Tunable Diode Laser (TDL) Based Hydrogen Chloride Gas (HCl) Continuous Emission Monitoring System (CEMS) Developments To Meet EPA's Draft Performance Specification 18

Presented at EUEC 2015
By
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A technical solution to meet every need

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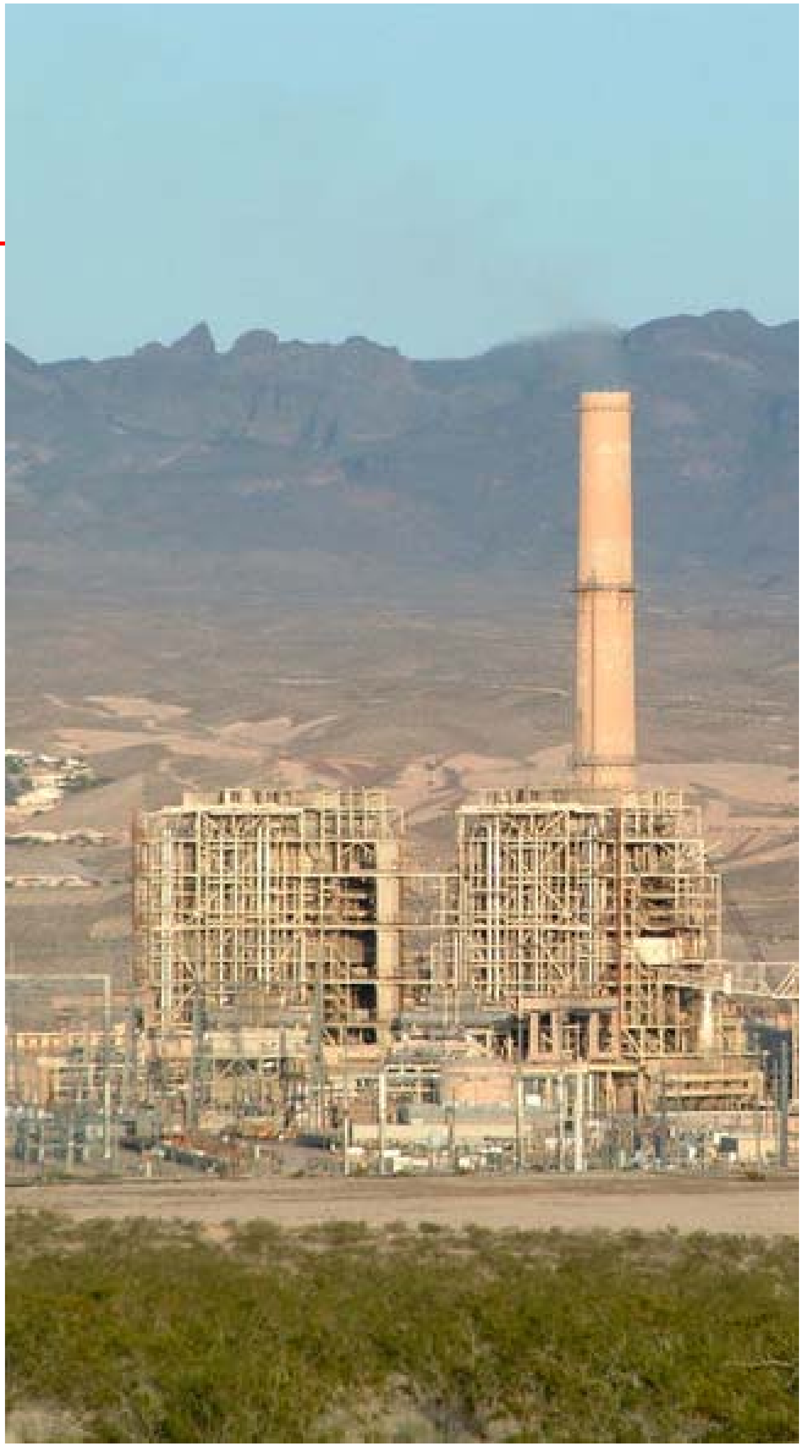


Outline

- Introduction – HCl Market Drivers
- HCl Monitoring Challenges
- Tunable Diode Laser (TDL) Technology
- TDL Theory of Operation & Technique
- Installation & Operating Advantages
- Calibration Features
- PS 18 for IP-CEMS Compliance Tests
- Draft Performance Specification 18 Tests
  - Interference Test
  - Limit of Detection Test
  - Response Time Test
  - Calibration Error Drift Test
  - Light Attenuation Test
  - Relative Accuracy Test Audit (RATA) Results
- Summary

Introduction – Drivers for Development of HCl CEMS

- **EPA Regulations:**
- **MATS: Mercury and Air Toxics Standards, 40 CFR Part 63 Subpart UUUUU**
- **PC MACT: Portland Cement Maximum Achievable Control Technology, Maximum Achievable Control Technology 40 CFR Part 63 Subpart LLL**
- **Boiler MACT: (40 CFR 63, subpart JJJJJJ**
  - **Emission Limits for Hydrogen Chloride (HCl) as a surrogate for all toxic acid gases**
    - **Performance Specification 18 developed - Performance Criteria Specific, not technology specific**
- **HCl Process Monitoring**
  - New mines in Illinois, western Kentucky, and Indiana have high Chlorine content
    - Chlorine could will increase HCl production in the boiler.
    - Chlorine induced boiler tube Corrosion

HCl Difficult to Measure

- **Water Soluble and Reactive gas**
  - **HCl removed and Reacts forming Acid Mist**
- **Maintaining temperature can be difficult**
- **Absorption onto components**
- **Potential leak issues**
- **Analyzer items**
  - **Potential Contamination & corrosion**
  - **Ultra low LOD limits – 0.2 ppm**
  - **Correcting for Interference background gases**
  - **Response time can be slow due to sample line lengths and dilution probes**
  - **Calibration gas availability for low levels**

✓ **Cross Stack TDL Monitor shown to be very successful overcoming HCl monitoring challenges**

TDL Proven HCl Monitoring Technique

- Tunable Diode Laser Absorption System TDLAS utilizing Cross Stack Measurement Technology -
- UNISEARCH first to develop TDLAS, with most experience
- Teamed up with CEMTEK 2004
- We have many HCL systems currently installed and operating in field at Coal Fired Power Plants

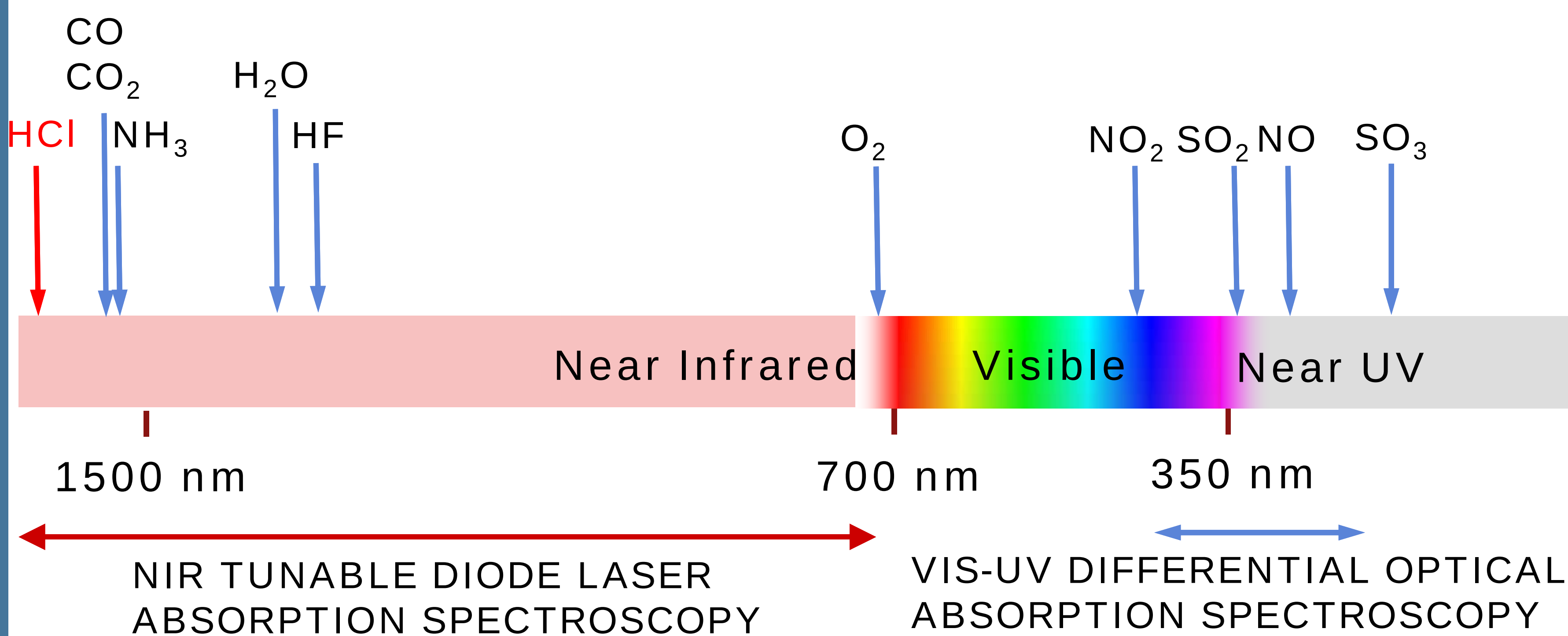
Basic Concepts of Optical Detection

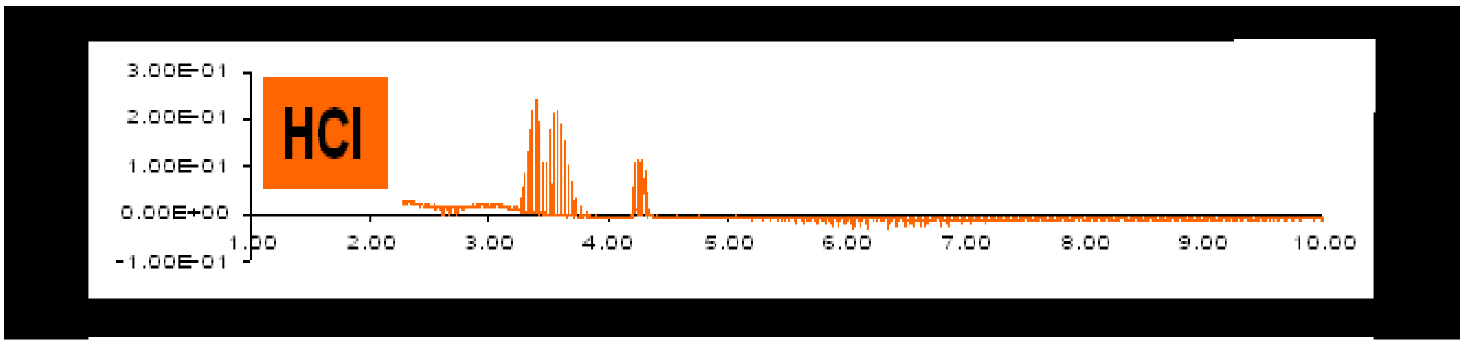
- **Most molecules absorb infrared (IR) light**
  - **The patterns of IR wavelengths (colors) they absorb are unique to each molecule**
  - **The amount of light they absorb is proportional to their concentration**

- **As a result:**
  - **The presence of specific compounds can be unequivocally determined by the absorption patterns**
  - **The concentration of the compounds can be measured by the strength of the absorption patterns**

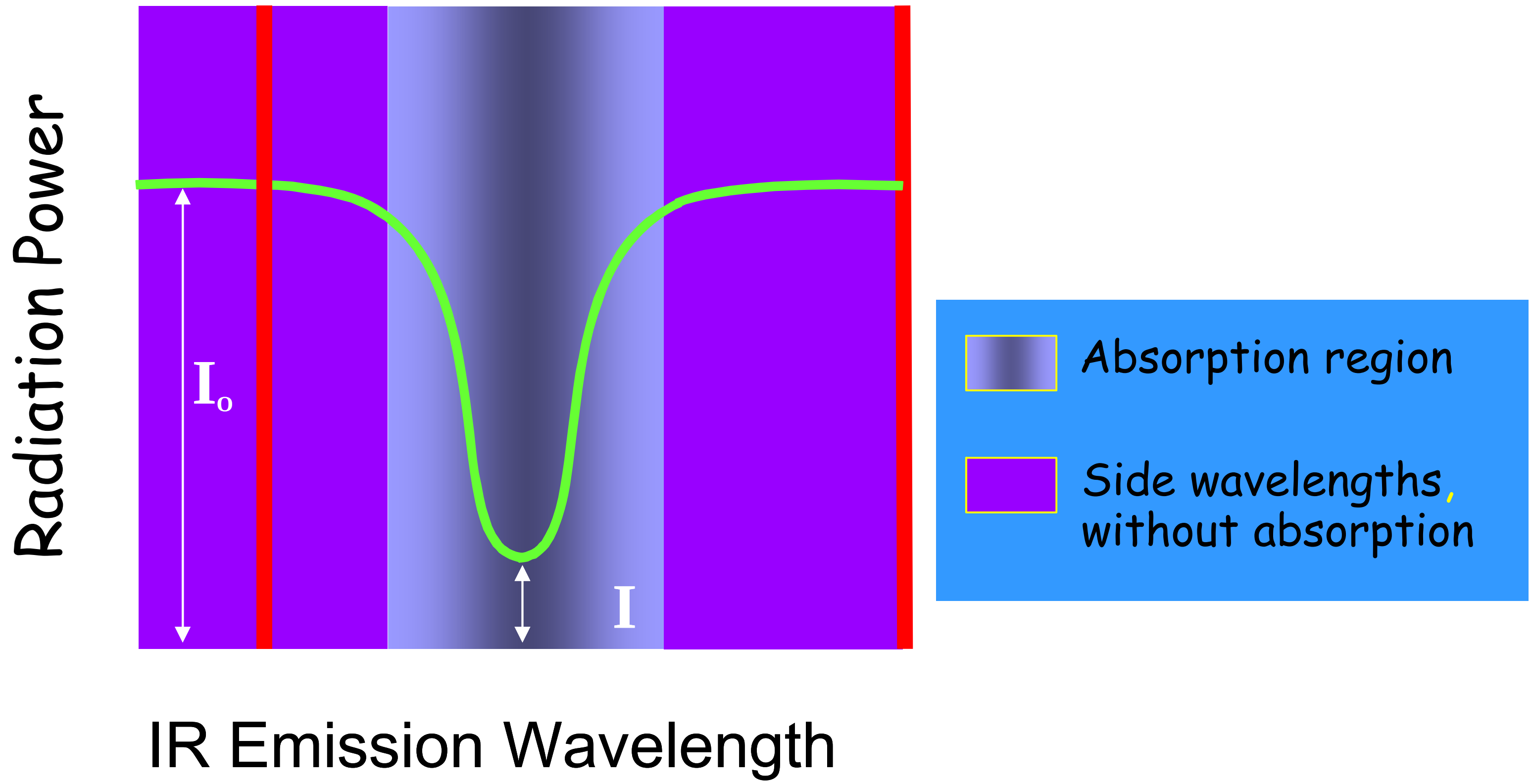
- **TDL, FTIR, NDIR, GFC, DOAS all use this principle**

Tunable Diode Laser Measurement Technique





TDL: What's happening at wavelength scale



Spectroscopy: Beer-Lambert Law

- **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**

TDL System Components

- **DIODE Laser**
- **Reference Cell**
- **Multiplexer**
- **Audit Cell**
- **In-situ Optics (stack/duct) Single pass, dual pass**
- **Flow Thru Calibration Gas Audit Cell**

Diode Laser

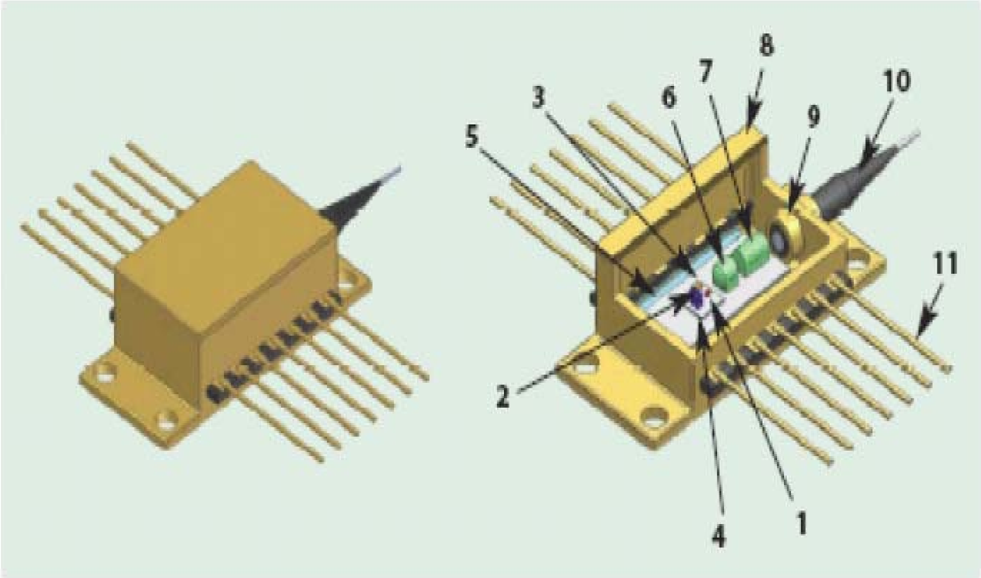


Figure A-7
Typical Type of DFB (Distributed Feedback) Laser that is Fiber Coupled in a Butterfly Package for Telecom and Spectroscopic Applications, Showing the Laser Chip (1), Monitor Photodiode (2), Thermistor (3), Chip Carrier (4), Thermoelectric Cooler (5), Lens (6), Optical Isolator (7), Component Package (8), Window for Light Output (9), Fiber Pigtail (10) and Electrical Leads (11)

Reference Signal

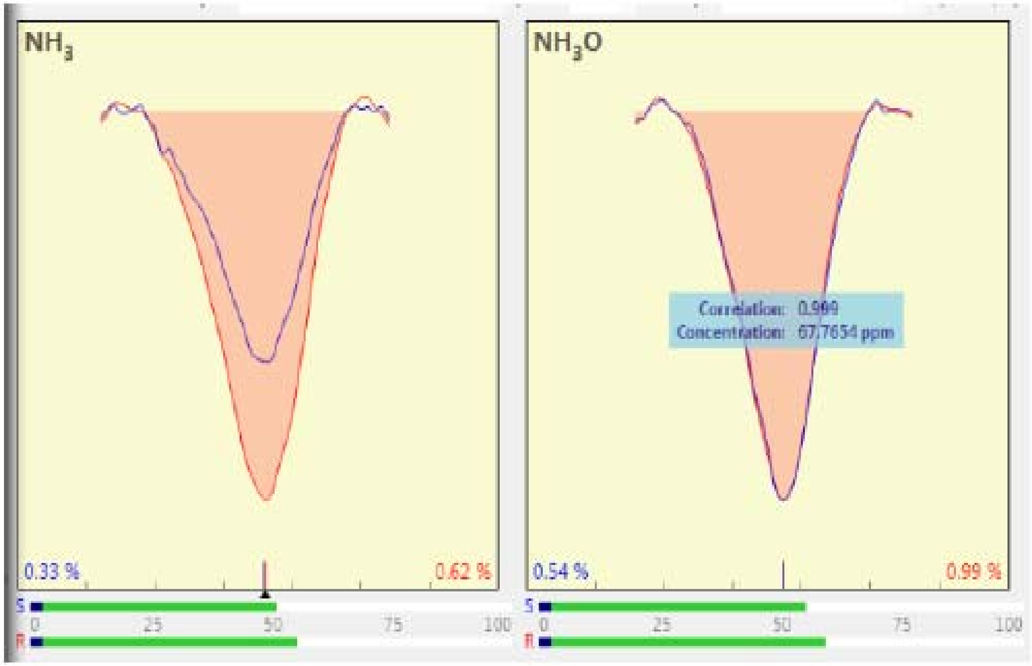


Figure A-10
Reference Cell (Red) Response which has 5% of the Laser Light, and the Measured Paths (Blue) which has 95% of the Laser Light

Tunable Diode Laser Reference Cell / Audit Method

Internal Audit Module

- **TDL Reference cell – Tuned allowing line lock - No calibration requirements**
- **Module spiked with known amount of target gas**
- **Isolated cell measurement**

Internal Audit Module

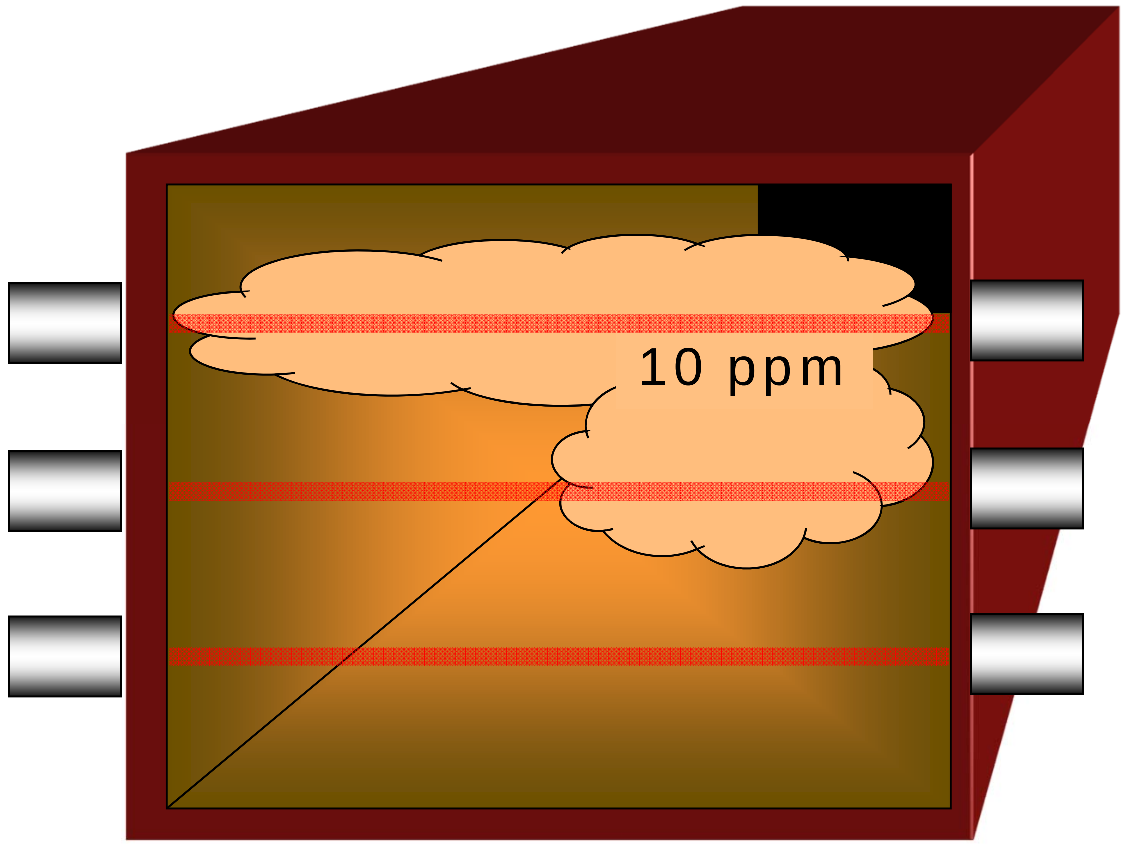
Multiplexed Optical Signal

- **The near IR TDL used by Unisearch has its emission fiber coupled**
- **This has the very advantageous feature of being able to incorporate optical elements as beam splitters and multiplexers to direct the beam over multiple paths.**
- **A multiplexer can direct the optical signal for a multi-path array configuration with up to eight lines of sight**
- **Multiplexing splits the signal by time instead of power**
    - **Multiplexing sends approximately 95% of signal power to each measurement path, with 5% being used as a reference**
    - **Competitors use Beam splitting which sends approximately 25% of signal power to each measurement path (4 path array) which limits optical path lengths to short distances in coal-fired power plant applications**
- **Multiplexed optical signal allows for not only use in heavy dust laden applications with longer path lengths but is very cost effective as one instrument needs to have only optical elements mounted on the stack or duct with the instrument fiber coupled to the elements but in a thermally controlled environment.**

Cost Effective

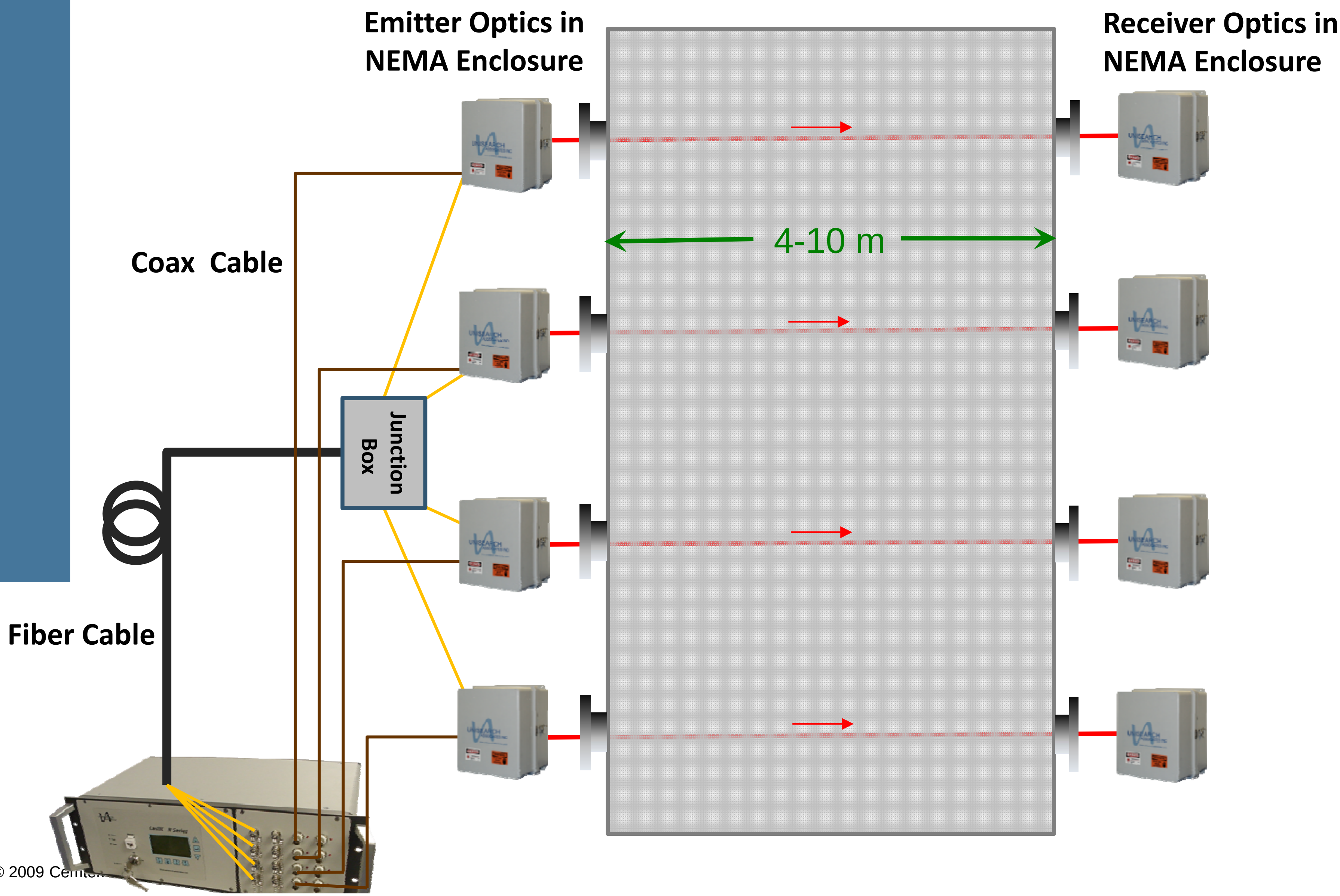
Figure A-12
4-channel Multiplexer

Multi-Path Array Configuration



Measurement is integrated over path length

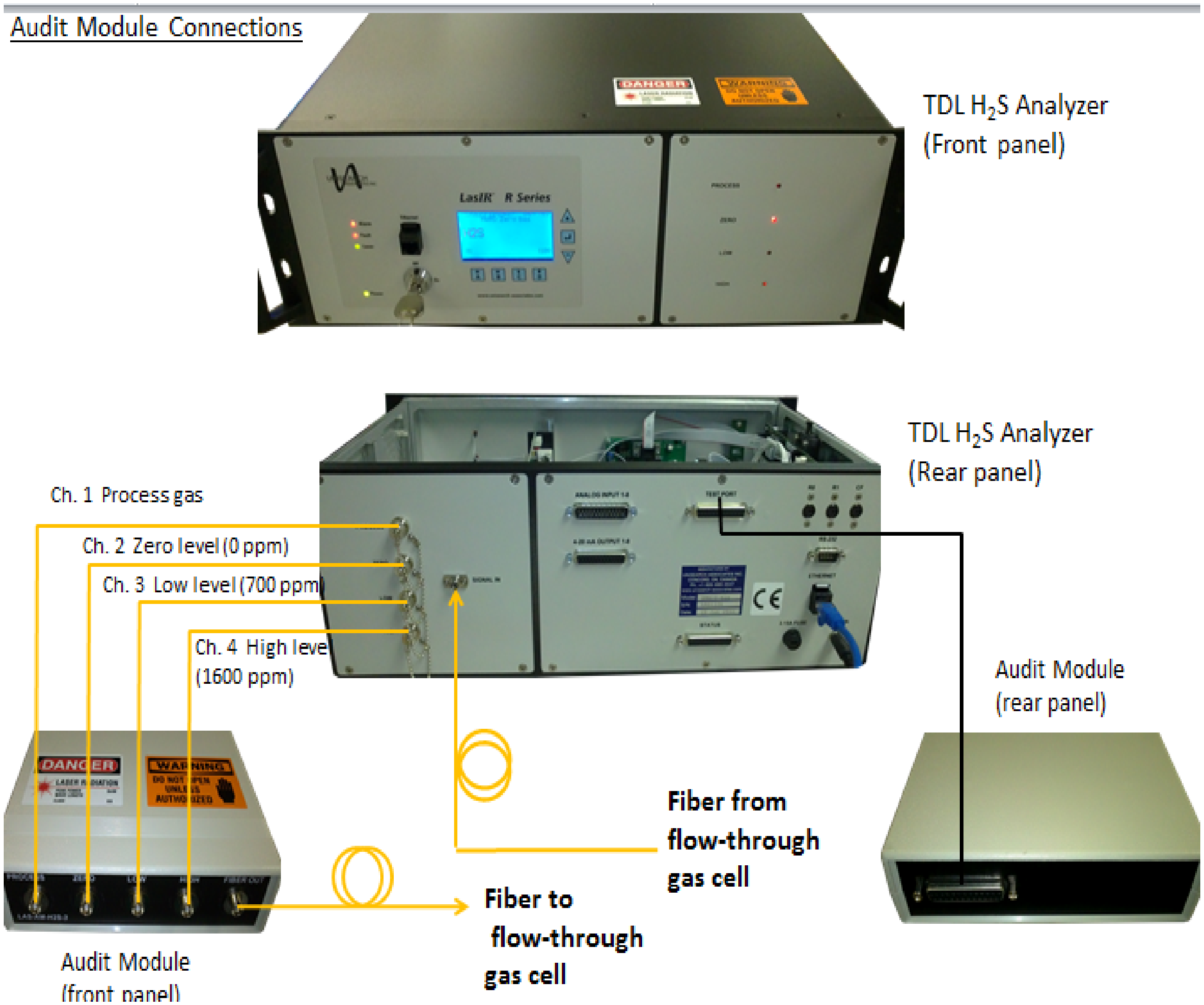
Multiplex Array Example



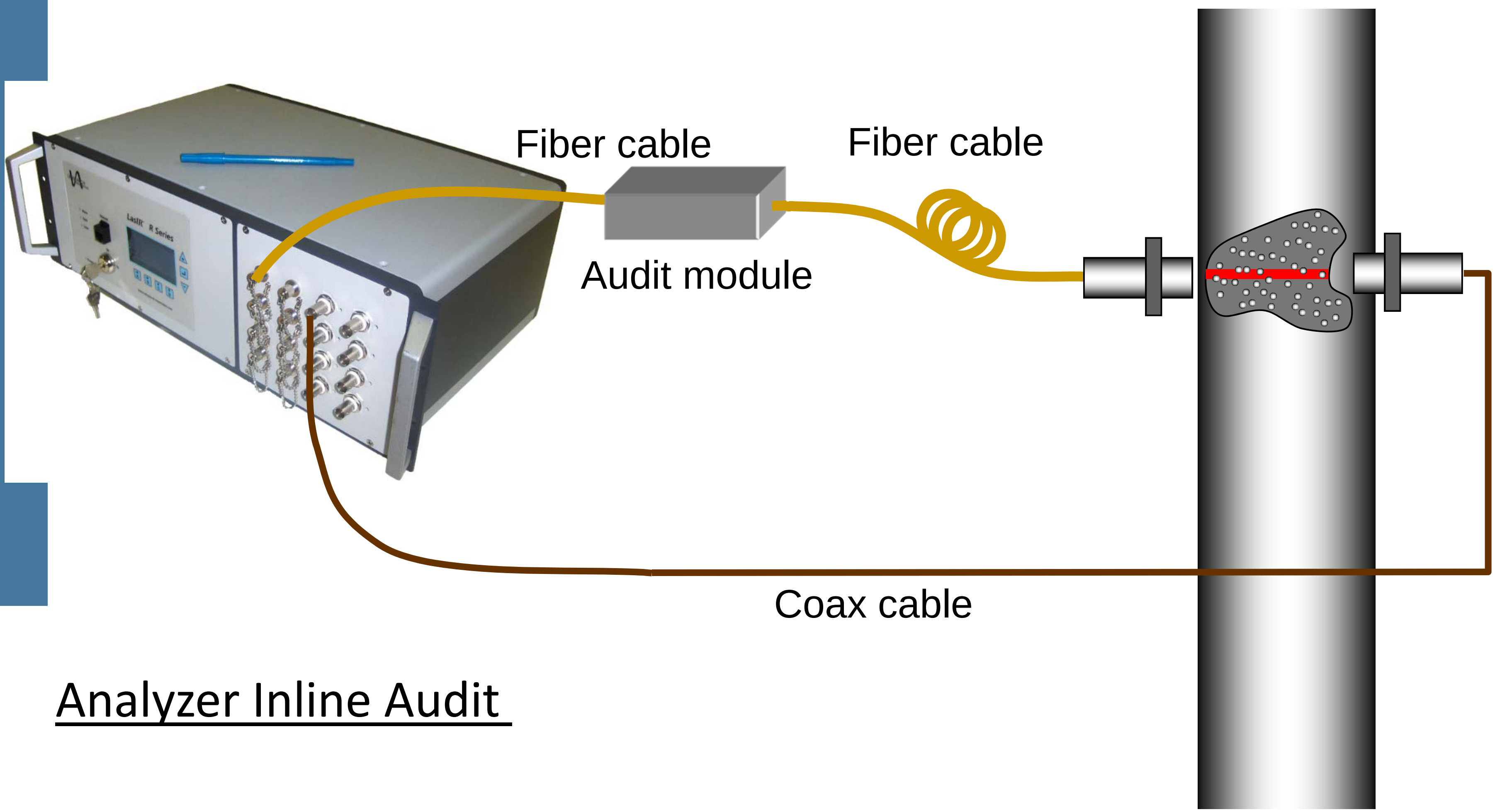
Multiplex Array Installation

Audit Cell Instead of Gas

- **Pictured is one example of the use of audit cells instead of calibration gas**
- **Three levels are used, one at zero, second at 700 ppmV (low) and third at 1600 ppmV (high)**

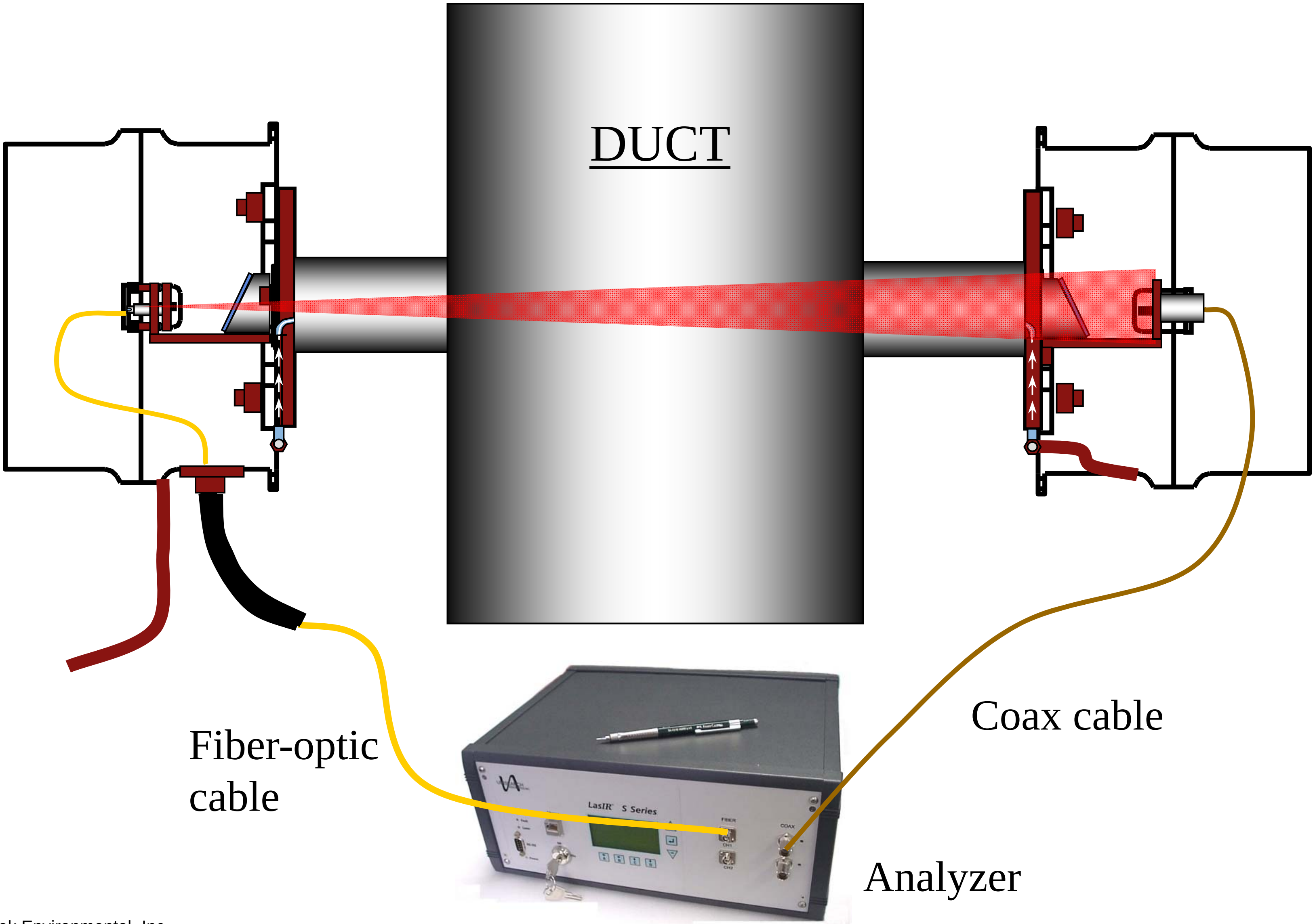


Audit Cell Inline Audit

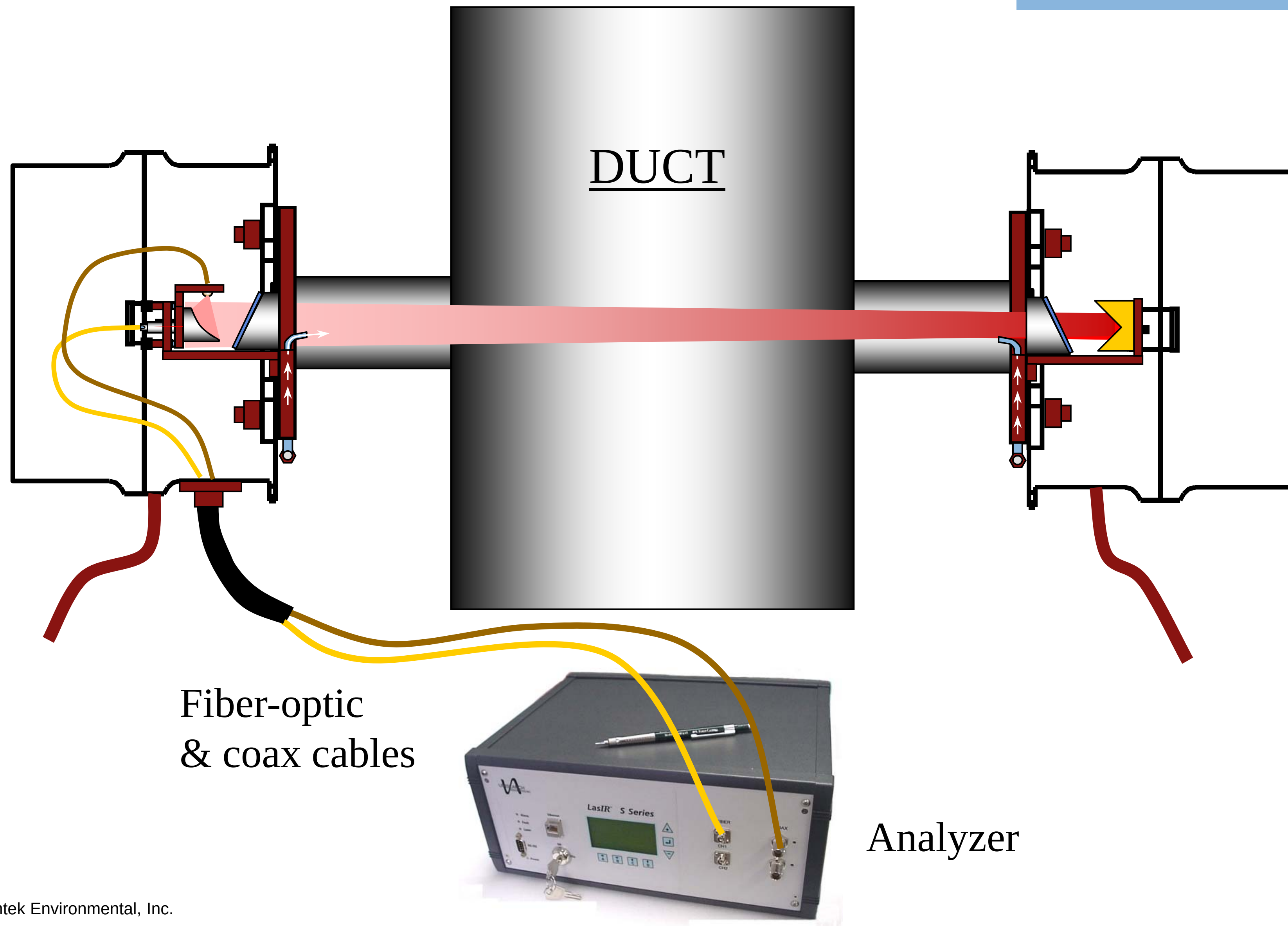


Analyzer Inline Audit

Single Pass Bistatic Stack Configuration

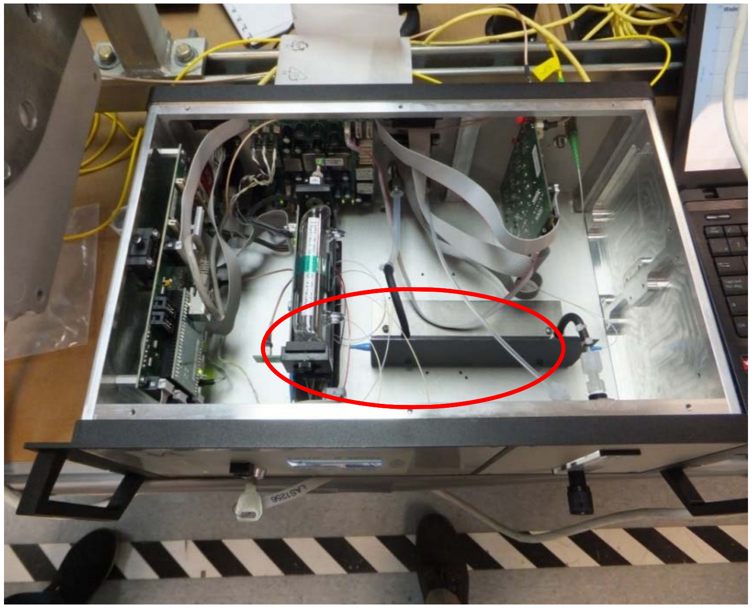


Dual Pass Monostatic Stack Configuration

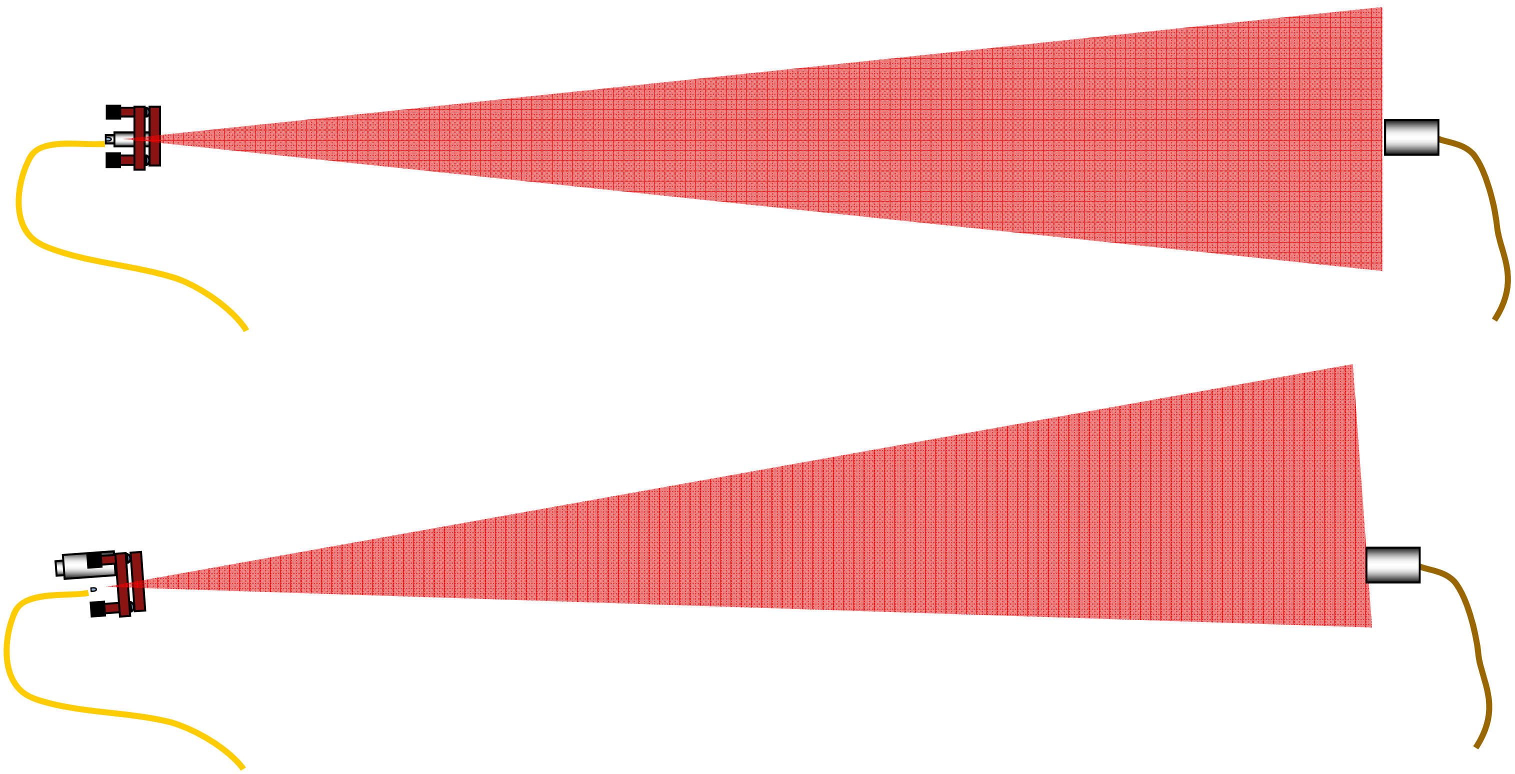


Dynamic Spiking Flow-thru Calibration Cell

- Internal to analyzer
- Used to flow Cylinder gas of known concentration of HCl gas
- Directly connected inline with stack optics
- Does not require Ultra Low HCl calibration gas. 40ppm vs 4 ppm
  - NIST gases available at higher ranges



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**

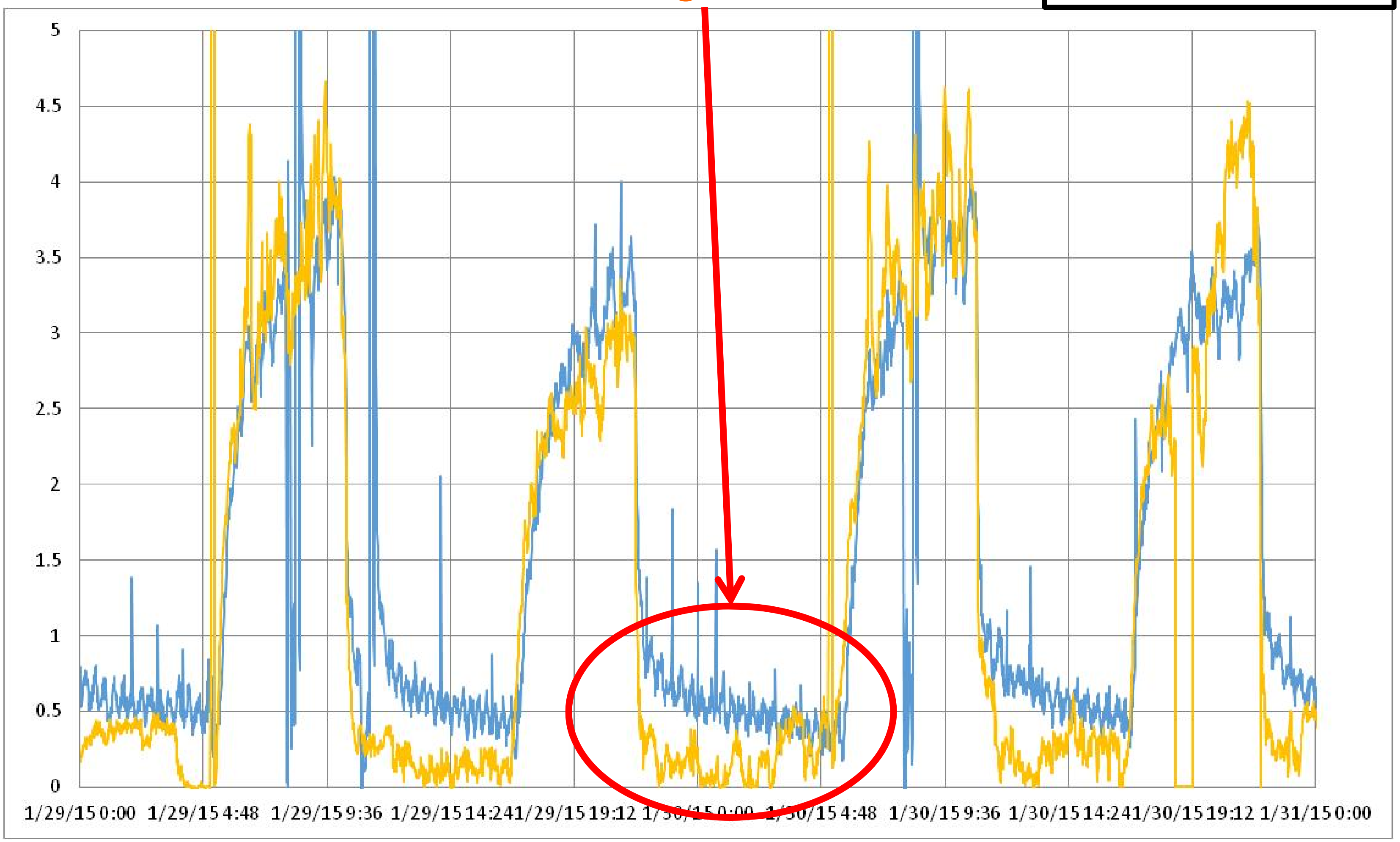
Data Comparison with Hot/Wet Extractive FTIR

Quick Response

No Lag Time

TDL HCl

FTIR HCl

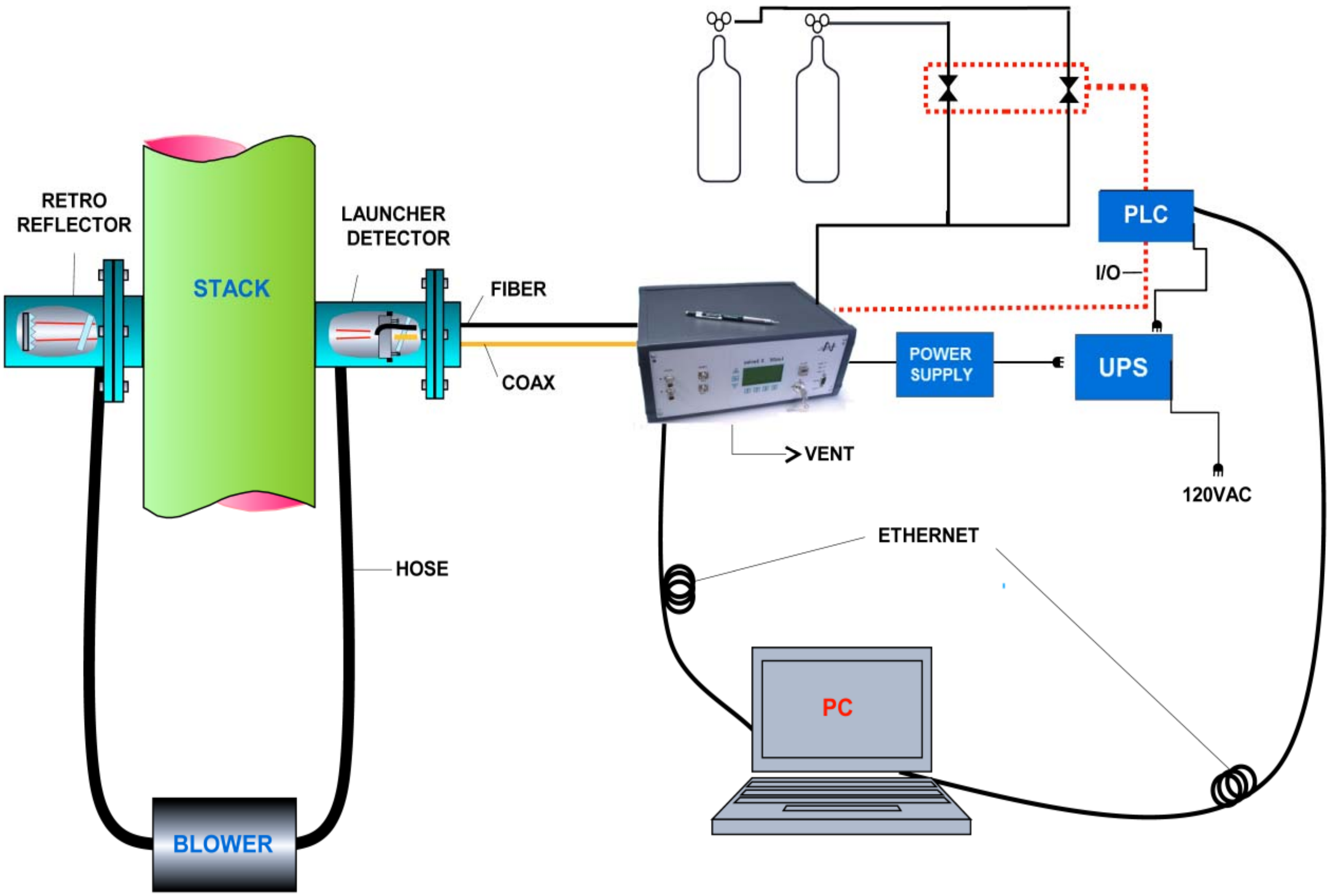


PS 18 for IP-CEMS Compliance Tests

- **Interference Test**
- **Limit of Detection (LOD) Determination**
- **Response Time Test (No longer required for IP-CEMS)**
- **Calibration Drift Test**
- **Calibration Gas Audit CGA Test**
- **Light Attenuation Test**
- **Relative Accuracy Test or Dynamic Spiking Test**

- **Note Stratification Test was not conducted**

PS 18 for IP-CEMS
HCl TDL Test Configuration



PS 18 for IP-CEMS
HCl TDL Test Configuration

PS 18 for IP-CEMS Interference Test (no HCl)

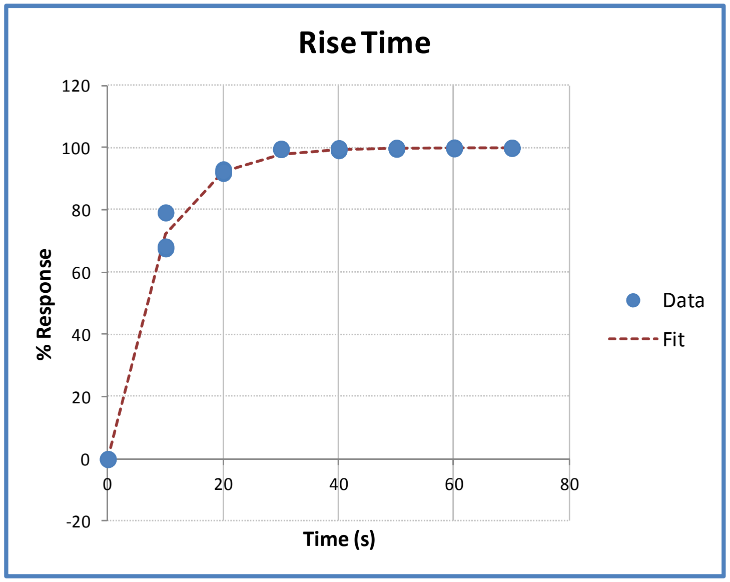
Test Gas	Interference (ppmv)
CO_2	0.079 ± 0.13
CO	-0.0053 ± 0.0036
CH_4	-0.13 ± 0.05
NO_2	Not Tested
SO_2	0.071 ± 0.057
O_2	0.06 ± 0.09
H_2O	Not Tested
Nitrogen	

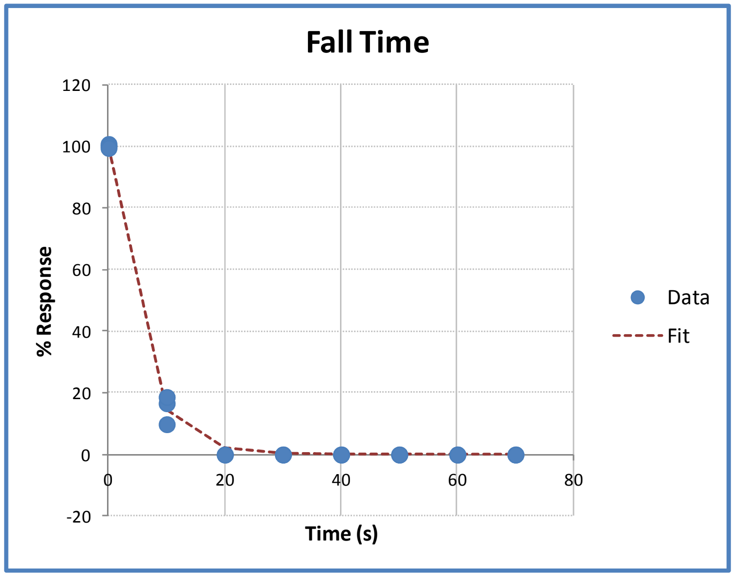
PS 18 for IP-CEMS – Limit of Detection LOD Test

- 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**.

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 Error Drift (CD) Test - Zero

Day	Date	HCl Zero Reading (ppm)	HCl Zero Reading Standard Dev	Cal. Drift
0.0	10/16	-0.00103	0.00008	0.00%
1.0	10/17	0.00000	0.00000	0.00%
2.0	10/18	0.00473	0.00126	0.02%
3.0	10/19	-0.00020	0.00009	0.00%
4.0	10/20	-0.00088	0.00012	0.00%
5.0	10/21	-0.01445	0.00076	-0.05%
6.0	10/22	0.00743	0.00073	0.02%
7.0	10/23	0.00212	0.00021	0.01%
8.0	10/24	0.00000	0.00000	0.00%

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

Day	Date	HCl Baseline (ppm) [A]	Analyzer Response (ppm) [B]	Analyzer Spike Response (ppm) [A-B]	Expected Response at Tavg (ppm) C=[A-B]Tavg	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 Calibration Gas Audit Test (Dry Stack)

	Cal gas Value ppmV	Type	HCl_Low ppmV	Percent Difference %		HCl_High ppmV	Percent Difference %
	0.00	Primary	0.00	0.00		0.00	0.00
	5.88	Primary	5.71	2.89%		5.88	0.00%
*1	15.17	Primary	14.30	5.74%		14.21	6.33%
	33.37	Primary	33.48	0.33%		33.44	0.21%
	0.00	Backup	0.00	0.00		0.00	0.00
	5.88	Backup	5.65	3.91%		5.74	2.38%
*1	13.69	Backup	13.70	0.07%		13.73	0.29%
	33.37	Backup	33.58	0.63%		33.51	0.42%

Note cylinder was changed after spurious results from first cylinder

Cylinder was older steel cylinder and replaced with glass lined alluminum cylinder

PS 18 for IP-CEMS
Calibration Gas Audit Test (Wet Stack)

Cal gas Value ppmV	Type	HCl_Low ppmV	Percent Difference %		HCl_High ppmV	Percent Difference %
0.00	Backup	0.00	0.00		0.00	0.00
1.61	Backup	1.68	4.35%		1.61	0.00%
3.61	Backup	3.84	6.37%		3.78	4.71%
5.73	Backup	5.79	1.05%		5.74	0.17%

PS 18 for IP-CEMS
Light Attenuation Test Results

Calibration Value ppmV	Power µW	% Reduction	% Transmission	HCL_LOW ppmV	Percent Different %	HCL_High ppmV	Percent Different %	Iris Size Diameter (in)
33.37	520	0.0%	100.0%	33.41	0.1%	33.51	0.4%	
33.37	215	58.7%	41.3%	33.58	0.6%	33.45	0.2%	
33.37	56	89.2%	10.8%	34.15	2.3%	34.06	2.1%	
33.37	32	93.8%	6.2%	32.8	1.7%	33.56	0.6%	
33.37	20	96.2%	3.8%	33.23	0.4%	33.85	1.4%	

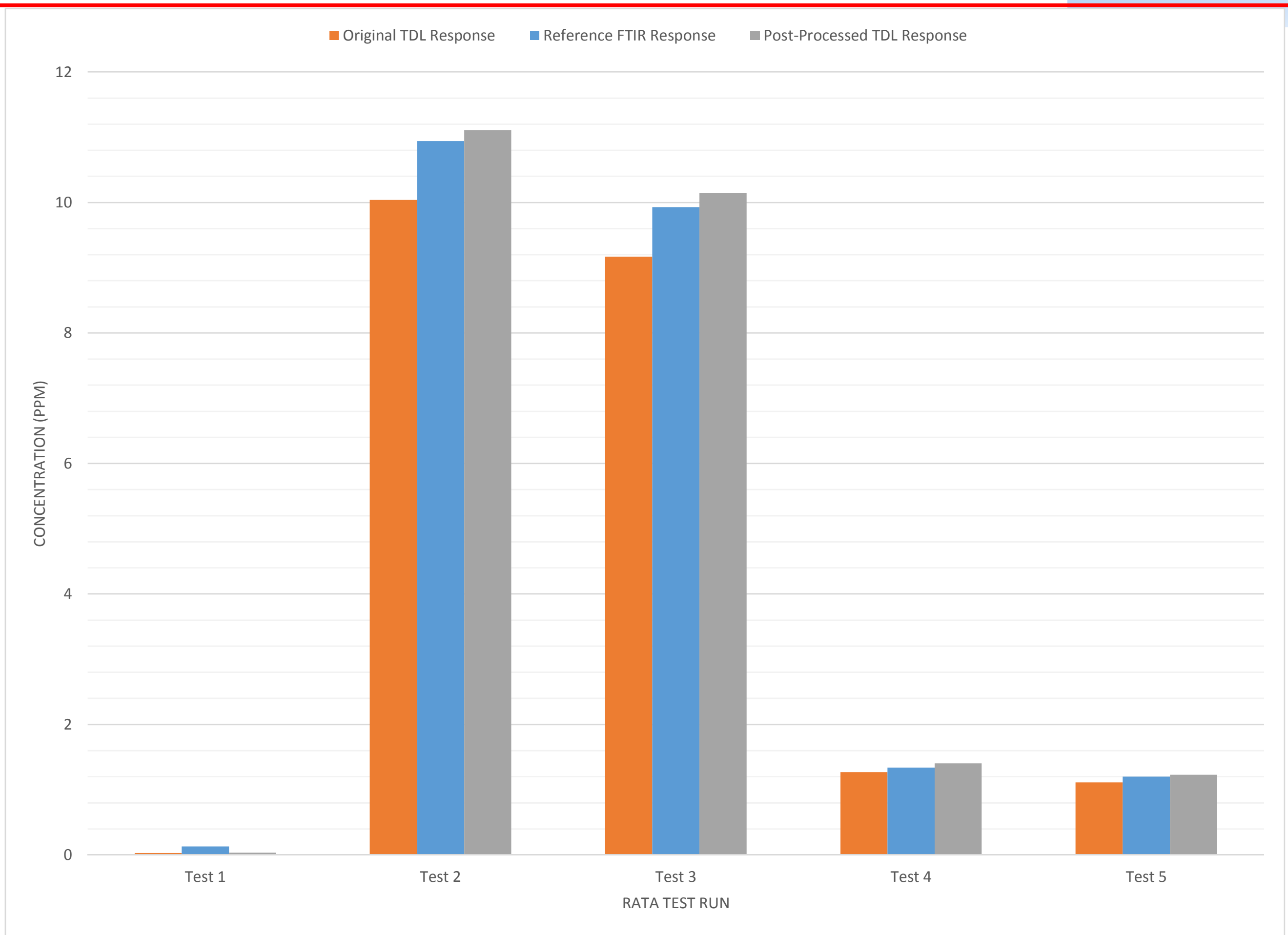
PS18 for IP-CEMS
Relative Accuracy Test Results

Test Condition	Two Mills On	Two Mills Off	Two Mills Off	One Mill On	One Mill On
# of Runs	9	18	15	17	14
CEMS Avg	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%

- **TDL RA was <20% of the RM or <10% of the emission standard**

Relative Accuracy Results at a Cement Plant via Method 321

PS18 for IP-CEMS Relative Accuracy Test Results



- **Relative Accuracy Test or Dynamic Spiking Test results showed the TDL RA was <20% of the RM or <10% of the emission standard**

Relative Accuracy Results at a Cement Plant via Method 321

TDL BENEFITS

The TDLAS is an accurate and reliable HCl monitoring system meeting Performance Specification 18 Certification Requirements (Draft)

- No interference from other gases
- No interferences from particles
- High sensitivity (ppb to percent levels)
- Fast response time (0.1 s and higher)
- Alignment stability
- Compact (3 – 5 kg)
- Relatively easy to install and operate
- Maintenance and Safety - TDL & Electronics located in Controller
- Multiplexing - cost effective
- No field calibration required (audit available)
- Path lengths - 0.1 m to a kilometer

Questions?

Cemtek Environmental, Inc.

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