REINHOLD ENVIRONMENTAL Ltd.

2013 APC Round Table & Expo Presentation

July 8-9, 2013, in St. Louis, MO / Hosted by Ameren

Tunable Diode Laser (TDL) Based HCl CEMS for MATS Compliance

Reinhold Environmental
2013 APC Round Table

a technical solution to meet every need…

Cemtek Environmental Inc.
3041 S. Orange Ave.
Santa Ana, CA 92707
800-400-0200
www.cemteks.com

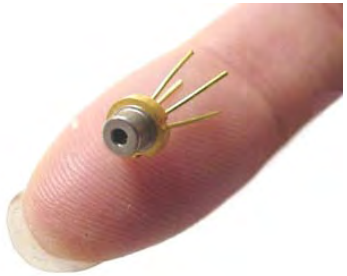
HCl CEMS

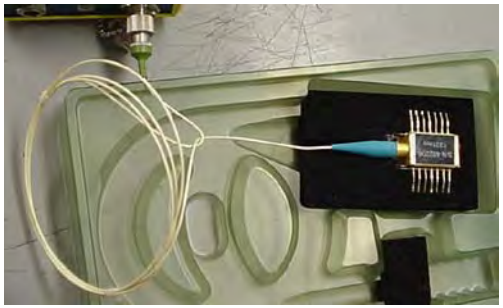
- **Tunable Diode Laser**
  - **Track record of proven installation based both on ammonia slip monitoring as well as HCl monitoring on coal fired stack and cement kiln demonstration testing**
- **FTIR**
  - **Readily accepted technology in cement industry**
  - **Reluctance to installation by utilities due to concerns of credible evidence rules**
- **NDIR**
  - **Detection limits may not be low enough for MATS and Portland Cement MACT emissions limits**
- **Cavity Ring Down**
  - **Highly sensitive down to ppb levels**
  - **Dilution extractive**
  - **Early stages of field demonstration**
  - **Maintainability concerns**

Tunable Diode Laser Measurement Technique

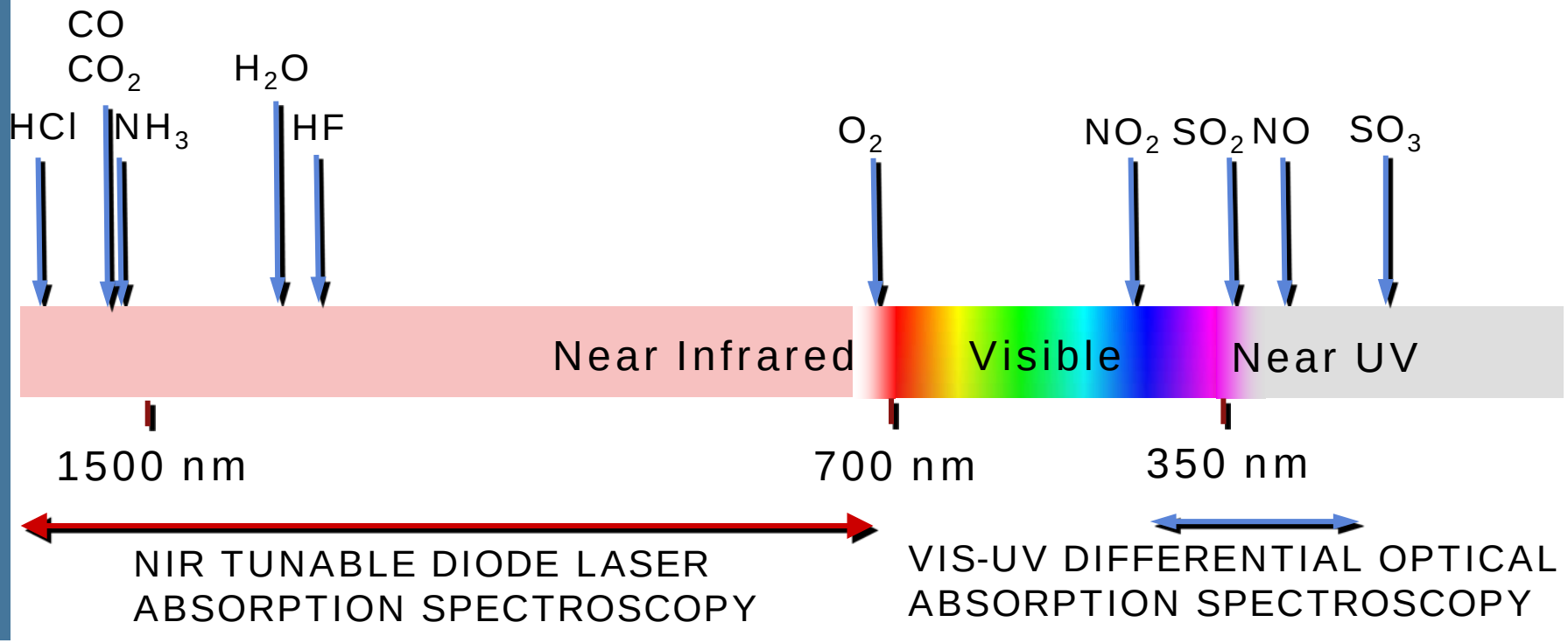
What are Tunable Diode Lasers (TDL)?

- **Lasers made of small crystals of Ga, As, Sb, P**
- **Lasers similar to those used in telecommunication, CD players and Laser Printers**
  - **Rugged construction**
  - **Commercially available at low cost**
- **Emits laser radiation in near infrared region when an electric current is applied**





Tunable Diode Laser Measurement Technique



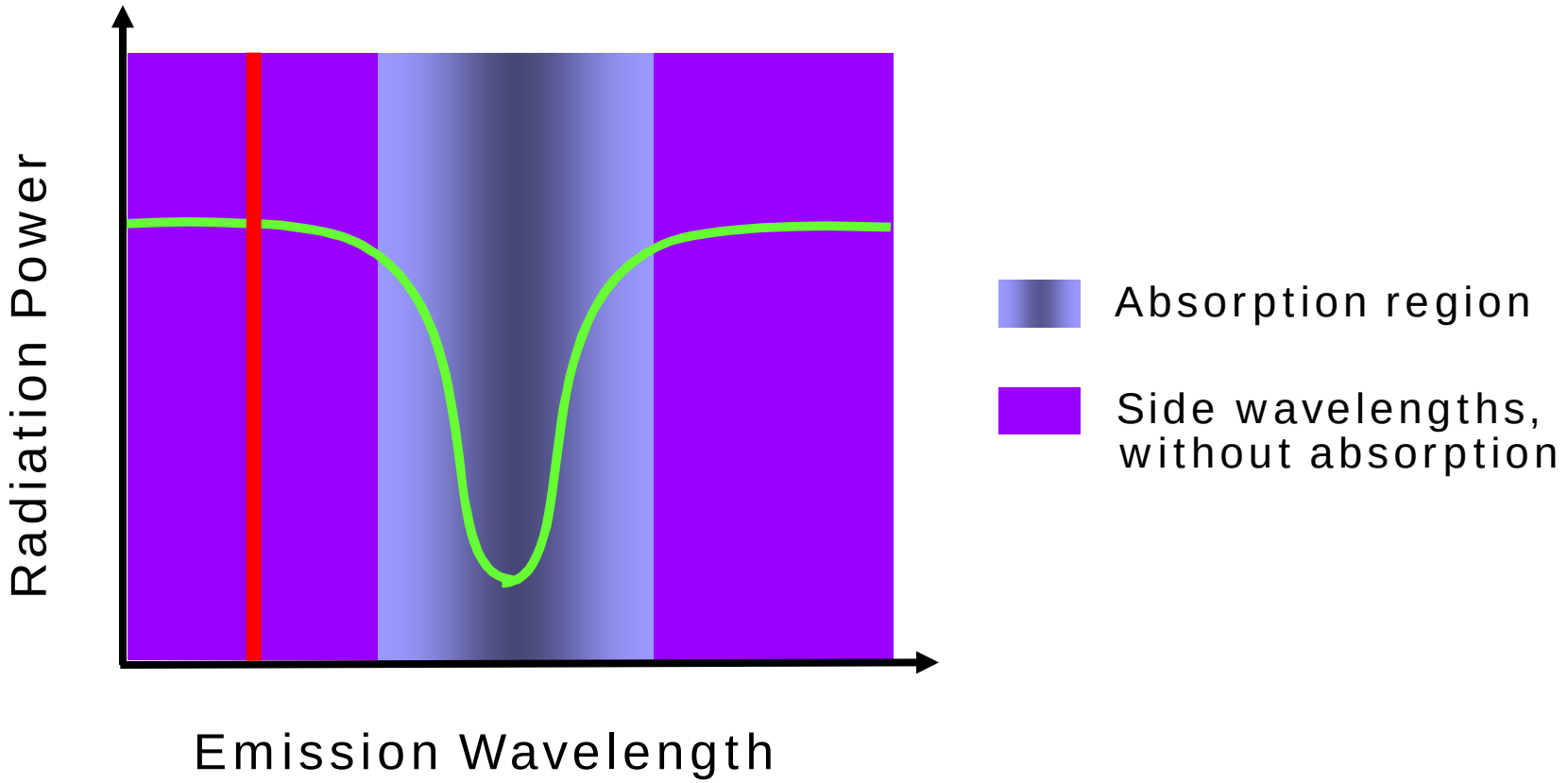
Tunable Diode Laser Measurement Technique

How do Tunable Diode Lasers (TDL) Operate?

- **Laser center wavelength depends on composition of crystal**
- **Laser wavelength can be changed over narrow range by changing current or over a wider range by changing laser operating temperature**
- **By temperature controlling the laser, changing the electric current permits scanning over entire absorption feature**
- **By scanning the entire absorption feature, interference from dust is eliminated as the laser signal power is continuously measured.**

Tunable Diode Laser Measurement Technique

In the Region of Wavelength Absorption



Tunable Diode Laser Measurement Technique

- **Concentration of the desired molecule done via the Beer-Lambert Law**

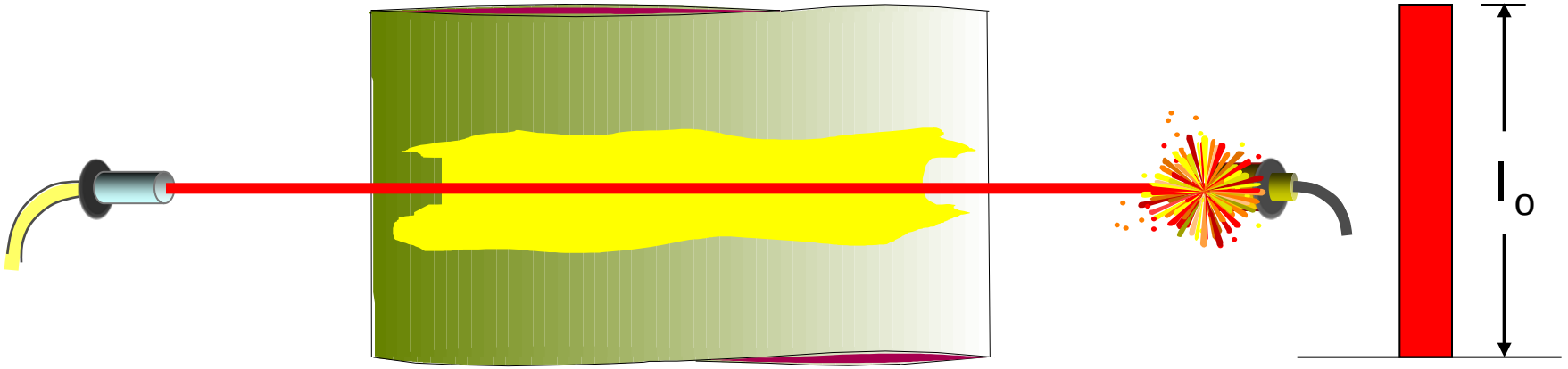
$$\frac{I}{I_0} = \exp\left[-\varphi(\phi) \times N \times L\right]$$

- **where**
  - **I = transmitted power**
  - **I_0 = incident power**
  - **L = path length [cm]**
  - **N = concentration [# molecules / cm^3]**
  - **φ(Φ) = absorption cross-section of molecule [cm^2 / molecule]**

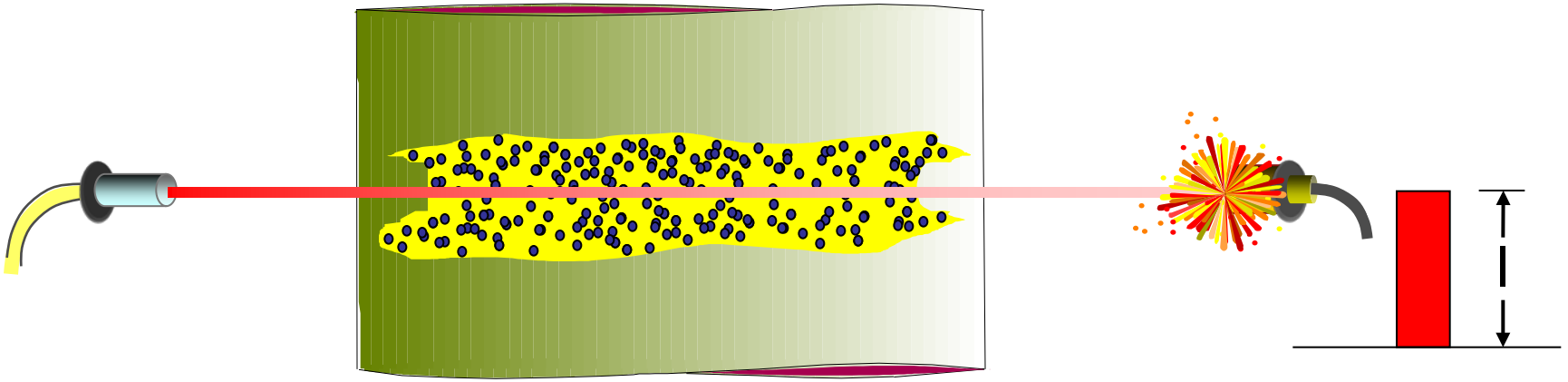
- **Which provides a simple mathematical solution as:**
  - **I and I_0 are measured by the analyzer**
  - **Path length, L, and absorption coefficient, φ(Φ), are constants that are input into the analyzer**
  - **All parameters are known except for concentration, N (in ppmV) which what is solved and reported**

Tunable Diode Laser Measurement Technique

When no gas present/off peak...



When gas present/on peak...



Absorbed intensity, $\delta I = I_o - I$

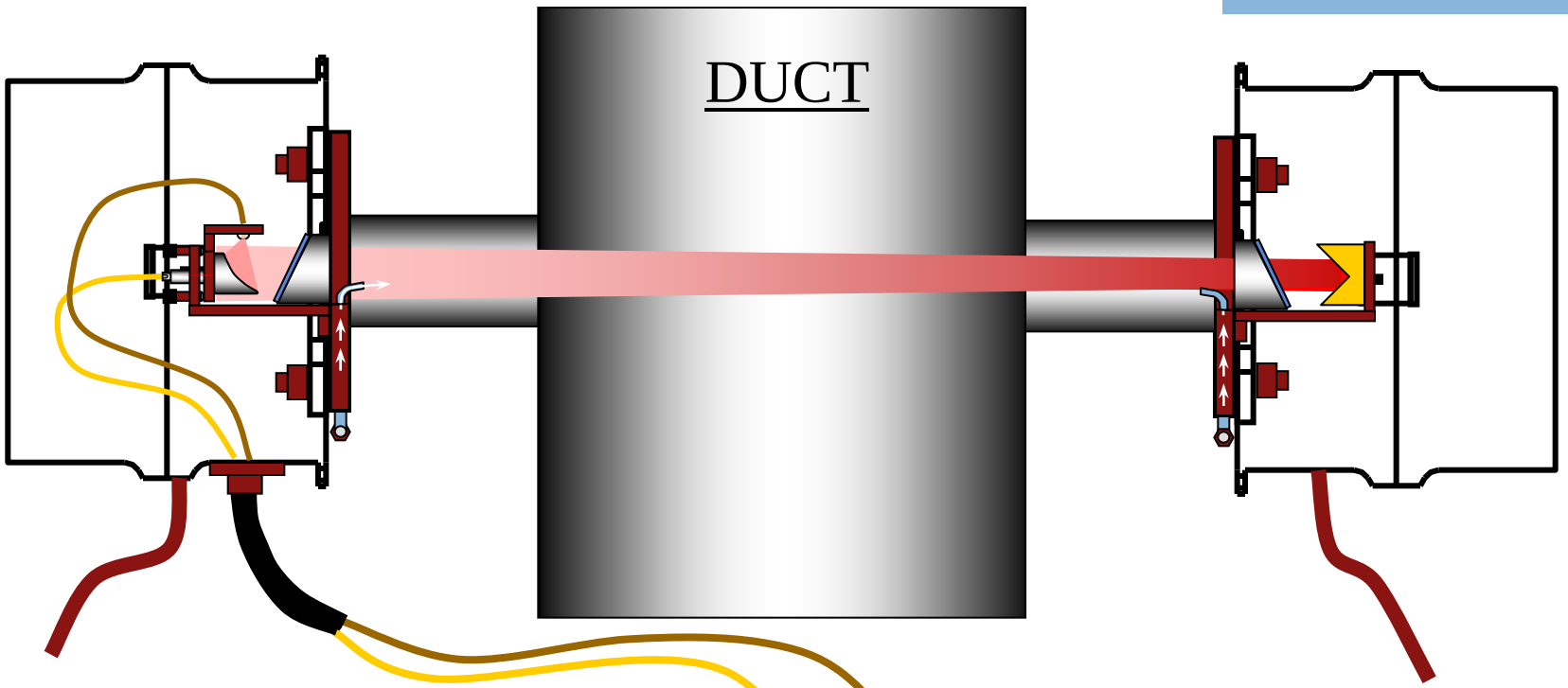
Tunable Diode Laser Measurement Technique

Tunable Diode Laser (TDL) Detection Limits

- **Detection limits are a factor of both path length and path measurement time and the molecule being measured.**
- **For tunable diode lasers operating in the spectral band, the detection limit is in the range of 0.1 to 5 ppm-meters.**
- **Path Length**
  - **The longer the path length, the higher the absorption and the better the sensitivity and the lower the detection limit. Therefore, longer path lengths result in better detection of low concentrations.**
- **Measurement Time**
  - **Detection limit scales approximately as the square root of the measurement time.**
  - **For example:**

    Increasing the time from one-second to one-minute enhances the detection limit approximately seven fold

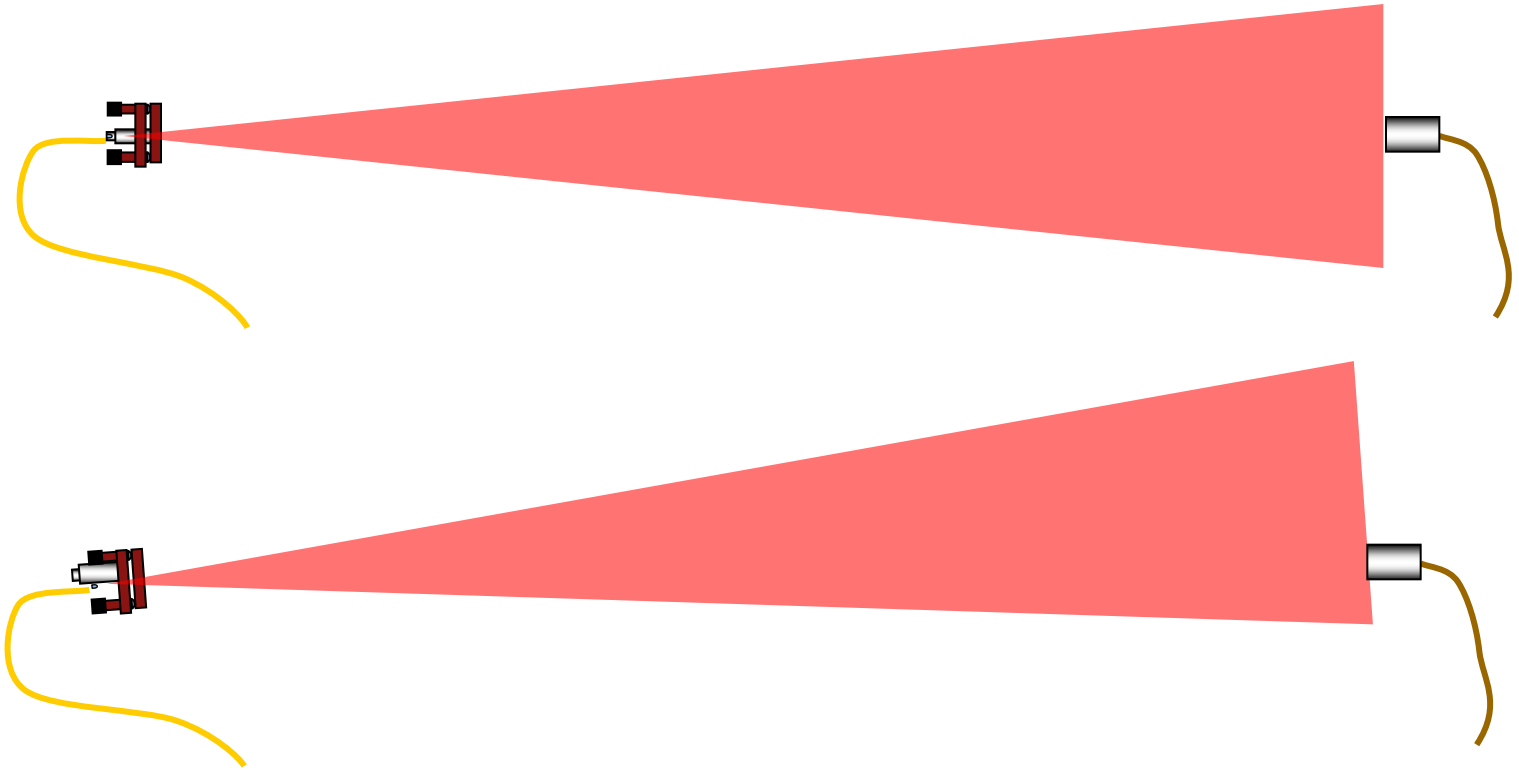
Dual Pass (Mono-static) Duct Configuration



Fiber-optic
& coax cables

Analyzer

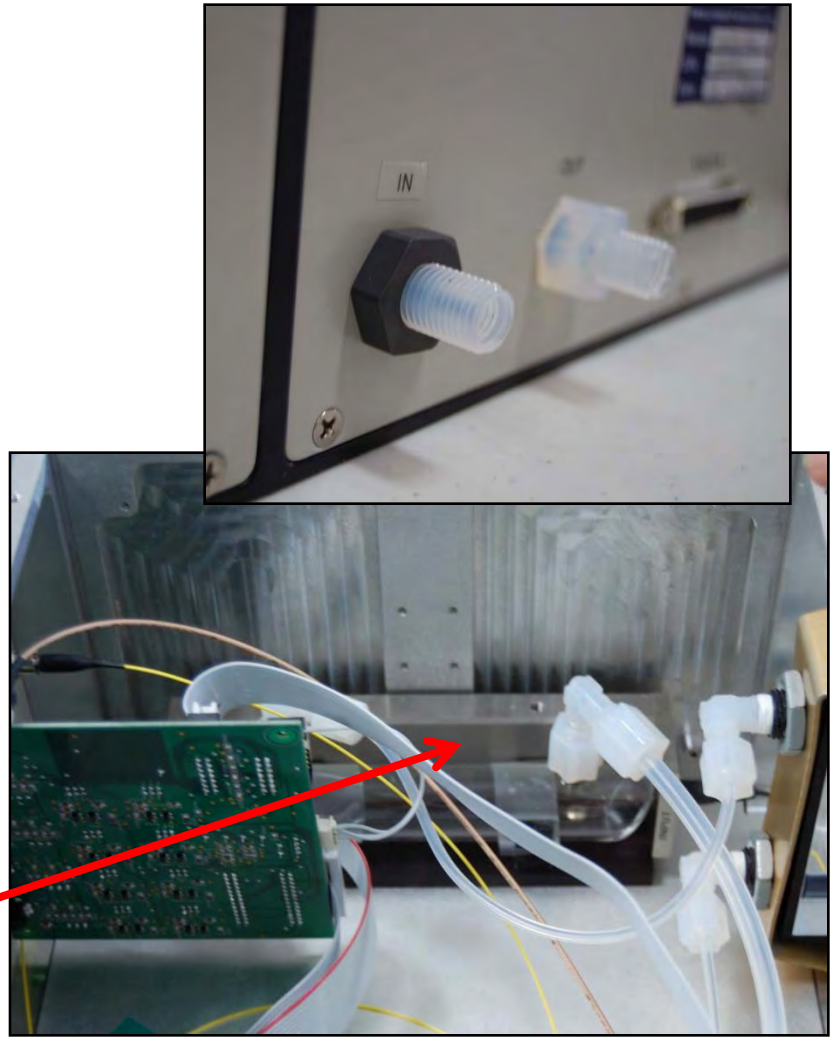
Tunable Diode Laser Measurement Technique



- **Higher laser powers allow beam expansion to attain alignment stability**
- **By de-focusing the beam, overfill of the detector optics allows for alignment changes**

Tunable Diode Laser Internal Audit Method

- Dynamic spiking audit
- Temperature correction factor used to account to difference between flow through cell and flue gas temperatures



Tunable Diode Laser Purge Options

Instrument Air

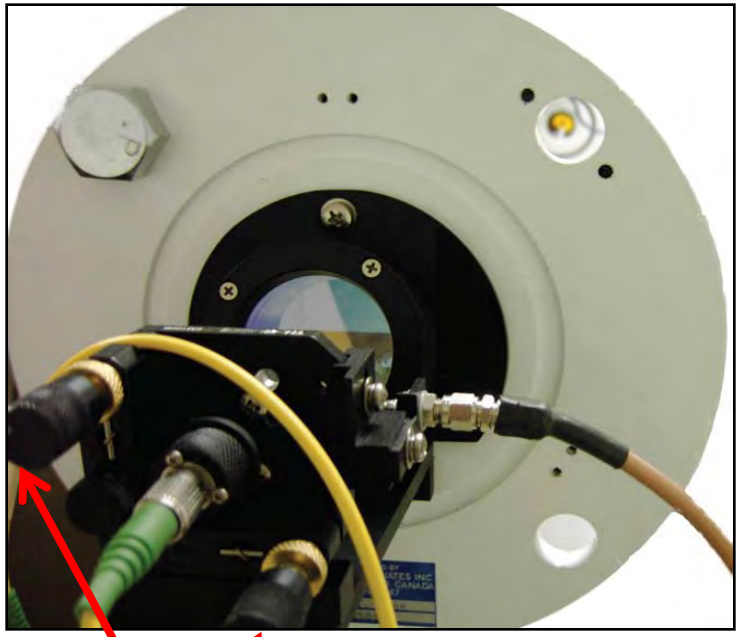
Opacity Type Blower

Tunable Diode Laser Maintenance & Adjustment

Maintenance

Lens Removal for Cleaning

Alignment

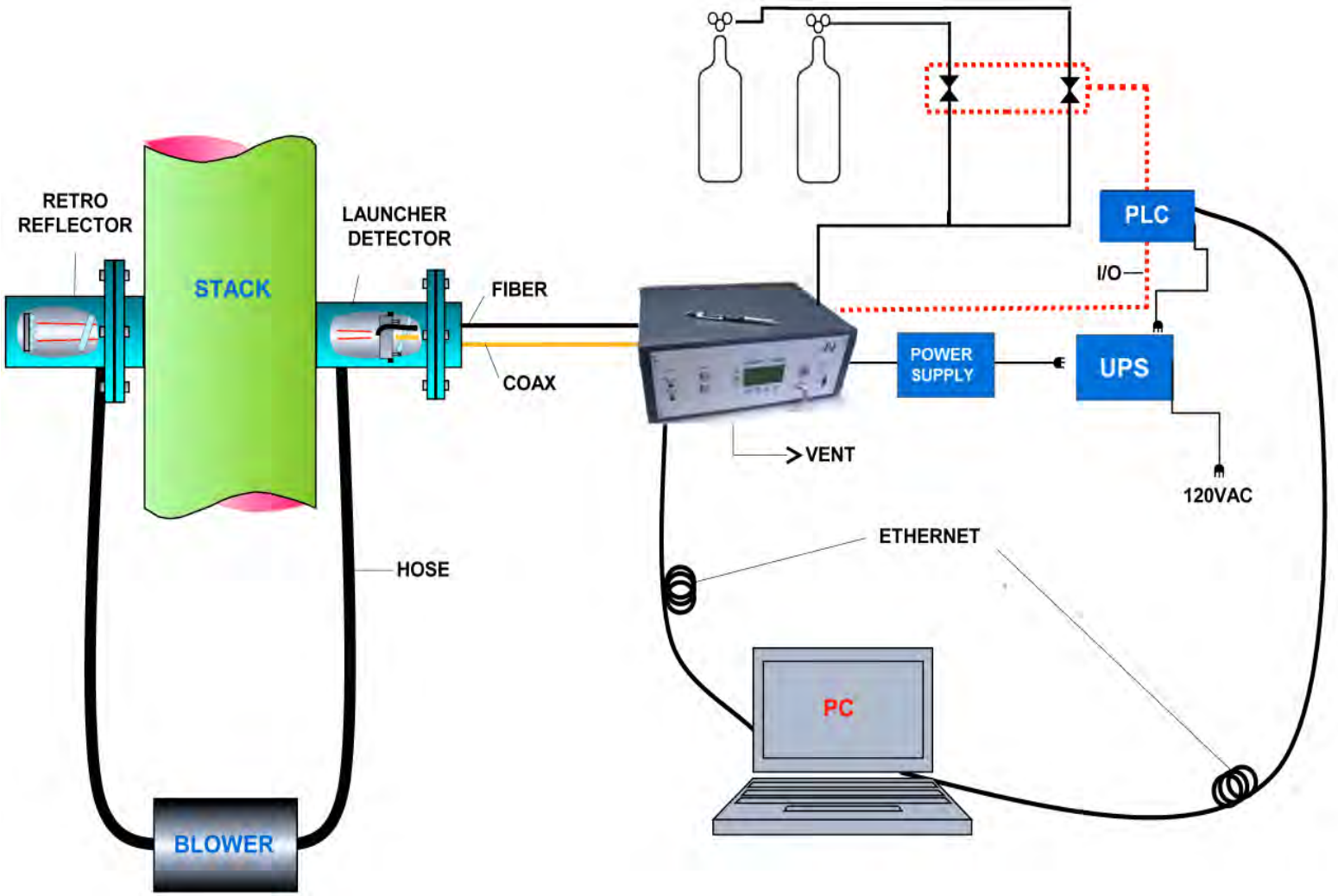


Micro Adjustment Screws

Tests conducted PS 18 for Integrated Path (IP) CEMS

- Interference Test
- Limit of Detection (LOD) Determination
- Response Time Test
- Calibration Error (CE) Test
- Seven Day Calibration Drift Test
- Stratification Test
- Relative Accuracy Test or Dynamic Spiking Test

HCl TDL Test Configuration



HCl TDL Test Configuration

PS 18 for IP-CEMS Interference Test

Test Gas	Interference (ppm_v)
CO_2	0.079 ± 0.13
CO	-0.0053 ± 0.0036
CH_4	-0.13 ± 0.05
NO_2	Not Tested
SO_2	0.071 ± 0.057
O_2	0.06 ± 0.09
H_2O	Not Tested
Nitrogen	

PS 18 for IP-CEMS Interference Test

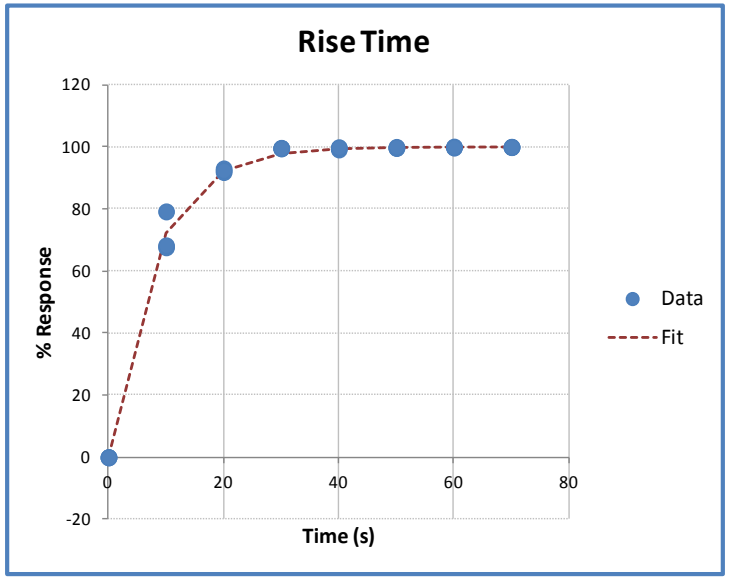
- Follow-up / Additional Testing
- Re-test the conditions above with the proper temperature and pressure conditions.
- Re-test to include the omitted test gases as they were not available on hand to measure.
- Increase the integration time to 1 minute or more from 10 seconds to improve the detection limit. This will not be required if the path length is increased such that the detection limit is lowered sufficiently.
- Have a method of automating the switching of the calibration gases via a manifold. This will speed up the data acquisition portion of the test.

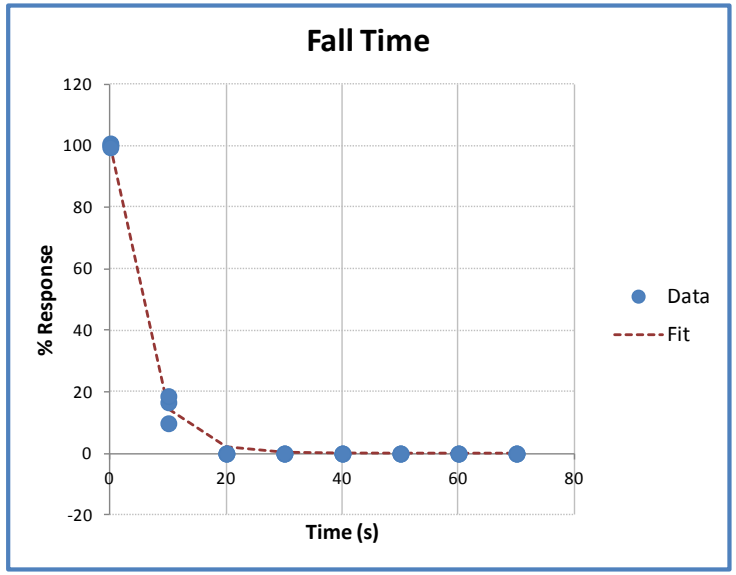
PS 18 for IP-CEMS
Limit of Detection (LOD) Test

- Successively decreasing spike gas concentrations into in-line audit cell by means of diluting the 318 ppm audit gas.
- Diluted spike concentration of 9.9 ppm is equivalent to an effluent HCl concentration of 0.165 ppm and was clearly distinguishable from the zero HCl concentration response of -0.005 ppm observed for the effluent after the spike was discontinued.
- The LOD for the TDL system as installed under real world conditions is **≤ 0.16 ppm**.
- Lower concentrations were spiked into the audit cell, however it was difficult to distinguish the presence of the response from the apparent zero value.

PS 18 for IP-CEMS
Response Time Test

Test Run	Rise Time (s)	Fall Time (s)
1	25.10	16.24
2	25.14	17.20
3	19.74	12.81
Average	23	15
Standard Deviation	3	2





PS 18 for IP-CEMS
Calibration Drift (CD) Test

Day	Date	HCl Baseline (ppm)	Analyzer Response (ppm)	Analyzer Spike Response (ppm)	Expected Response at T_{avg} (ppm)	Cal. Drift
0.0	10/16	-0.00001	5.322	5.322	5.195	0.42%
1.0	10/17	5.45112	11.888	6.437	6.170	0.89%
2.0	10/18	-0.00034	5.585	5.585	5.366	0.73%
3.0	10/19	-0.00021	5.640	5.640	5.405	0.78%
4.0	10/20	-0.00105	5.596	5.597	5.410	0.62%
5.0	10/21	-0.01180	5.277	5.289	5.248	0.14%
6.0	10/22	0.45991	7.136	6.676	5.896	2.60%
7.0	10/23	0.00377	5.787	5.783	5.374	1.36%
8.0	10/24	0.00068	5.778	5.778	5.435	1.14%

PS 18 for IP-CEMS Relative Accuracy Test

Test Condition	Two Mills On	Two Mills Off	Two Mills Off	One Mill On	One Mill On
# of Runs	9	18	15	17	14
Standard Deviation	0.03	10.04	9.17	1.27	1.11
RM Avg	0.13	10.94	9.93	1.34	1.20
Average Difference	-0.10	-0.90	-0.76	-0.06	-0.09
Standard Deviation	0.04	0.43	0.30	0.36	0.13
Confidence Coefficient	0.03	0.22	0.17	0.19	0.07
Relative Accuracy	104%	10.2%	9.3%	18.7%	13.6%
Relative Accuracy ppm	0.13	-	-	0.25	0.16
Emission Standard	3	-	-	3	3
Relative Accuracy % of STD	4.4%	-	-	8.3%	5.5%

Conclusions

- Interference Test was incomplete and further testing will be conducted
- Limit of Detection (LOD) Determination showed for this installation to be ≤ 0.16 ppm
- Response Time Test indicates the TDL is rapid in response to gases introduced to the flow through cell < 25 seconds
- Calibration Error (CE) Test was formally conducted
- Seven Day Calibration Drift Test showed the TDL was repeatable over eight consecutive days and within 3% of expected response
- Stratification Test was not conducted (no evidence of any)
- Relative Accuracy Test or Dynamic Spiking Test results showed the TDL RA was <20% of the RM or <10% of the emission standard

Questions?

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