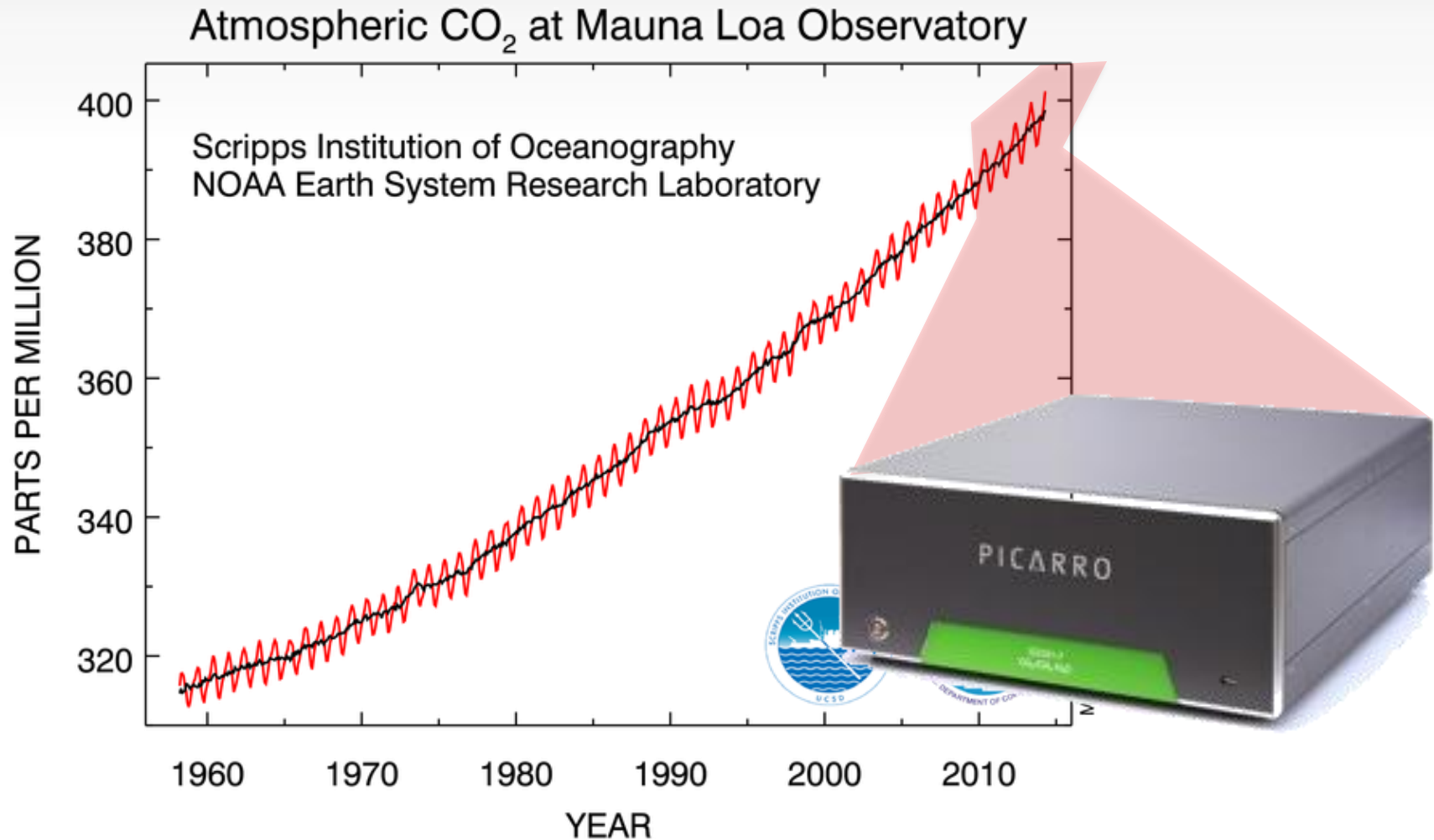- World class customer service and technical support

CRDS Analyzer $CO_2 + CO + CH_4 + H_2O$
Model G2401

The world's only field-deployable analyzer capable of measuring the four main atmospheric trace gases simultaneously and continuously.
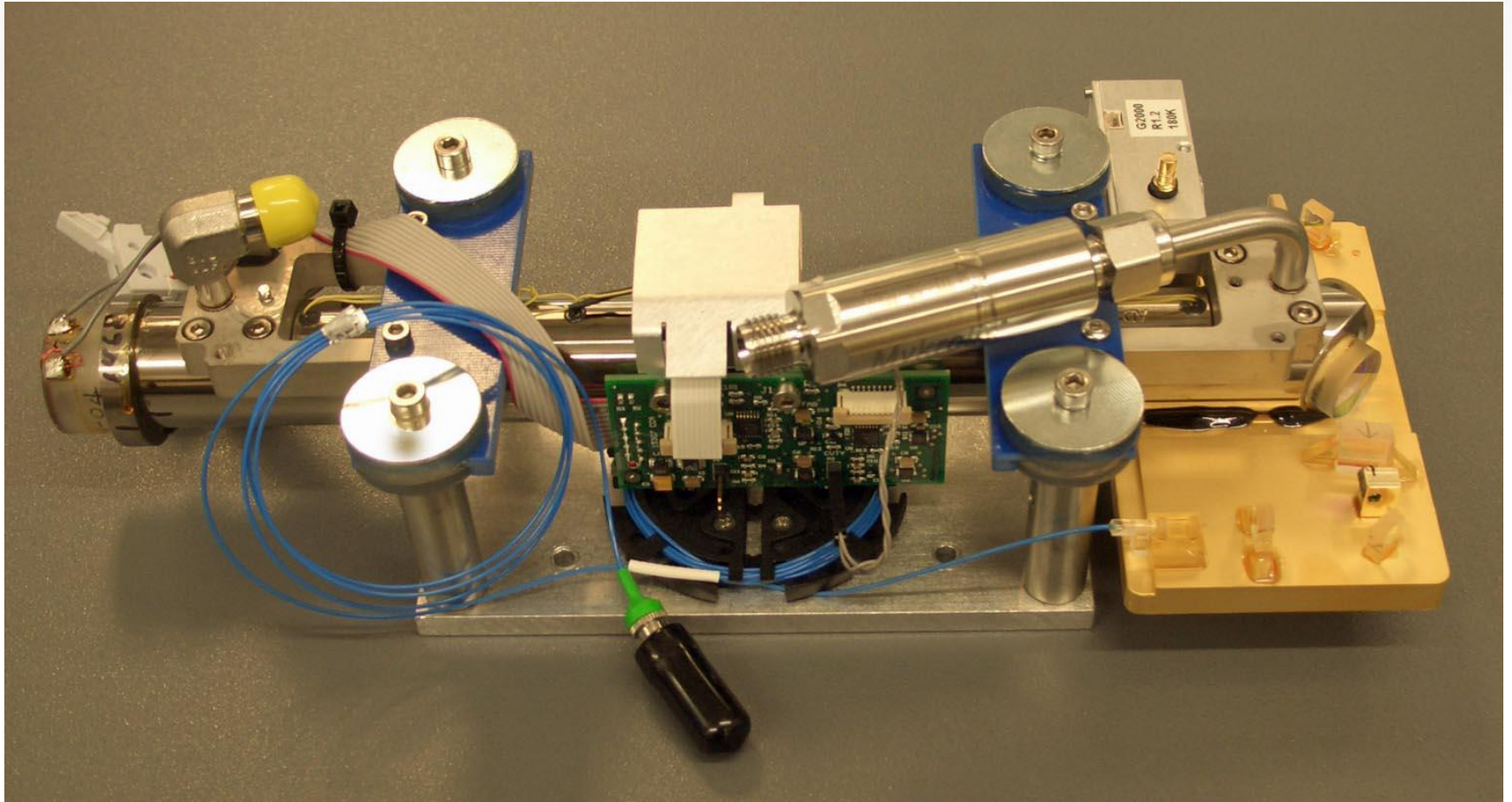
- Global #1 in precision, accuracy, and portability
- Capable of meeting WMO Data Quality Objectives for CO, CO_2 & CH_4
- Guaranteed lowest drift of any continuous greenhouse gas measurement instrument
- Unique water correction automatically reports dry gas mol fractions

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GHG Measurements: The Mauna Loa CO$_2$ Record

Atmospheric CO$_2$ at Mauna Loa Observatory
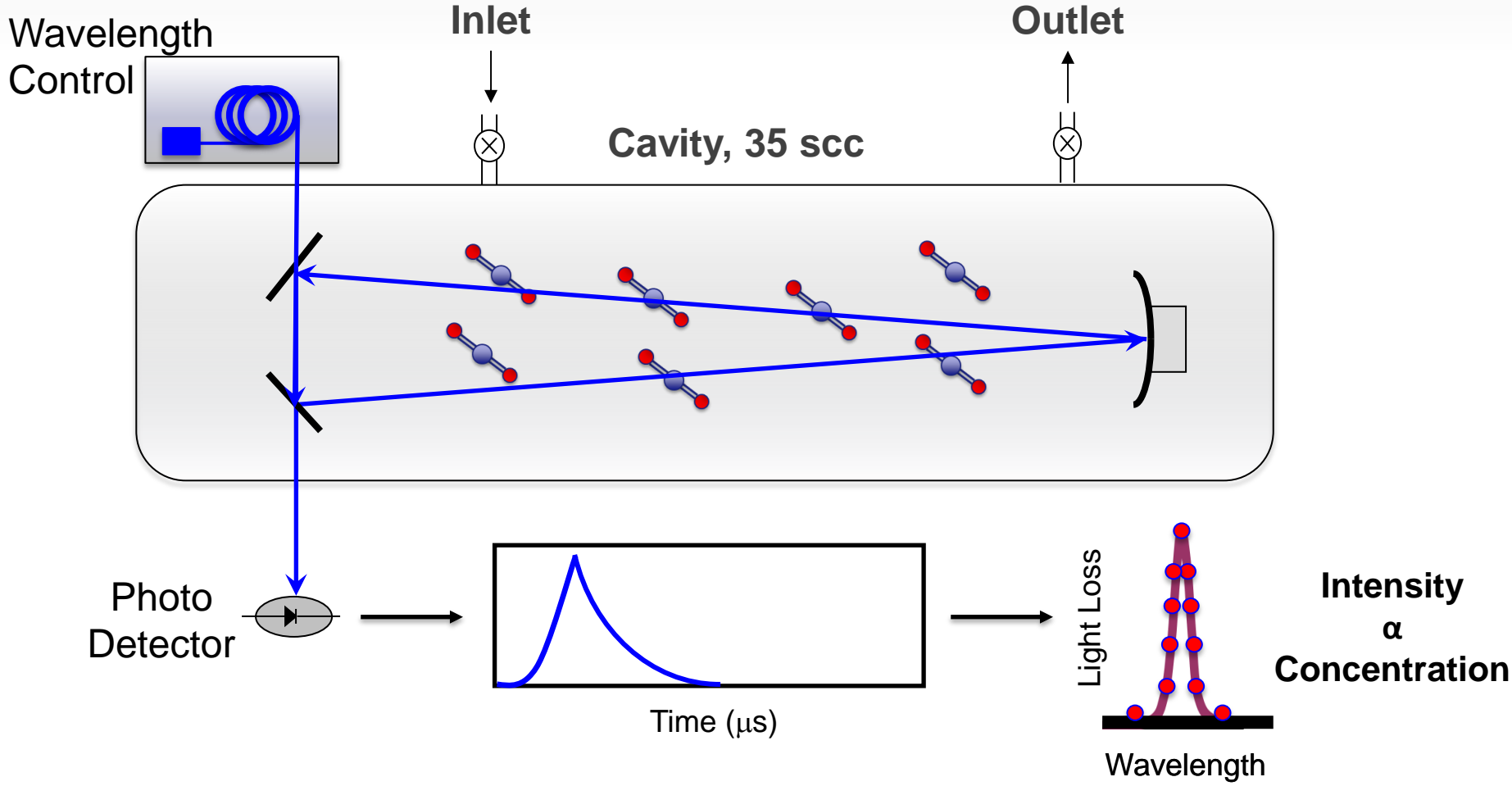
Scripps Institution of Oceanography
NOAA Earth System Research Laboratory

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The measurement cell – small and robust
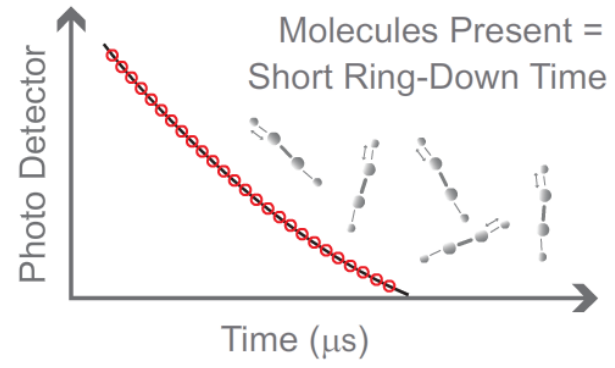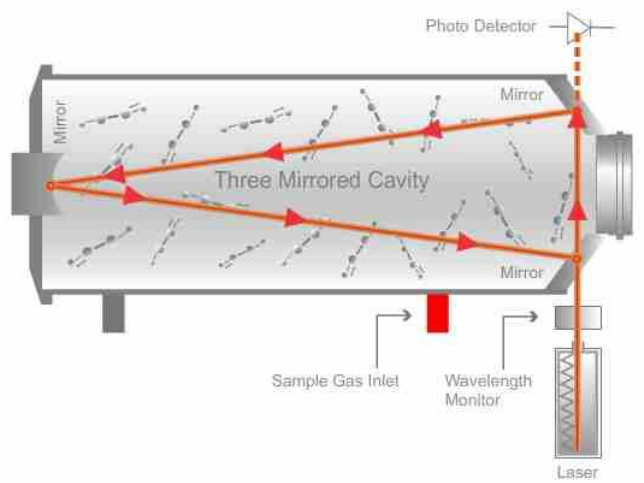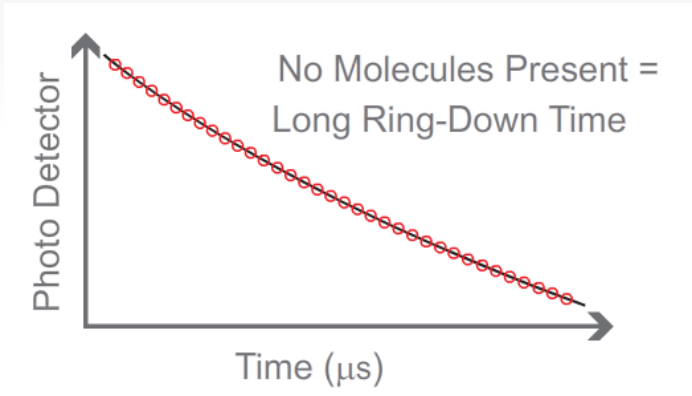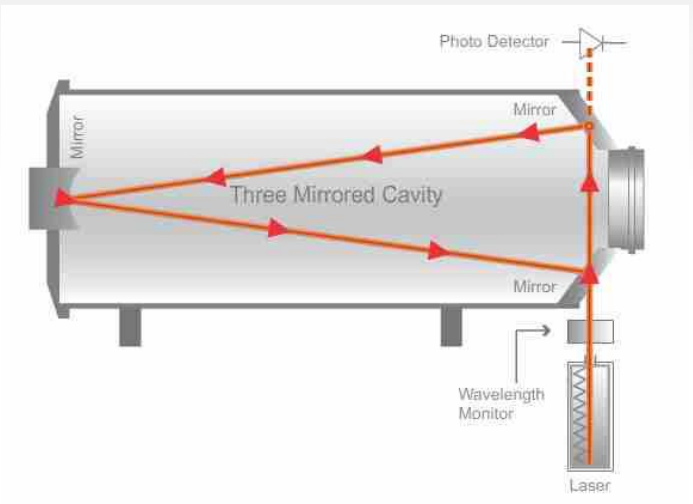
30 cm

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Cavity Ring-Down Spectroscopy – Hardware

- Laser light at a wavelength that the molecule does absorb light

Stronger light absorbance -> shorter ring-down time

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Pressure and temperature stability

Tightly control the conditions inside the cavity, so that variations of the environmental conditions* have no signifcant effect on:

Cavity Temperature Stability (± **0.007 ºC**)

Cavity Pressure Stability (±**0.00002 atm**)
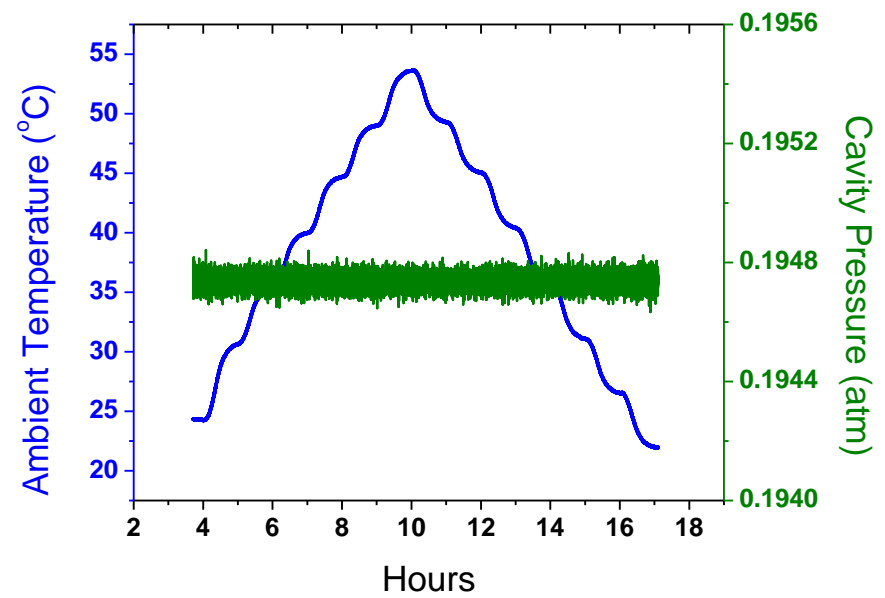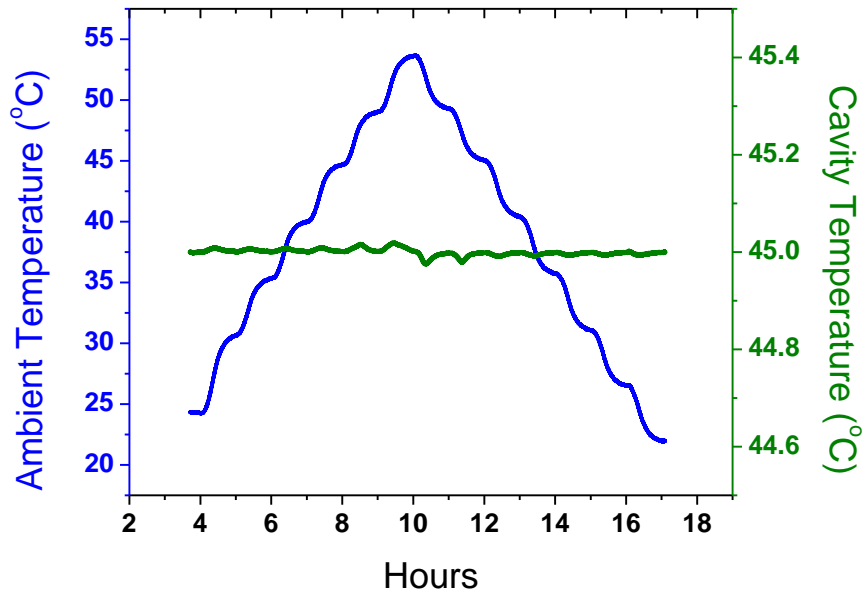
*The analyzer is placed in an environmental chamber where the temperature is ramped up (then down), while measuring a cylinder of compressed air.

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What Makes a Great GHG Instrument?

- Stability, Stability, Stability!
  - The more unstable the instrument is, the more you have to calibrate, and calibration gases are:
    - Costly
    - Difficult to deploy remotely (it's not so easy to ship gas bottles from NOAA to Greenland or Borneo or wherever the station is)

- Small sample size
  - The ability to measure a small amount of gas means that the expensive calibration standard lasts a long time

Cavity Ring-Down Spectroscopy – Low Drift

The long-term effects of this control and stability are clear

Two Analytes,
One Month
Zero Calibration

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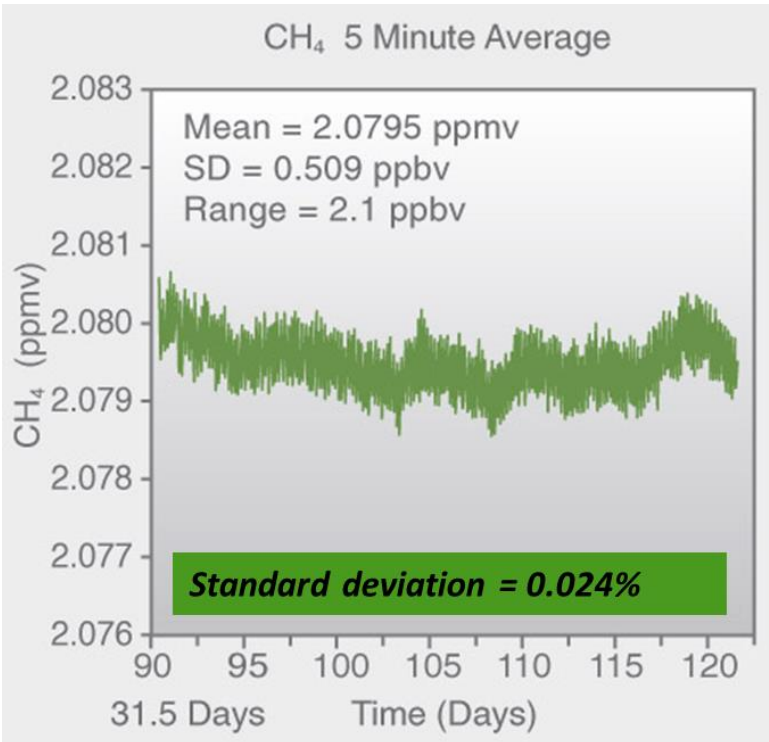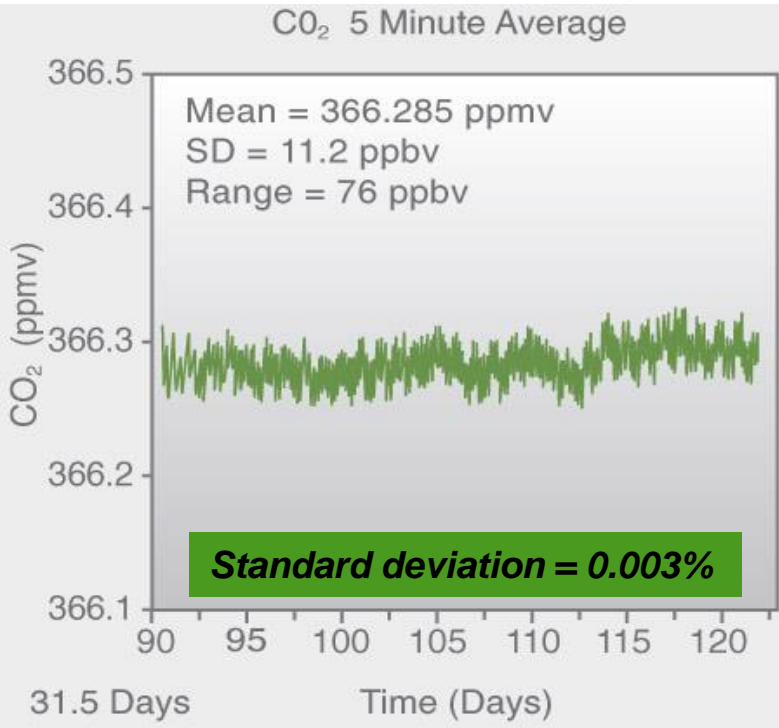
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Picarro G2401 meets WMO /GAW specifications

| Performance Specifications, in dry air	CO₂	CO	CH₄	H₂O
Precision (5 sec / 5 min, 1-σ) *Guaranteed for below specified range & conditions - reference gas not needed*	<150 ppb / <50 ppb	<30 ppb / < 2 ppb	< 1 ppb / < 0.7 ppb	< 200 ppm / < 50 ppm
Max Drift at STP (over 24 hrs / 1 month) (peak-to-peak, 50-minute average) *Guaranteed for below specified range & conditions - reference gas not needed*	150 ppb / 500 ppb	15 ppb / 50 ppb	1 ppb / 3 ppb	100 ppm ± 5% of reading
Max Uncertainty Using Reference Gas* **(1hr average, 2-sigma)** *Meets WMO Data Quality Objective for GAW Stations*	< 50 ppb	< 2 ppb	< 1 ppb	n/a
Automated Determination of Dry Mol Fraction	Included	Included	Included	n/a
Operating Range	0 – 1000 ppm	0 – 5 ppm	0 – 20 ppm	0 - 7 %v H_2O / 39 °C dew pt (non-condensing)
Guaranteed Specifications Range	300 – 500 ppm	0 – 1 ppm	1 – 3 ppm	0 - 3 %v H_2O / 25 °C dew pt (non-condensing)
Measurement Interval	< 5 seconds	< 5 seconds	< 5 seconds	< 5 seconds
Rise/Fall time (10 - 90 % / 90 - 10%)	< 5 seconds	< 5 seconds	< 5 seconds	< 5 seconds

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"Calibrate-ability" (that is, drift) in a CRDS Instrument

(Actually, what follow is true of most optical instruments)

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Calibration, is it needed?...yes it is
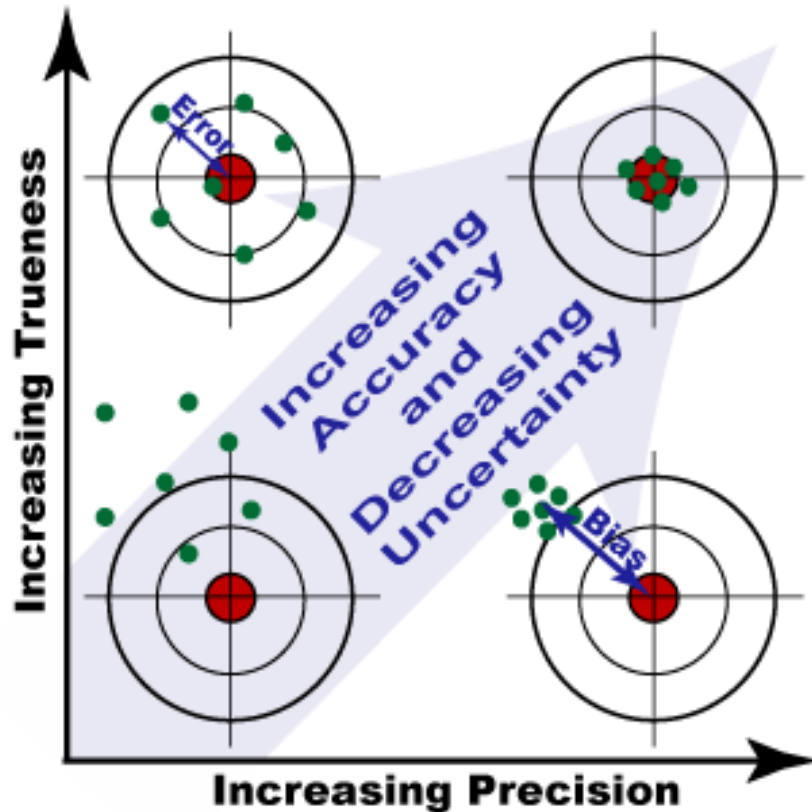
1)
Even a perfect instrument with
a 1-sigma standard deviation of ~0
Does not report the **"Truth"** and has
a non-zero **Bias**

2)
At Picarro we build instruments that
have very high **precision** and very low
drift

Precision:
Precision is the closeness of agreement between independent measurements of a quantity under the same conditions. It is a measure of how well a measurement can be made **without reference to a theoretical or true value**.

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How Calibration Is Performed

compare

+1.500 ppm difference

381.500

380.000 ppm

Cal gas

CRDS

Adjust the instrument readings
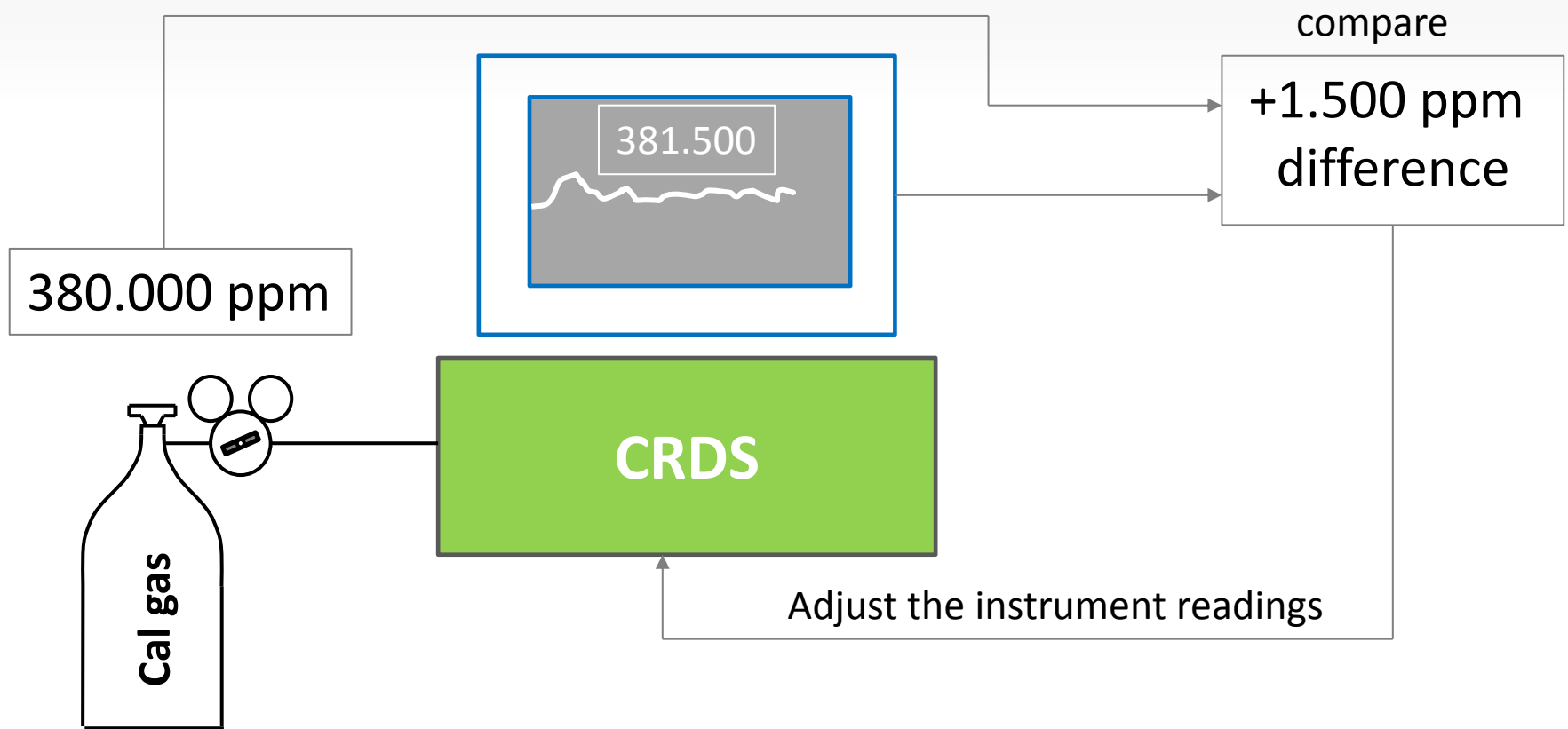
What is the physical basis of the difference?

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The basic elements of optical spectroscopy

$$[conc] = k[peak\ height]$$

k is a constant for a perfect optical spectrometer:

constant T & P and perfect λ & α

peak height

True baseline

Absorbance (ppb / cm)

Optical frequency (wavenumbers)

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The basic elements of optical spectroscopy

$$[conc] = xk[peak\ height] + \varepsilon$$

Both x and ε have both noise and drift

Absorbance (ppb / cm)

peak height

ε

True baseline

Fit baseline

Optical frequency (wavenumbers)

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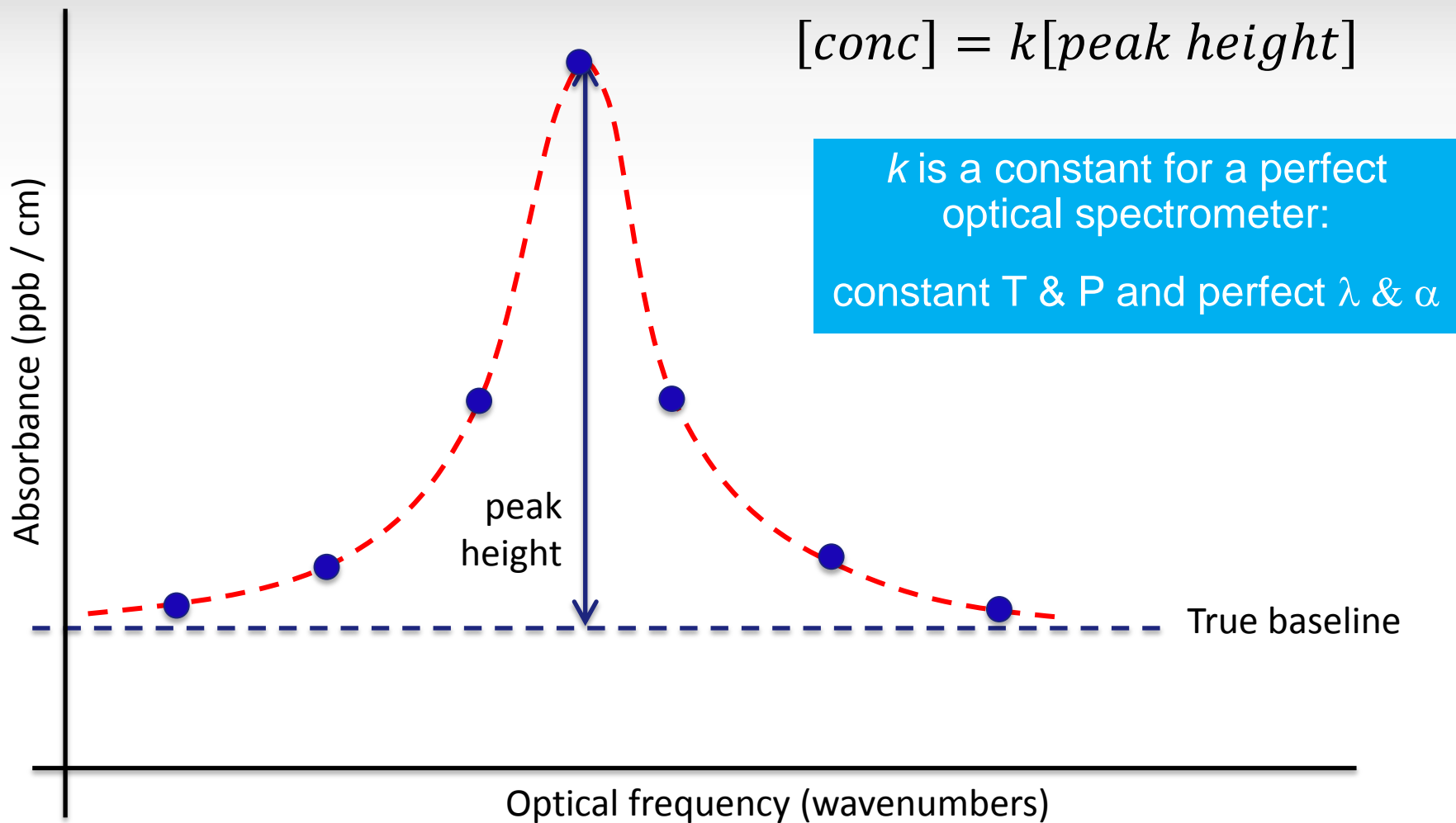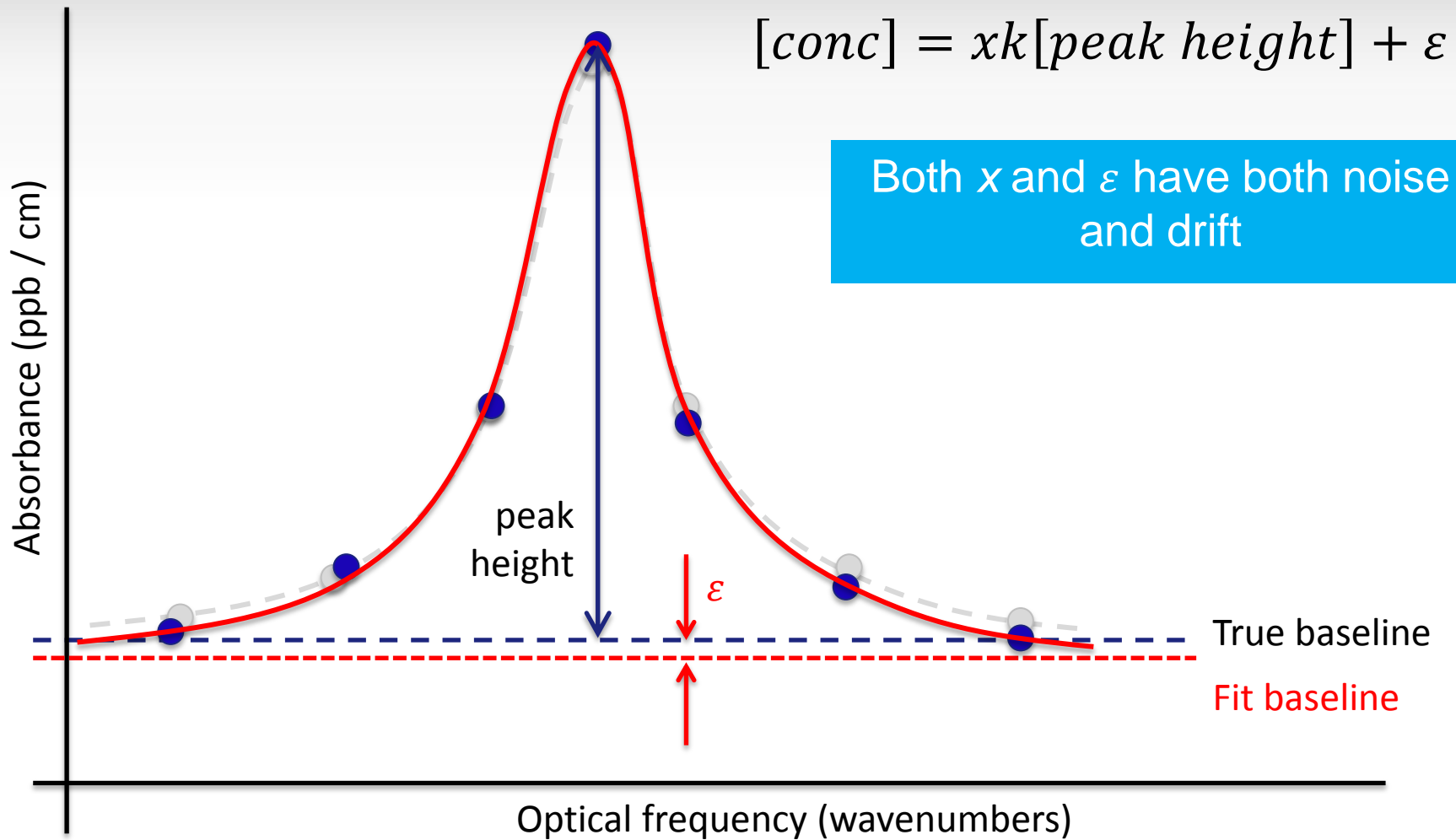
What if the Spectrometer Isn't Perfect?

True concentration   Measured peak height (and proportionality k)

$$c = xkm + \varepsilon$$
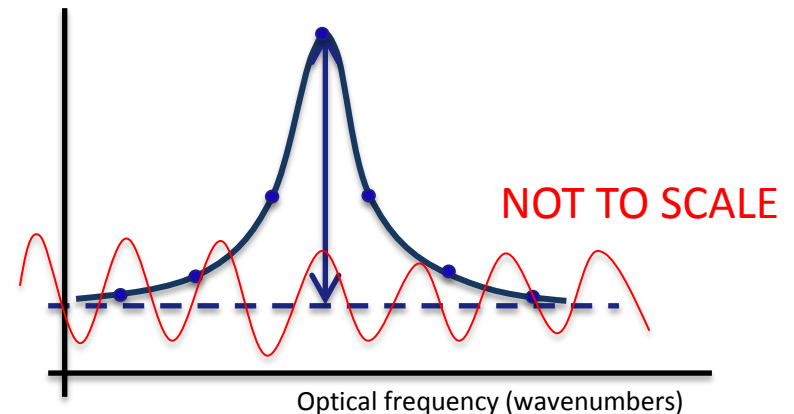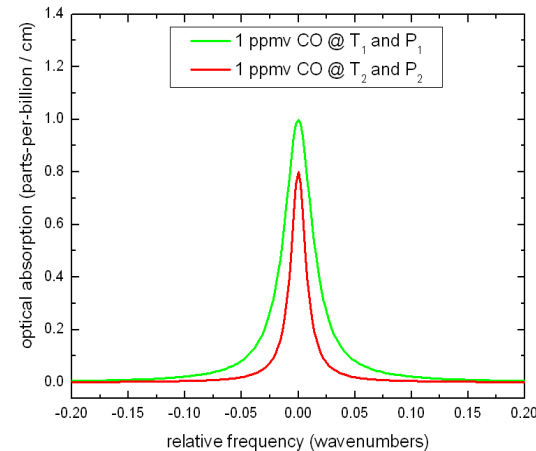
Span (x ~ 1)   Offset ($\varepsilon \sim 0$)

- "SPAN" drift
  - Incorrect temperature
  - Incorrect Pressure
  - Wavelength error
  - Spectral interference from other species

- "OFFSET" drift
  - "micro-etalons", or baseline ripple
  - Spectral interference from other species

NOT TO SCALE

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Calibration of GHG Concentration Instruments

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Drift in a G2401 (CFKADS)

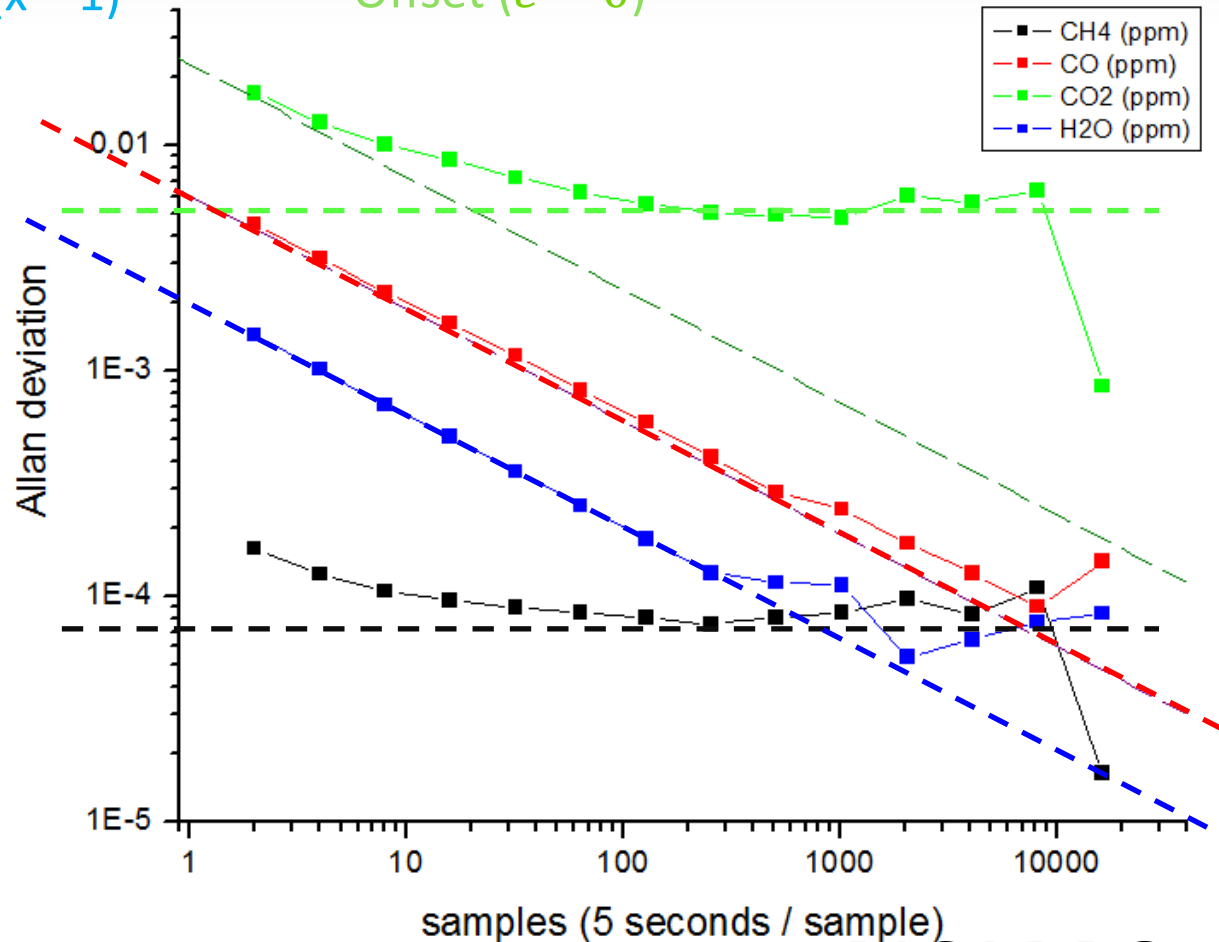True concentration   Measured peak height (and proportionality k)

$$c = xkm + \varepsilon$$

Span (x ~ 1)   Offset ($\varepsilon \sim 0$)

- "SPAN" drift dominates CH_4 and CO_2
  - Time scale is minutes to hours

- "OFFSET" drift dominates CO and H_2O (only at low water levels)
  - Time scale is hours to days

Legend:
- CH4 (ppm)
- CO (ppm)
- CO2 (ppm)
- H2O (ppm)

y-axis: Allan deviation (0.01, 1E-3, 1E-4, 1E-5)

x-axis: samples (5 seconds / sample) (1, 10, 100, 1000, 10000)

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Typical Calibration Strategy for GHGs

- Calibrate with 3-5 bottles infrequently (start of life, yearly, etc) to verify instrument linearity over full range of measurements

- Calibrate in the field on a daily / weekly / monthly basis with 2-3 bottles

- "Target Tank" - Always have one known bottle that does not participate as a calibration reference to validate that the sampling system and calibration methodology gives the right answer

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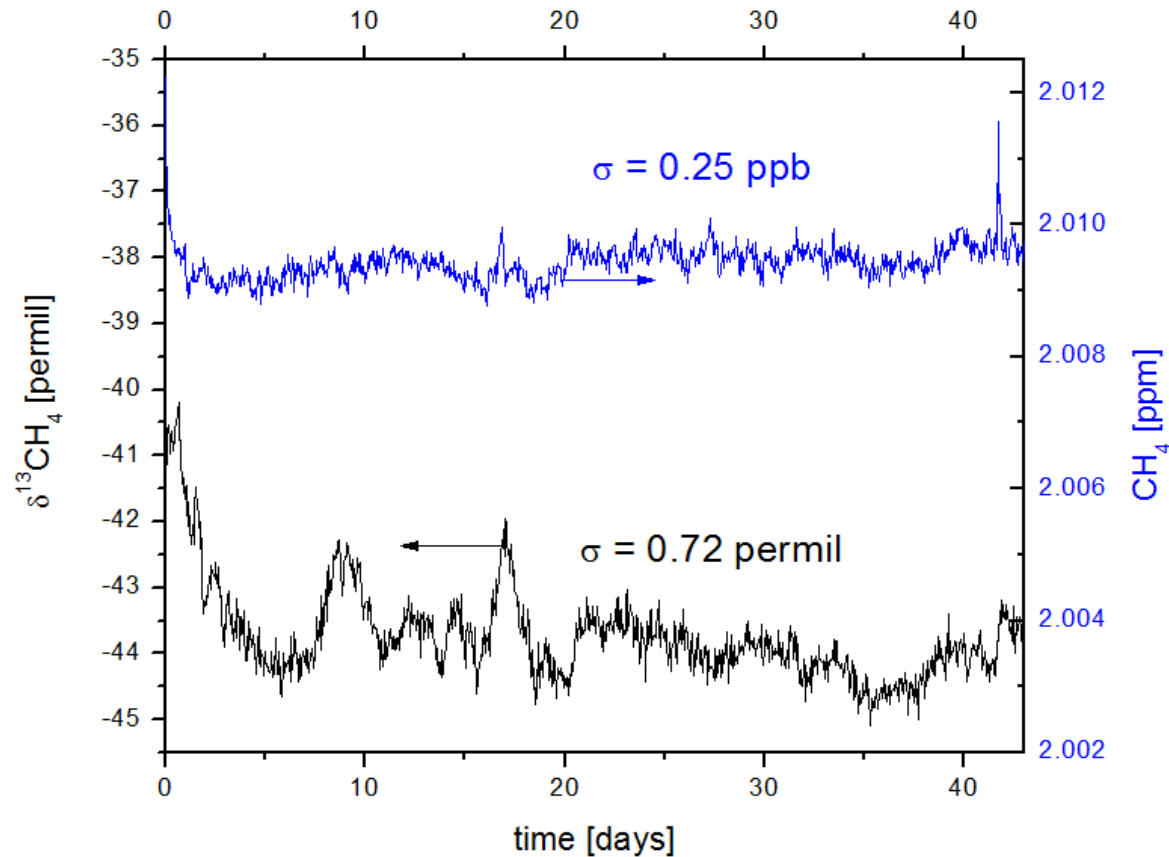# Calibration of $\delta^{13}CH_4$ and $\delta^{13}CO_2$ for atmospheric measurements

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Testing the Instrument: Precision and Drift

Precision, $\delta^{13}C$ in CH_4 (1-σ , 1 hr window)	< 0.8 ‰ guaranteed precision at > 1.8 ppm 5 min. average < 0.5 ‰ guaranteed precision at > 1.8 ppm, 15 minute average

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How Does Drift in an Infrared Isotope Spectrometer Manifest?

$$\delta_{13} = 1000\left(\frac{r_{sample}}{r_{VPDB}} - 1\right) \qquad r_{sample} = c_{13}/c_{12} \qquad c = \textcolor{cyan}{x}\textcolor{red}{k}\textcolor{black}{m} + \textcolor{green}{\varepsilon}$$

$$\delta_{true} = 1000\left(\frac{(x_{13}k_{13}m_{13} + \varepsilon_{13})/(x_{12}k_{12}m_{12} + \varepsilon_{12})}{r_{VPDB}} - 1\right)$$

Ignore ε_{12} when $m_{13} \ll m_{12}$, and $x_{13} \sim x_{12} \sim 1$

$$\delta_{true} = 1000\left(\begin{array}{l}\dfrac{k_{13}m_{13}/k_{12}m_{12}}{r_{VPDB}} - 1 \\[2mm] +(\dfrac{\boldsymbol{x_{13}}}{\boldsymbol{x_{12}}} - \boldsymbol{1})\dfrac{k_{13}m_{13}/k_{12}m_{12}}{r_{VPDB}} \\[2mm] +\boldsymbol{\varepsilon_{13}}/x_{12}k_{12}m_{12}r_{VPDB}\end{array}\right)$$

δ_{raw}

Delta span drift

[concentration]$^{-1}$ drift

$$\delta_{true} = \delta_{raw} + B(\delta_{raw} + 1000) + \frac{A}{^{12}CH_4}$$

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A HI – LO Calibration Scheme

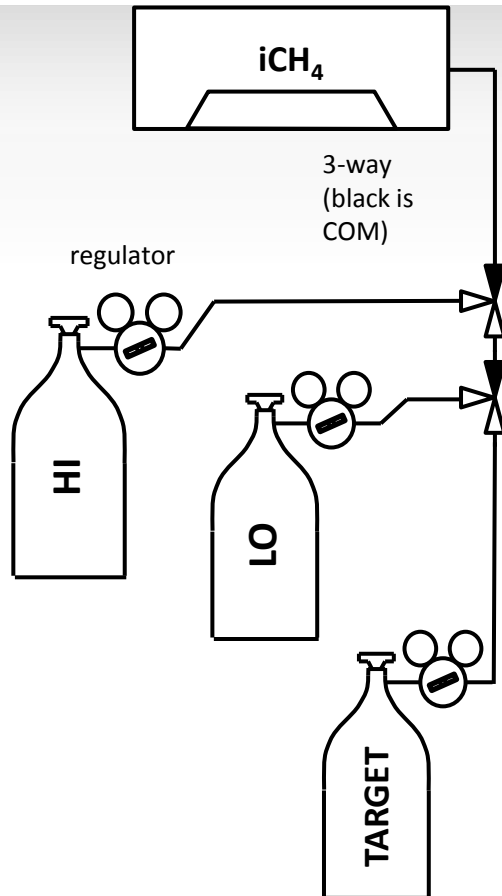$$\delta_{true} = \delta_{raw} + B(\delta_{raw} + 1000) + \frac{A}{^{12}CH_4}$$

– *delta span drift* affects high and low concentration equally

– *conc⁻¹ drift* affects low concentration bottles more

- Calibration Strategy: Use two known bottles, a HI (C_{HI} and δ_{HI}) and a LO (C_{LO} and δ_{LO}), to determine A_i and B_i in each calibration period τ_i

Define: $\Delta_H \equiv \delta_{HI} - \delta_{HI\ raw}$ and $\Delta_L \equiv \delta_{LO} - \delta_{LO\ raw}$
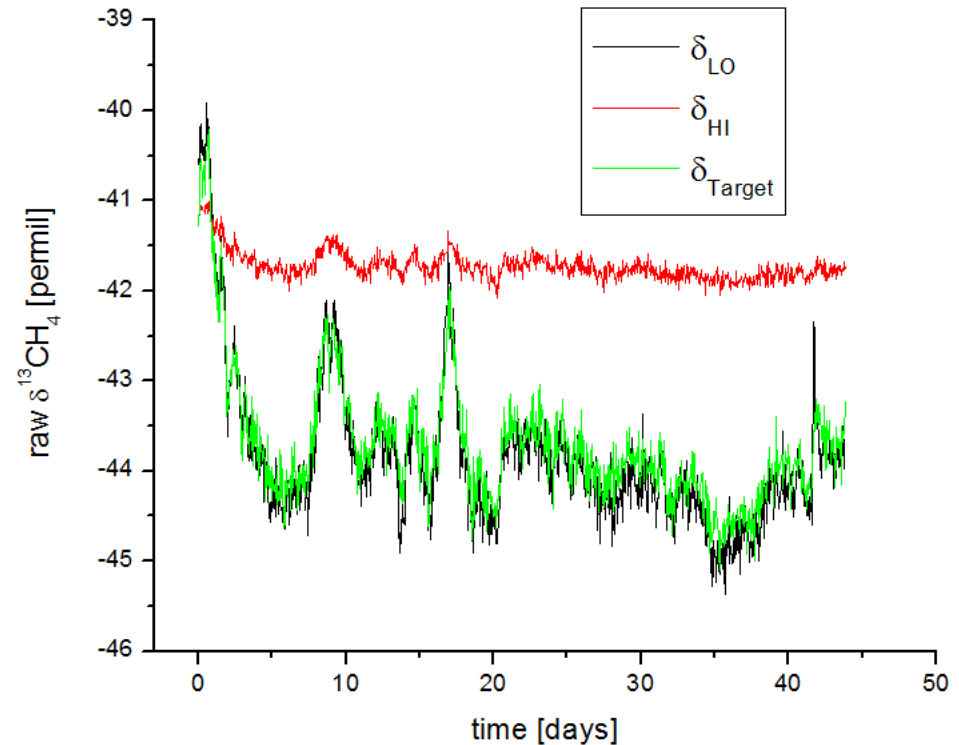
$$A_i = \left[\frac{\Delta_H(\delta_{LO\ raw} + 1000) - \Delta_L(\delta_{HI\ raw} + 1000)}{\frac{(\delta_{LO\ raw} + 1000)}{C_H} - \frac{(\delta_{HI\ raw} + 1000)}{C_L}} \right]_i$$

$$B_i = [(\Delta_H - A_i/C_H)/(\delta_{HI\ raw} + 1000)]_i$$
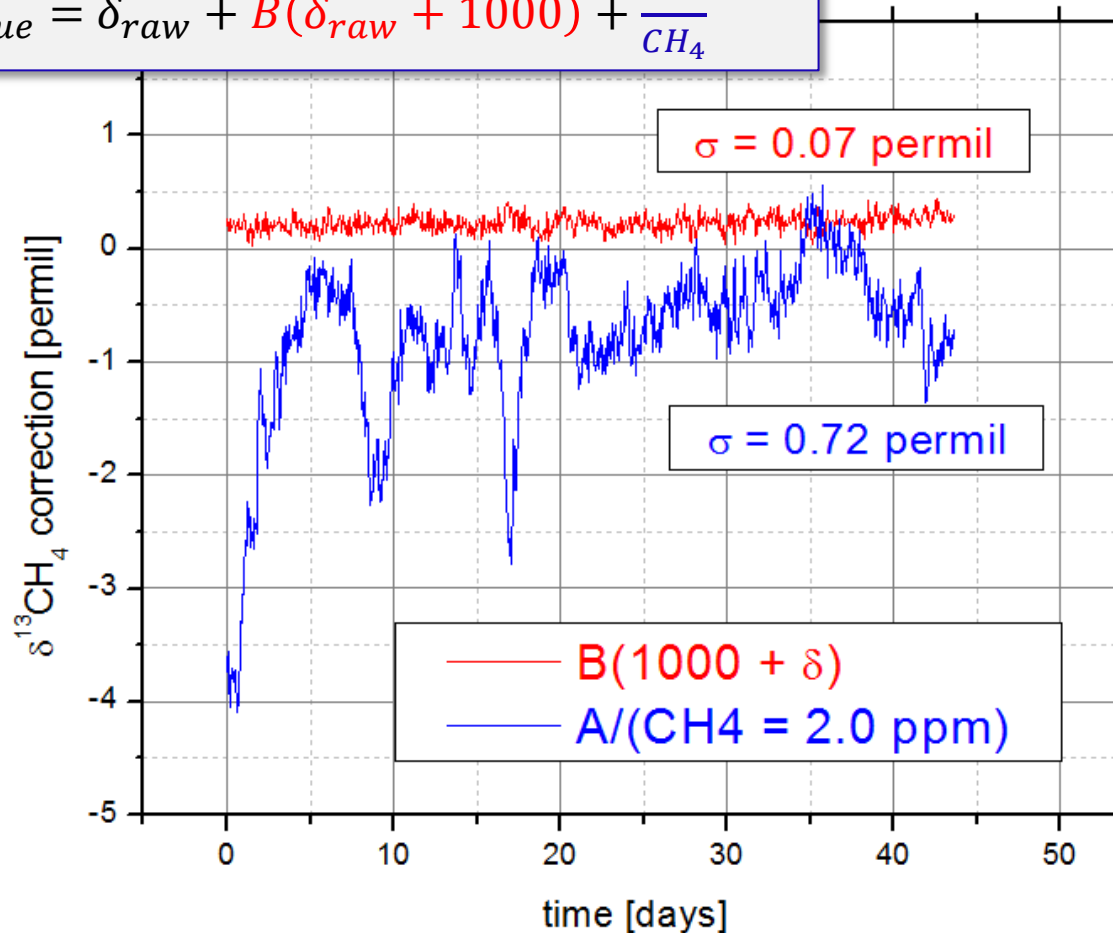
Testing the Scheme – 40 days and 40 nights

- Hourly measurement cycle
  - HI = 10.07 ppm / -41.7 ‰ (10 min)
 - LO = 1.80 ppm / -44.5 ‰ (25 min)
  - TARGET = 2.03 ppm (25 min)

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Calibration – [conc]⁻¹ Drift Dominates

$$\delta_{true} = \delta_{raw} + B(\delta_{raw} + 1000) + \frac{A}{CH_4}$$
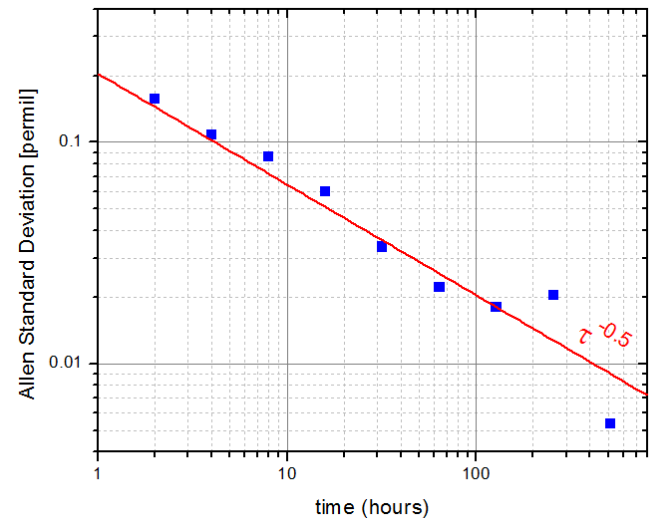

σ = 0.07 permil

σ = 0.72 permil

Legend:
- B(1000 + δ)
- A/(CH4 = 2.0 ppm)

Y-axis: δ¹³CH₄ correction [permil]

X-axis: time [days]

*>90% of the drift can be corrected using a single bottle and a **A / ¹²CH₄** correction factor*

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Target Tank Stability After Hourly Calibration

$$\sigma_{1\ hr} = 0.204\ \permil$$

$$\sigma_{24\ hr} = 0.046\ \permil$$

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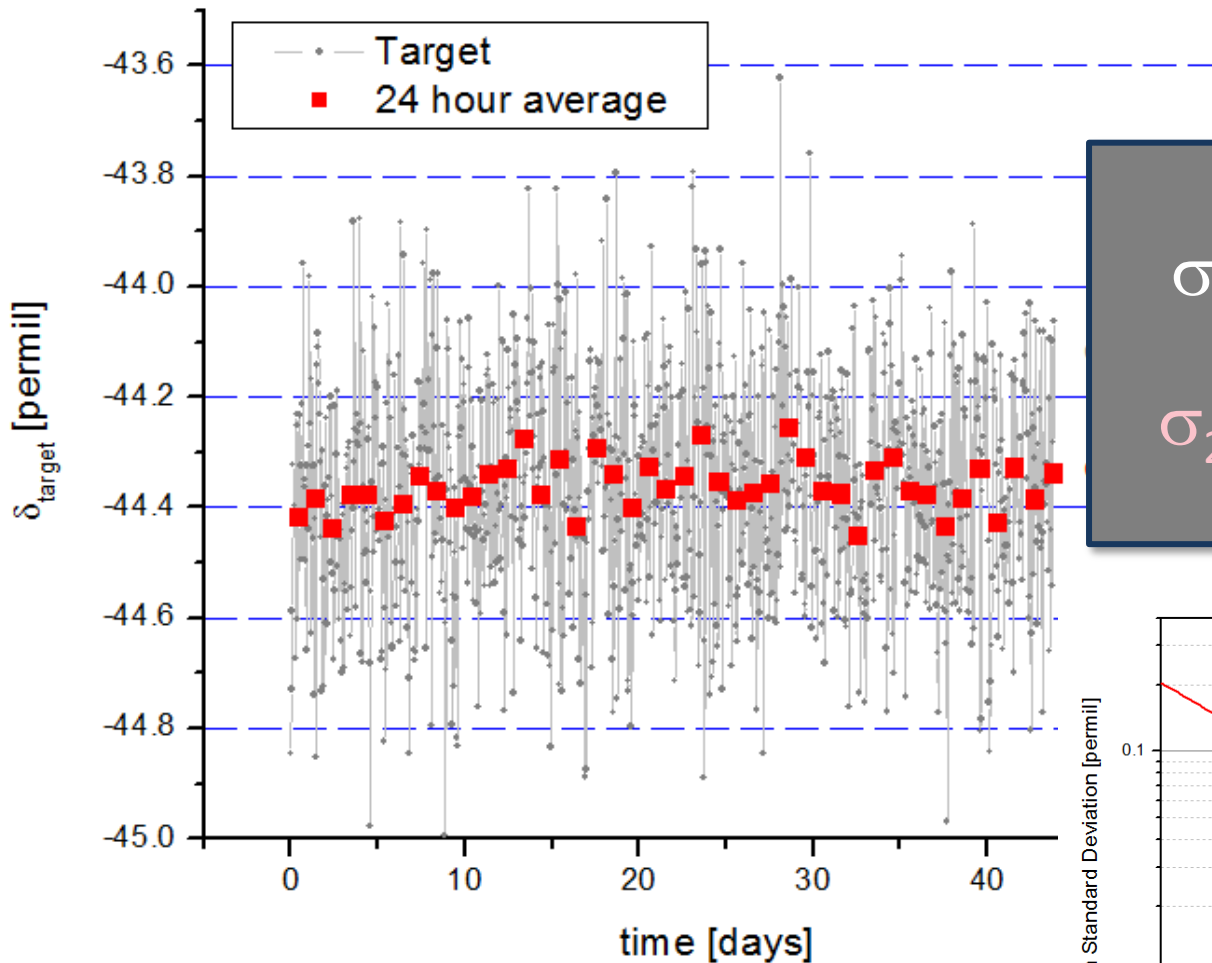
Recommended Calibration Strategy for isotopic measurements

- Calibrate with 3 (or more) ref. gases infrequently (start of life, yearly, etc) to verify instrument linearity over full range of isotopic and concentration range, and to characterize your working standards

- Calibrate in the field on every couple of hours / 2-times daily with 2 working standards bracketing the range in delta values and concentration (HI LO scheme)

- "Daily working standards" - Always have 1-2 bottles that has an isotopic composition close to the samples, and acts as a quality control (daily offset and drift)

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Thank you for your attention

Questions?

- Feel free to contact me:

  rwinkler@picarro.com

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*selected Picarro customers

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