



Proven Emerging Technologies

TDL, Hg, PM & Mass Emissions

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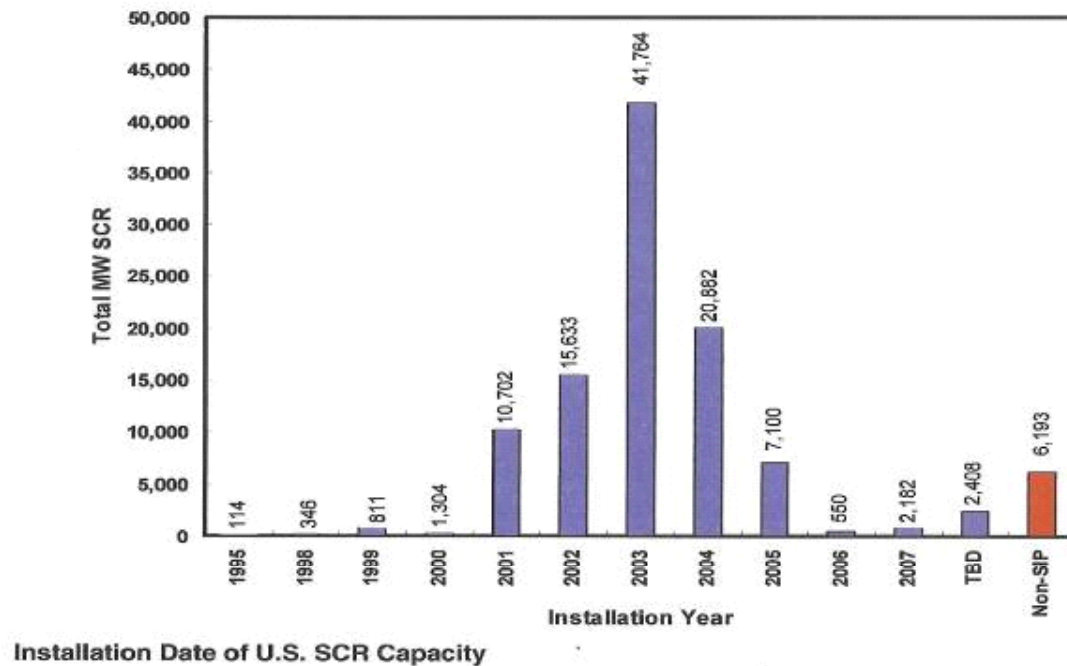
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SCR Deployment in the US

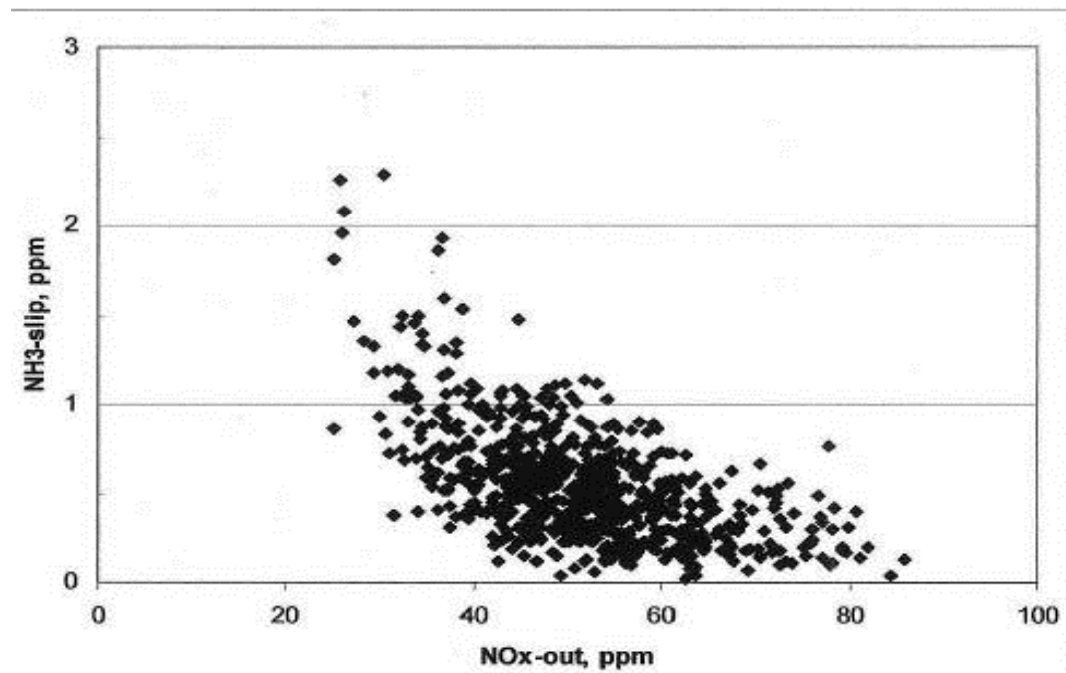
- The broad based deployment of post combustion NO_x control systems, such as SCR, in response to more stringent NO_x control mandates has highlighted the need for continuous ammonia monitoring capabilities.
- More than 100,000 MW of coal-fired utility boiler capacity has been retrofit with SCR technology.





Typical NH_3 Slip versus NO_x -Out

- Since the NO_x control mandates are typically represented by NO_x emission tonnage caps, increased NO_x reductions are often desirable, and can be achieved early in the catalyst life cycle through increased reagent injection, however this typically generates an increase in ammonia slip.





Why NH₃ Monitoring is Useful

Purpose for monitoring Ammonia (NH₃) Slip

- 1. Overall verification of efficiency for NO_x control**
- 2. Check of errors in over NH₃ injection**
- 3. Prevention of air preheater blocking specifically in minimization of ABS formation especially if using high sulfur coal**
- 4. Corrosion and maintenance of equipment**
- 5. Regulatory emissions limits for both NO_x and NH₃ slip**
- 6. Can be related to a measure of reduction of catalyst activity**
- 7. Economic Considerations:**
 - NO_x emission trading credit maximization**
 - Contamination of fly ash**
 - Cost of consumable ammonia/urea**

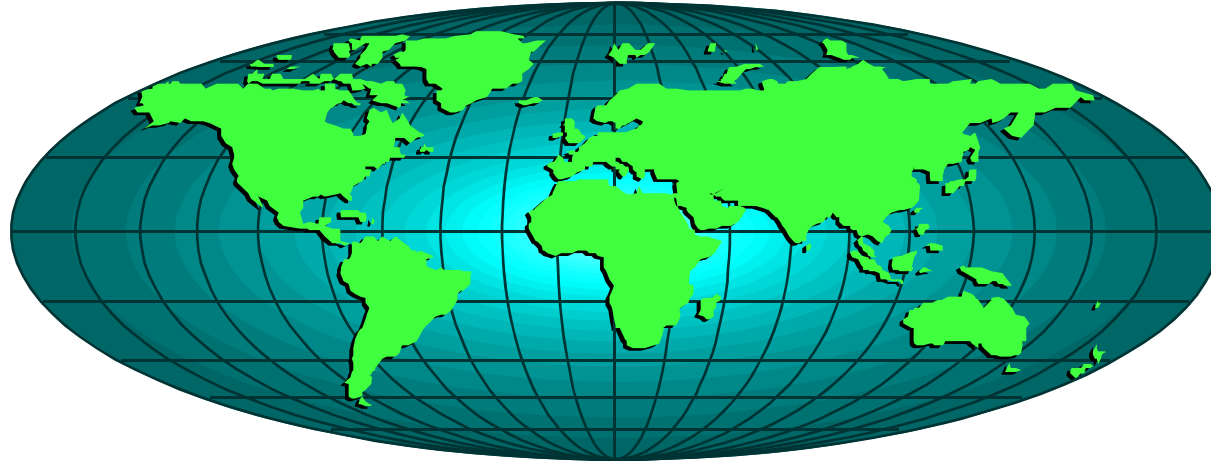


Outline

- **Introduction to Unisearch**
- **Basic Concepts of Optical Detection**
 - **Measuring NH₃**
 - **Tunable diode laser measurement technique**
 - **NH₃ spectrum of interest**
 - **Spectroscopy: Beer-Lambert Law**
 - **Fast scan direct absorption technique**
 - **TDL Detection limits**
 - **TDL's how they work**
 - **TDL: What's happening on the wavelength scale**
 - **Intensity (I) and (I₀)**
 - **TDL response**
 - **Bi-static configuration**
 - **Mono-static configuration**
 - **Beam expansion for alignment stability**
 - **Multiplexed optical signal, multi-path array configuration**
 - **Audit cell verification (internal and external)**
 - **Air purge options**
 - **Maintenance considerations and User Examples**



Unisearch TDLAS for NH_3



■ Unisearch

- Recognized as both pioneer and leader in tunable diode laser (TDL) spectroscopy
- Has many clients throughout the world especially in the coal-fired power industry
- Has worked extensively with EPRI in conducting projects where NH_3 monitoring has been required.



Basic Concepts of Optical Detection

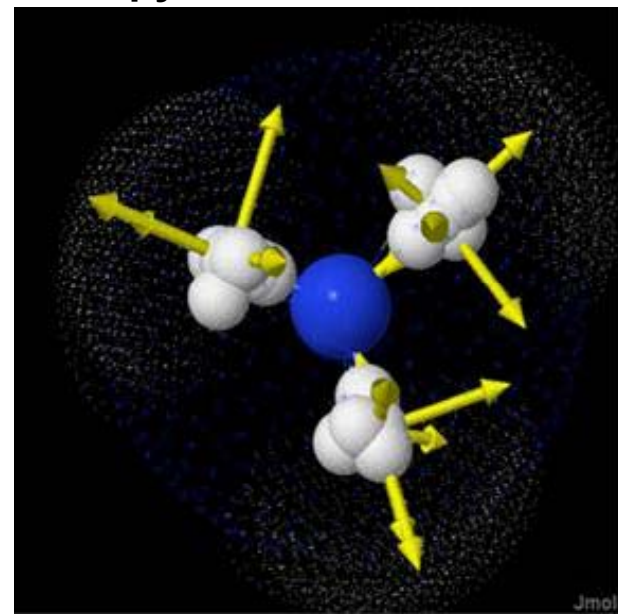
- **Most molecules absorb infrared (IR) light**
 - **The patterns of IR wavelengths (colors) they absorb are unique to each molecule**
 - **The amount of light they absorb is proportional to their concentration**

- **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**



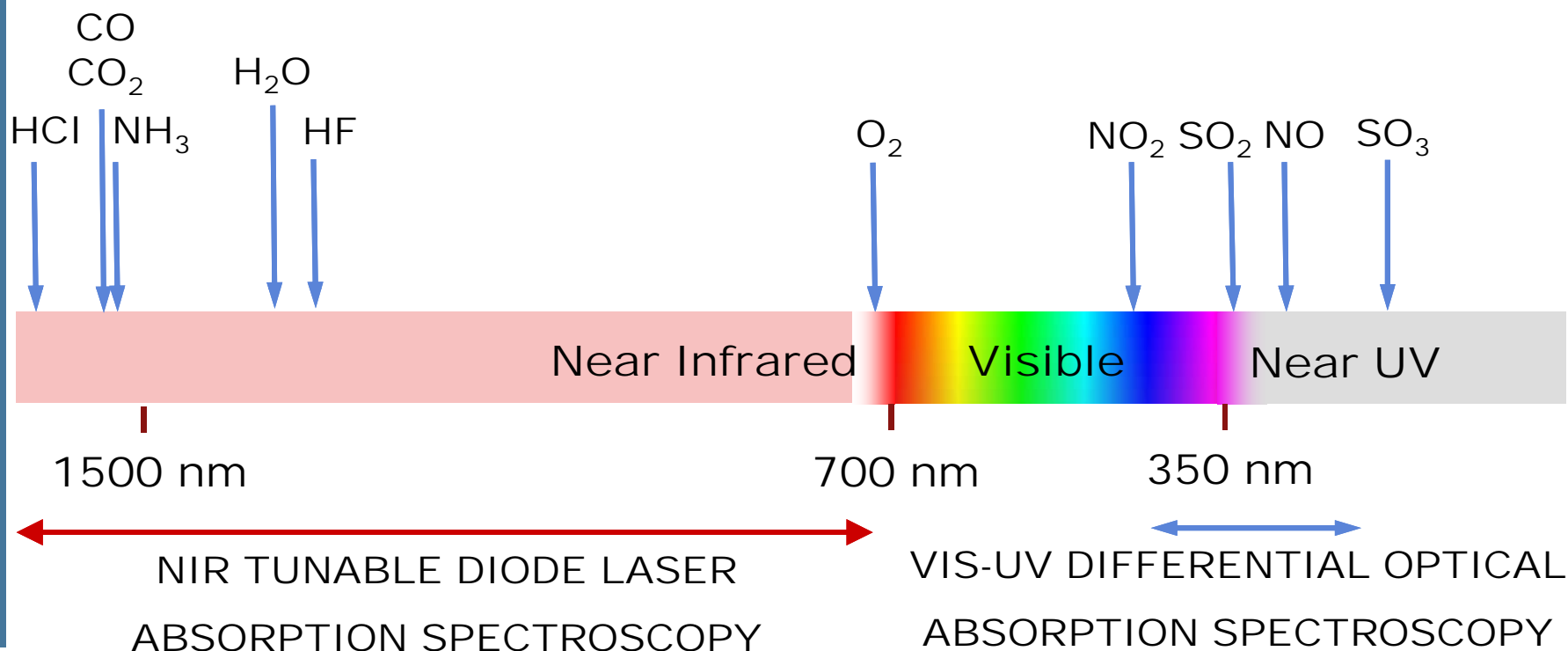
Measuring NH₃

- Diode lasers are ideally suited for overtone spectroscopy of molecules with chemical bonds such as C-H, O-H, and N-H in the near-IR region ~0.78–2.5 μm .
- Figure shows the dynamics of a NH₃ molecule which has a rich spectrum in the near-IR region.
- These spectral absorption features are from the vibrational and rotational characteristics of this molecule as it absorbs energy of a specific wavelength.
- In just the spectral range from 1450 to 1560 nm ~;6400–6900 cm^{-1} , 381 lines due to rotational–vibrational transitions in the combination band n1 to n3 and the overtone band at 2n3 have been characterized.
- Characterization has examined these lines for interferences, specifically moisture, and currently the best lines for monitoring purposes with near IR ammonia measurements are the lines at 1512.3 and 1514.1 nm.





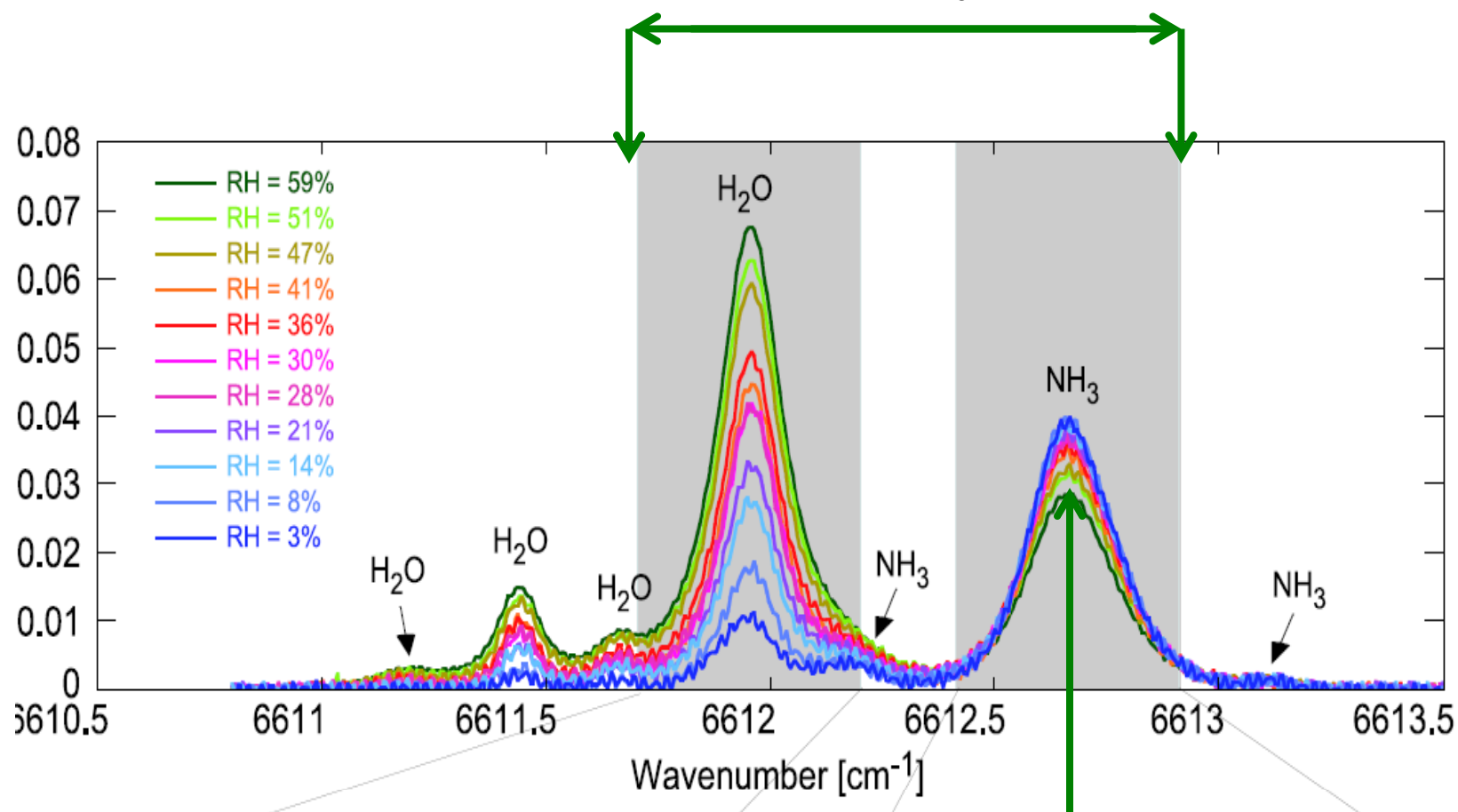
Tunable Diode Laser Measurement Technique





NH₃ Spectrum of Interest

Laser scanning range measures NH₃ and H₂O concurrently



Laser currently used by Unisearch



Spectroscopy: Beer-Lambert Law

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

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

- where

- I = transmitted power
- I_0 = incident power
- L = path length [cm]
- N = concentration [# molecules / cm³]
- $\phi(\Phi)$ = absorption cross-section of molecule [cm² / molecule]

- Which provides a simple mathematical solution as:

- I and I_0 are measured by the analyzer
- Path length, L , and absorption coefficient, $\phi(\Phi)$, are constants that are input into the analyzer
- All parameters are known except for concentration, N (in ppmV) which what is solved and reported



Fast Scan Direct Absorption Technique

- Advantages
 - **Very fast response time**
 - **Excellent sensitivity**
 - **Independent of extraneous radiation emissions from other sources as IR emission from hot boiler flue gas**
 - **Optical effects as etalons, which may perturb the background structure are easily compensated by taking background measurements when NH_3 levels are below detection limits**
 - **System does not require calibration as it is a pure, direct absorption measurement but can be easily audited with an internal reference cell or an external audit cell**
 - **Relatively inexpensive as it does not require shielded RF modulation electronics**
 - **Wide dynamic range; typically 5 orders of magnitude**
 - **Can easily correct in real time for wide power swings typical in heavily laden dust environments as found in coal-fired power plant flue gasses prior to the air heater via continuous measurement of laser power (I_0)**



TDL Detection Limits

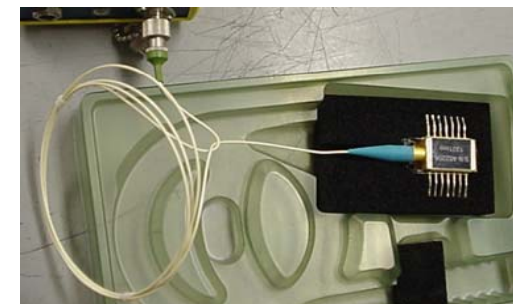
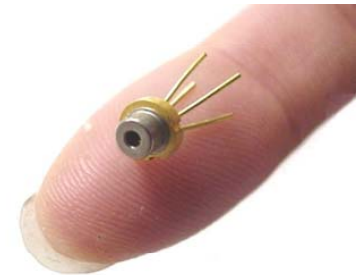
- **Factor of both path length, path measurement time, measurement temperature, pressure and species being measured**
 - **Normally longer path length = lower detection limit as long as the optical return power is above threshold (60 microwatts), laser initially are 10 milliwatts in power)**
 - **Longer path yields greater absorption and sensitivity of measured species but in heavily laden dust environments must yield enough return power**
 - **Scales by factor of square root of measurement time**
 - **E.g. 1 s → 1 min integration time = 7-fold enhancement of detection limit**
- **Typically 0.1 –0. 5 ppmV-m for NH₃ depending on pathlength and integration time**
- **For most coal-fired power plant applications, measurements at one-minute over 5 meters, yield better than 0.2 ppmV MDL's at 700 °F**



TDLs: How they work

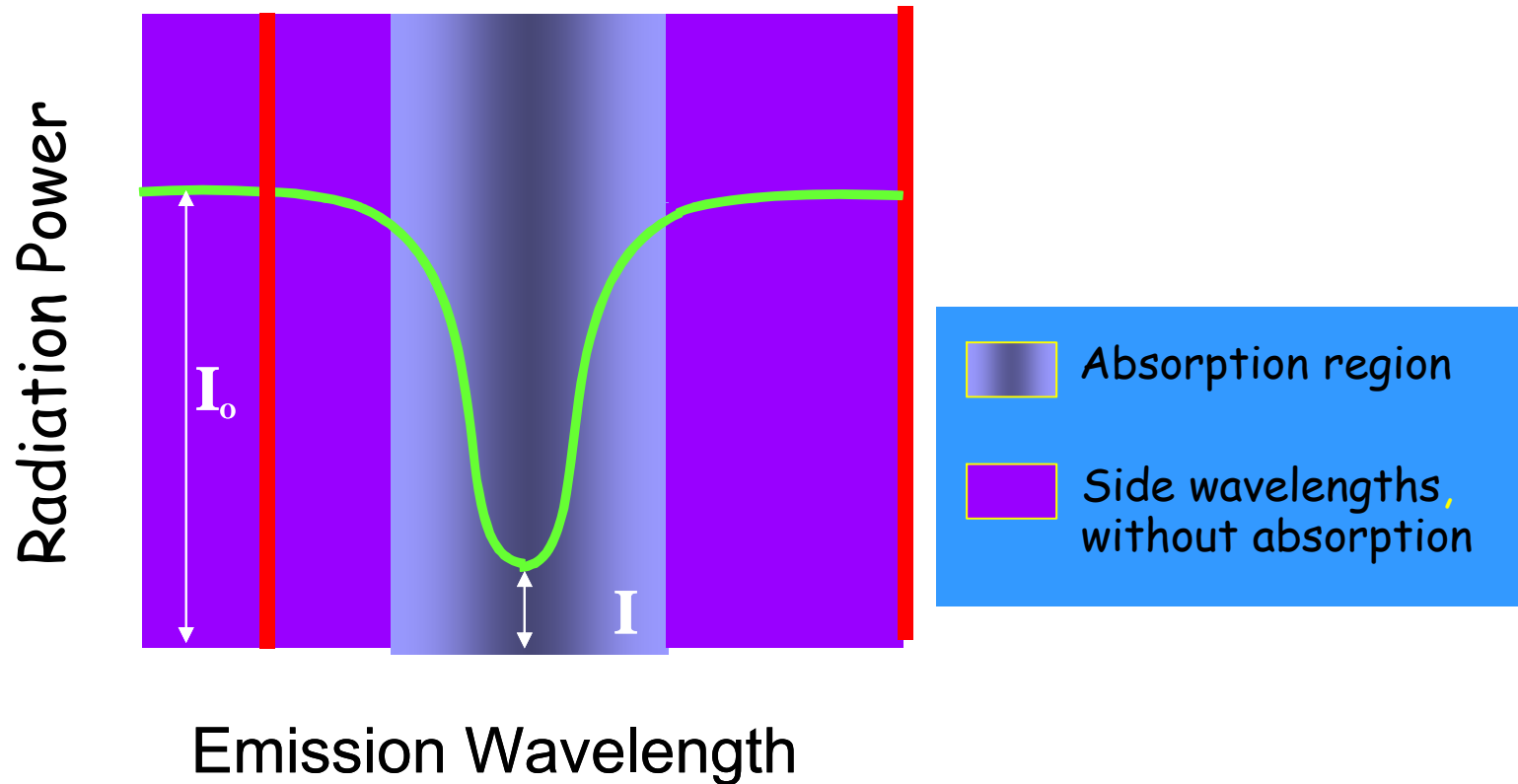
■ Tunable diode lasers

- Made of small crystals of Ga, As, Sb, P
- Similar to lasers used in telecommunications applications
 - Rugged
 - Long life
- Commercially available at a low cost
- Emits light emissions in the near-infrared region when an electric current is applied
- Laser center wavelength depends on composition of crystal
- Laser wavelength can be tuned over narrow range by changing current (fine) or by adjusting laser operating temperature (coarse)
- Output can be fiber coupled allowing easier installation and multi-channel capability





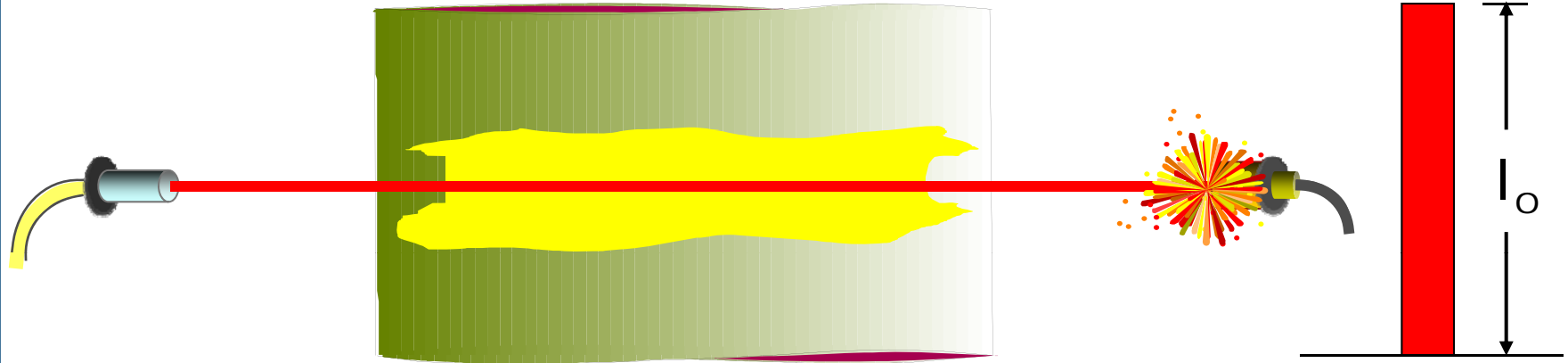
TDL: What's happening at wavelength scale



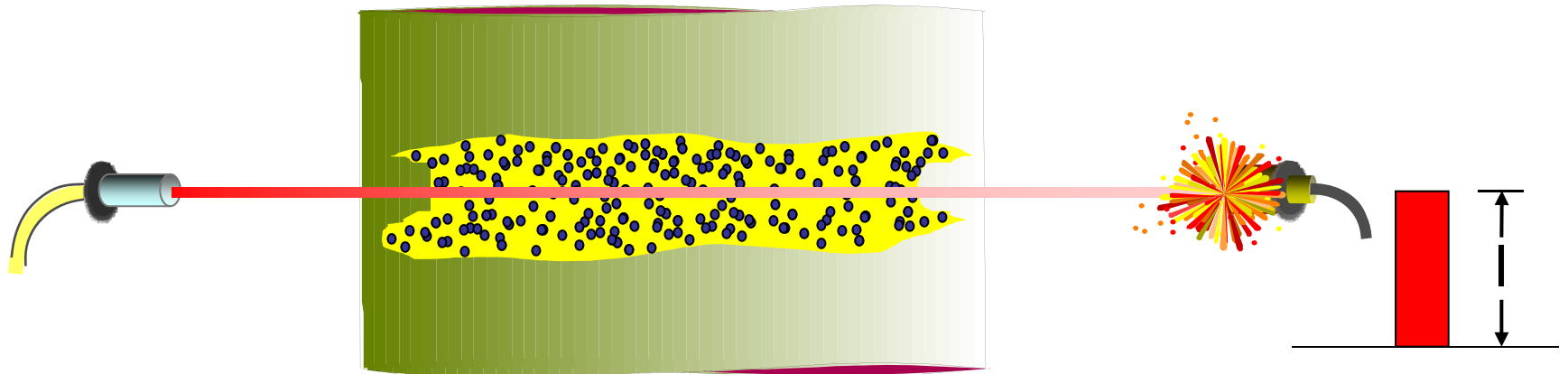


Intensity (I) and (I_0) Measurement

When no gas present...



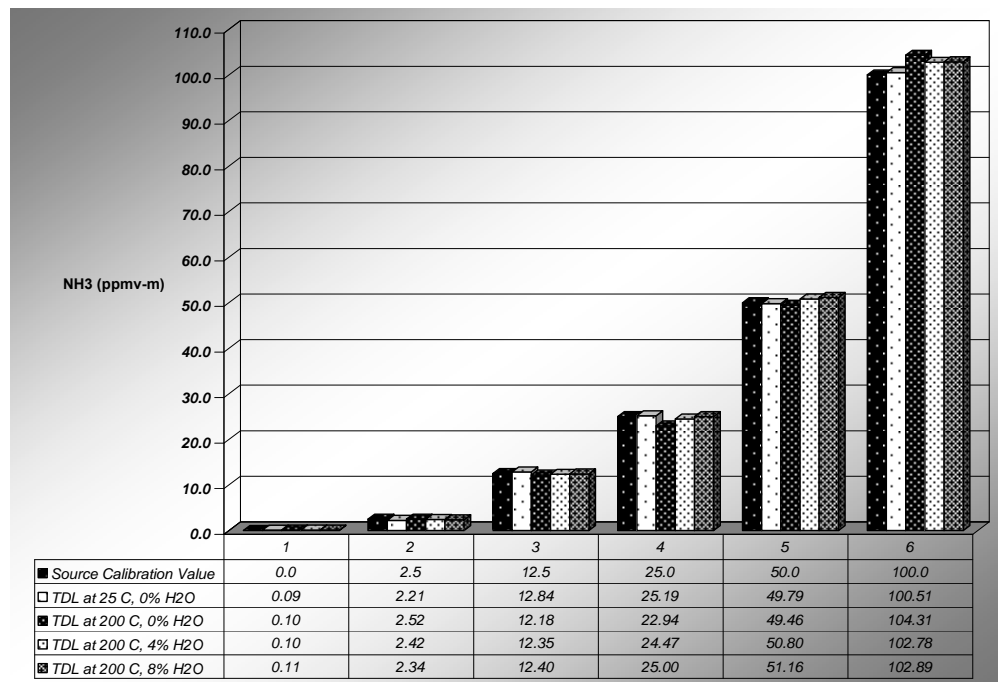
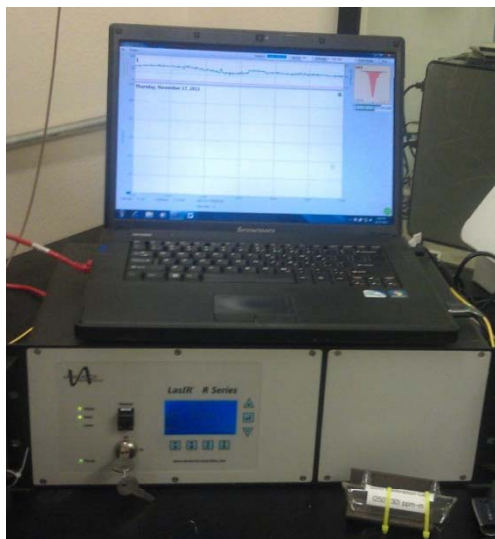
When gas present...



Absorbed intensity, $\delta I = I_0 - I$



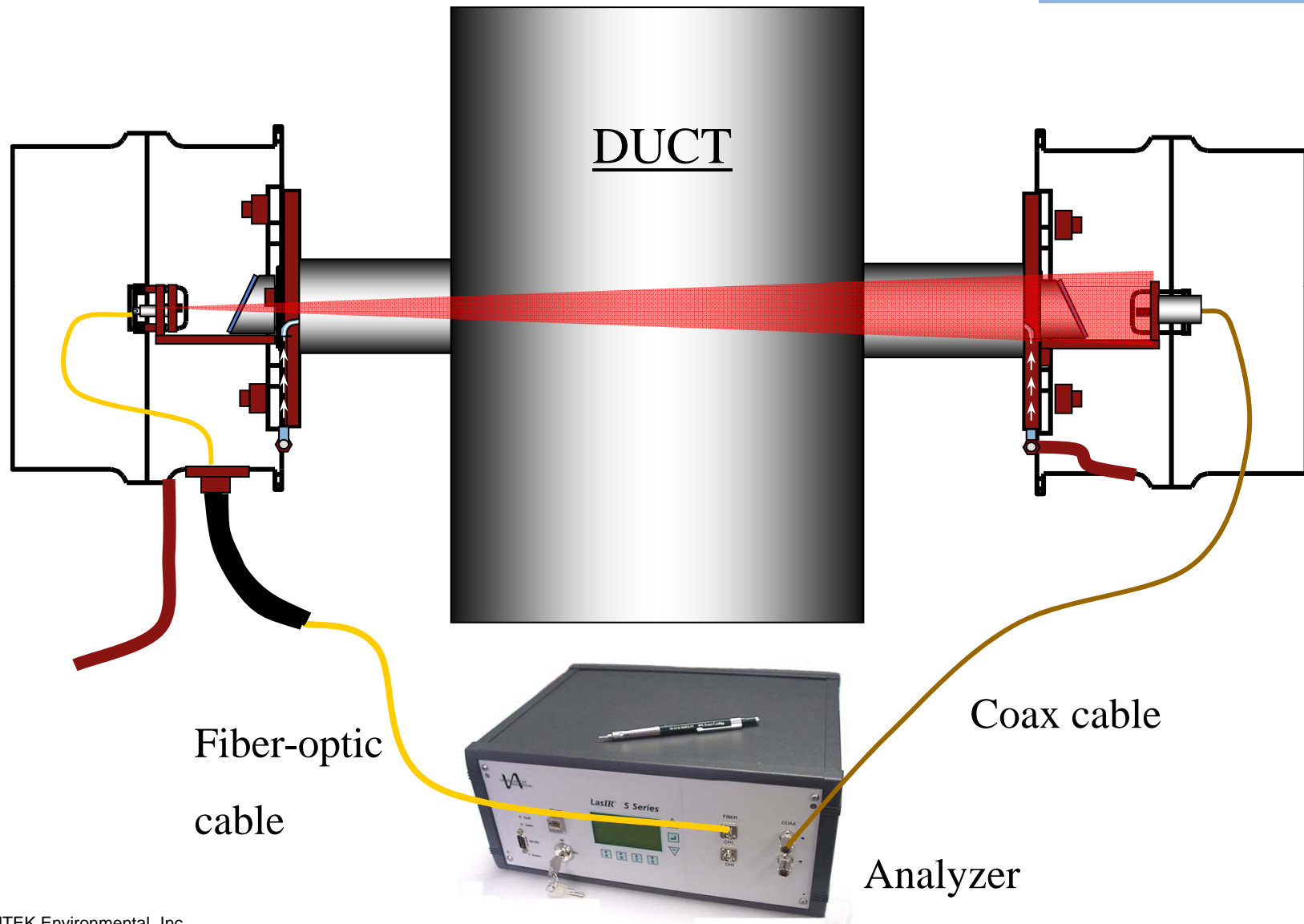
TDL Response

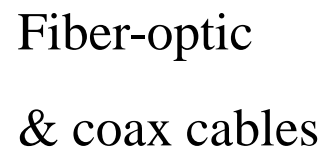


University of California at Riverside (CE-CERT) Laboratory results of the Unisearch TDL for NH₃ at temperatures and water content typical of combustion flue gasses (instrument currently running at a coal-fired power plant under an EPRI project) measuring NH₃ slip and H₂O , plot is courtesy of EPRI (Report number: EPRI 1014664, EPRI Contact Mr. R. Himes)



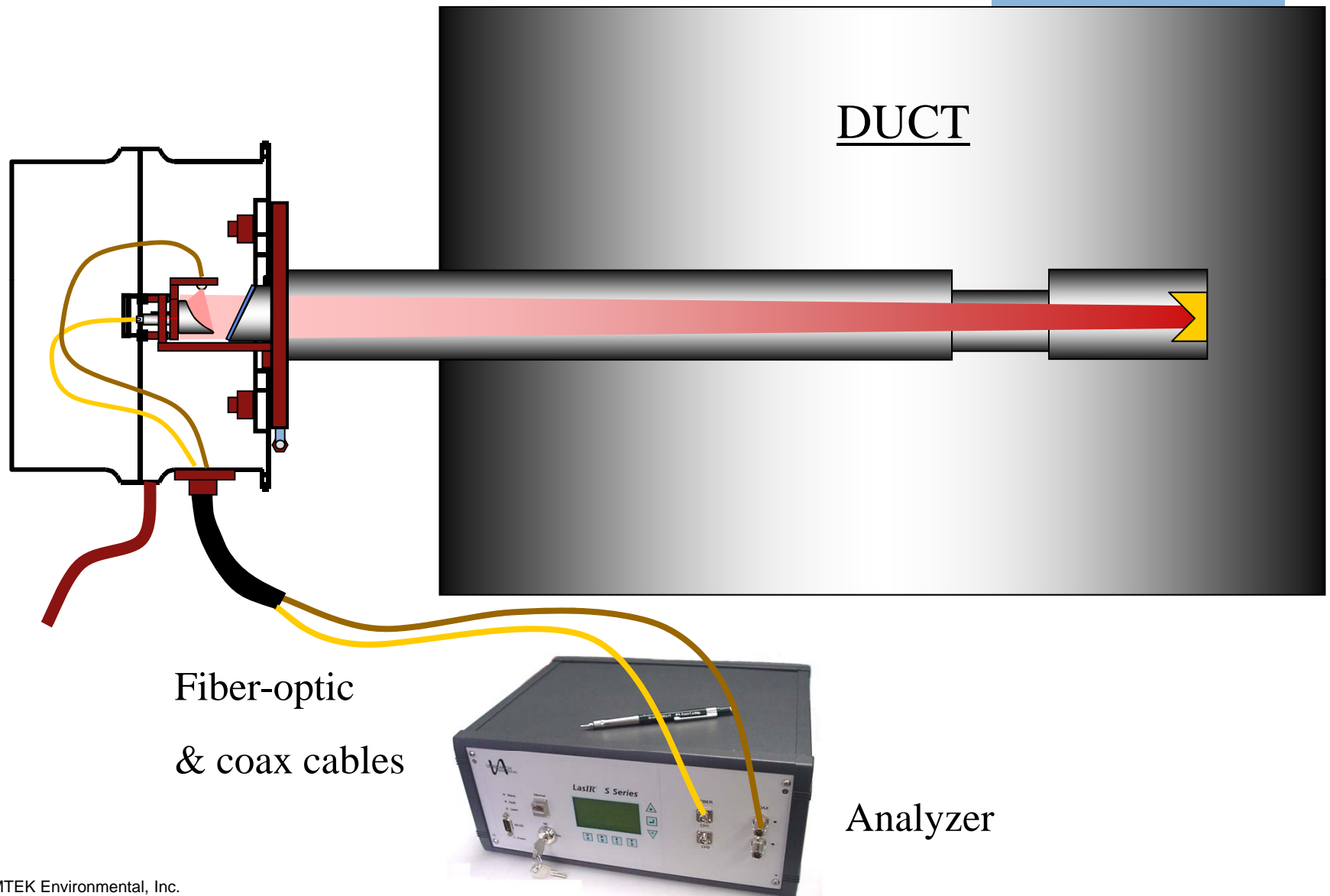
Single Pass (Bi-static) Duct Configuration







Dual Pass (Mono-static) In-Duct Configuration





Dual Pass (Mono-static) In-Duct Configuration



NH₃ measurement section

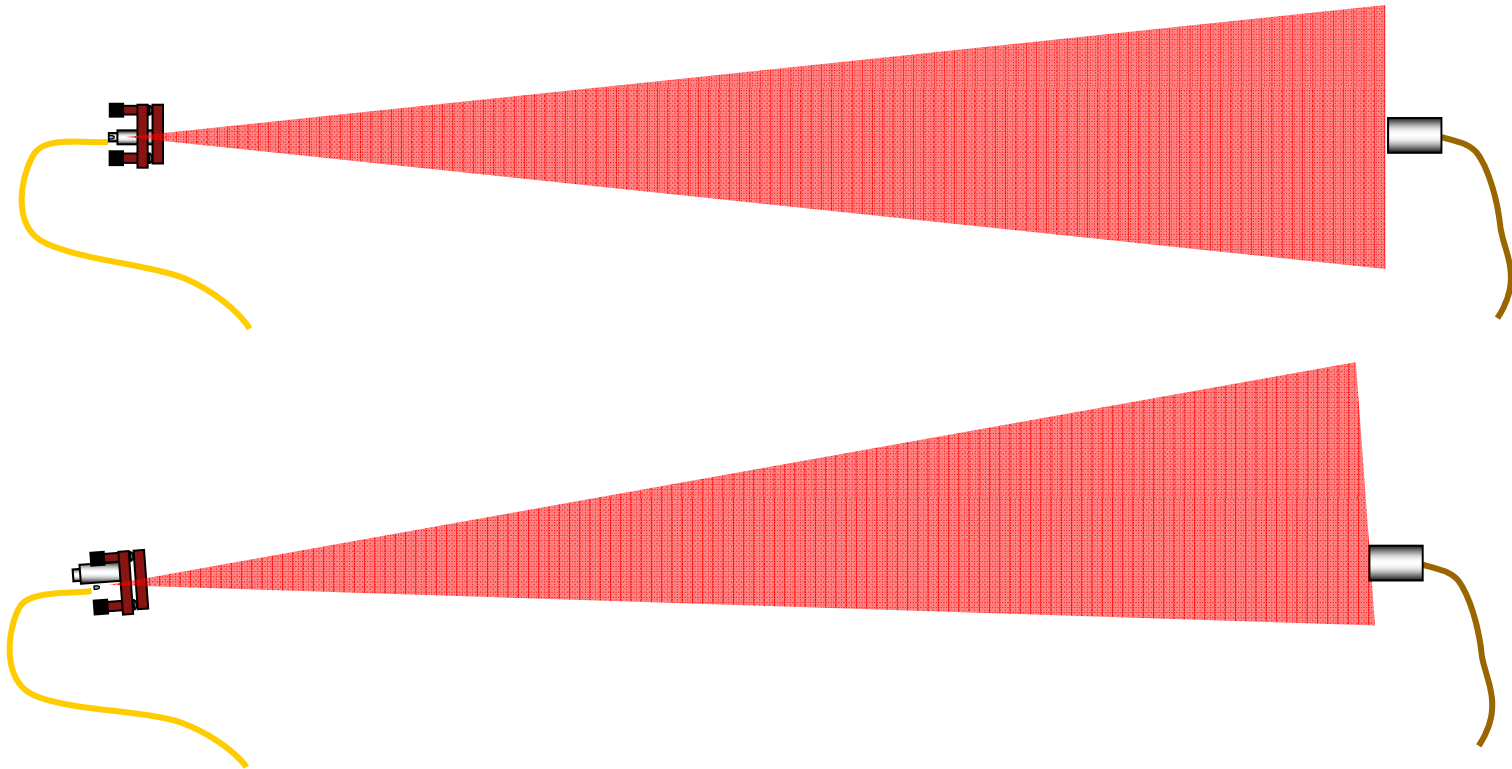
Sealed retro chamber



PDA w/cooler



Beam Expansion for Alignment Stability



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

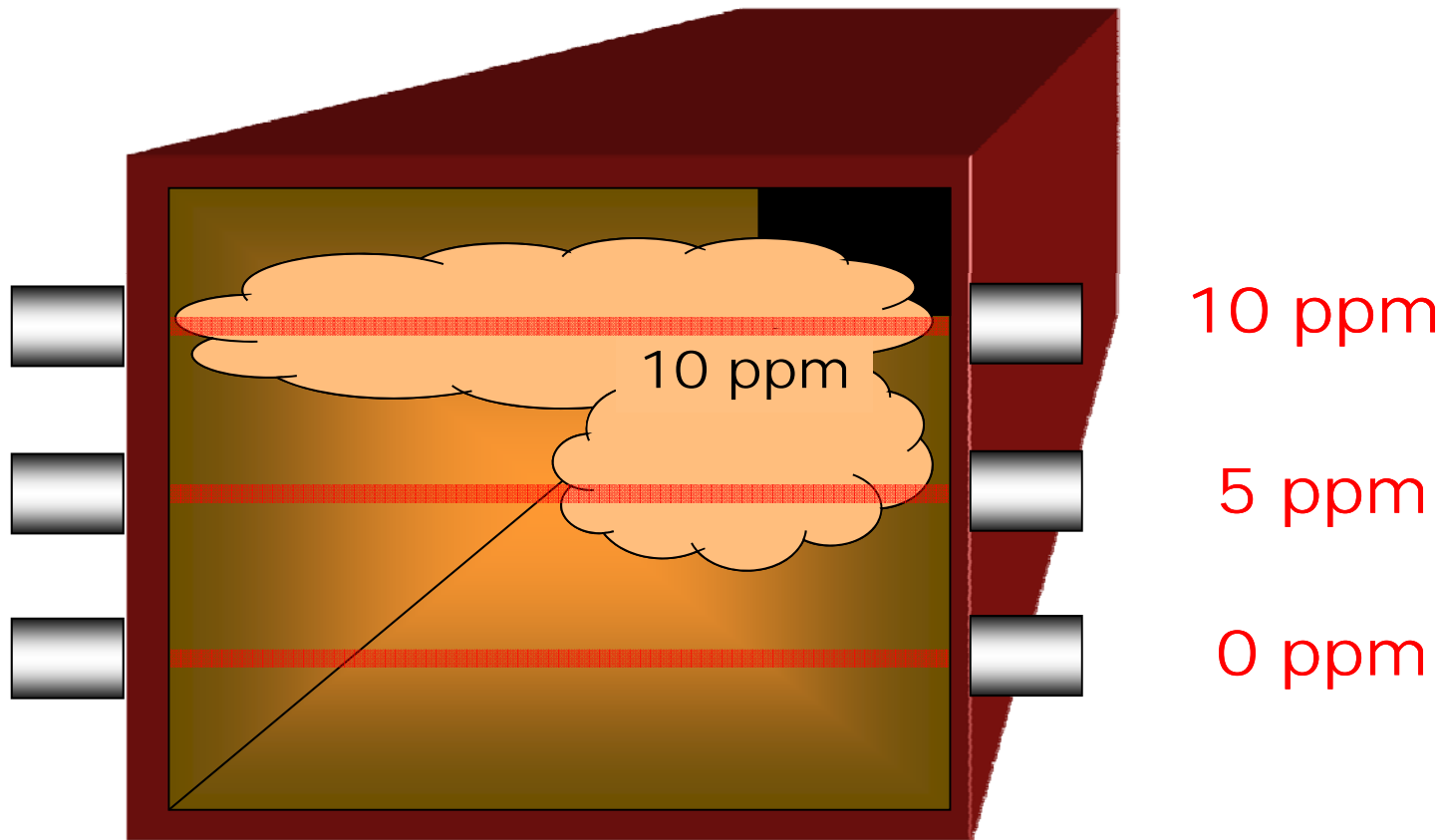


Multiplexed Optical Signal

- 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
 - Beam splitting 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 boiler duct with the instrument fiber coupled to the elements but in a thermally controlled environment.



Multi-Path Array Configuration

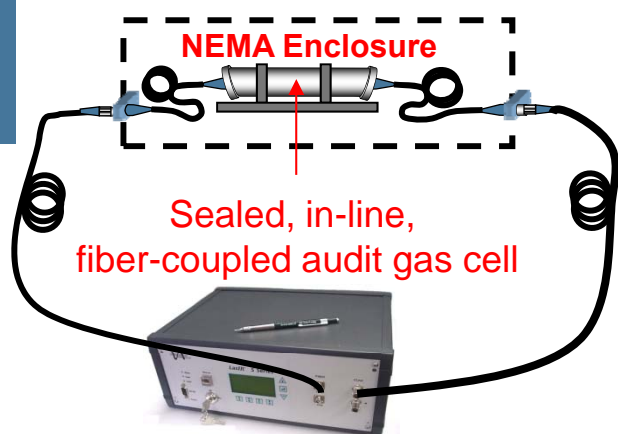


Measurements over multiple paths can spatially help isolate problem areas within the SCR reactor.

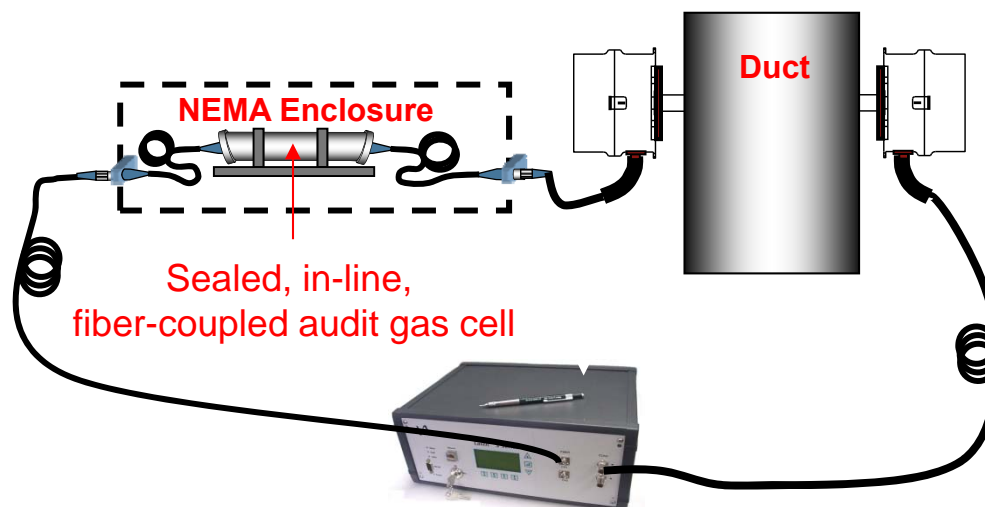


Tunable Diode Laser External Audit Method

- Diagnostic Tool
- Dynamic Spiking
- Analyzer Isolation



Analyzer Isolation Configuration



Dynamic Spiking Configuration



Tunable Diode Laser Internal Audit Method

- **Module spiked with known amount of target gas**
- **Isolated cell measurement**



Internal Audit Module





Tunable Diode Laser Purge Options

Instrument Air



Opacity Type Blower





Tunable Diode Laser Maintenance & Adjustment

Maintenance

Alignment



Lens Removal for Cleaning



Micro Adjustment Screws



Summary: Tunable Diode Laser Measurement Technique

Advantages

- **Real Time Process Feedback**
- **In-situ Measurement Integrated Across Path Length**
- **Multi-Path Grid Array**
 - **Stratified applications**
- **No Sample System Bias from Gas Transport**

Disadvantages

- **Alignment of Optics**
 - **Deformations in ducting due to heating and cooling can lead to misalignment. (Beam expansion mitigates this)**
- **Heavy Dust Loading Applications**
 - **Must be able to transmit light across path. Multiplexed signal allows for stronger signal transmittal across path (typically good to 22 feet, shields can be employed for longer path lengths).**



Coal Fired Boiler- Dry FGD HCl Application

HCl Measurement

■ ***Application Summary***

- Coal fired boiler with dry FGD scrubber
- 15 foot detection path with 0.2 ppm detection limit
- 478 foot distance between analyzer and stack optics
- On-stack blowers to keep optic windows clean
- System configured with flow-through audit cell using best quality HCl calibration gas cylinder available

■ ***Lessons Learned***

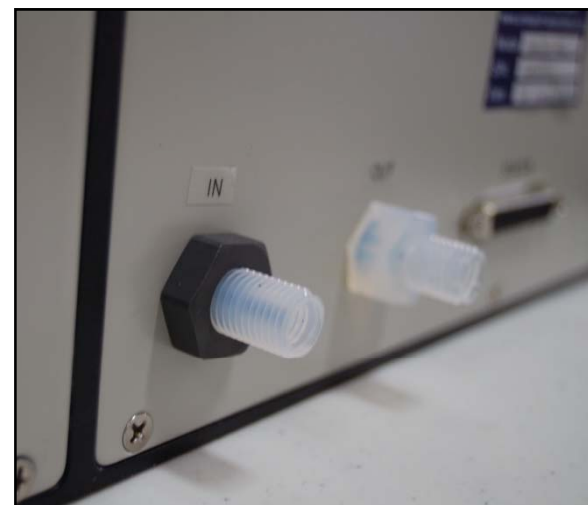
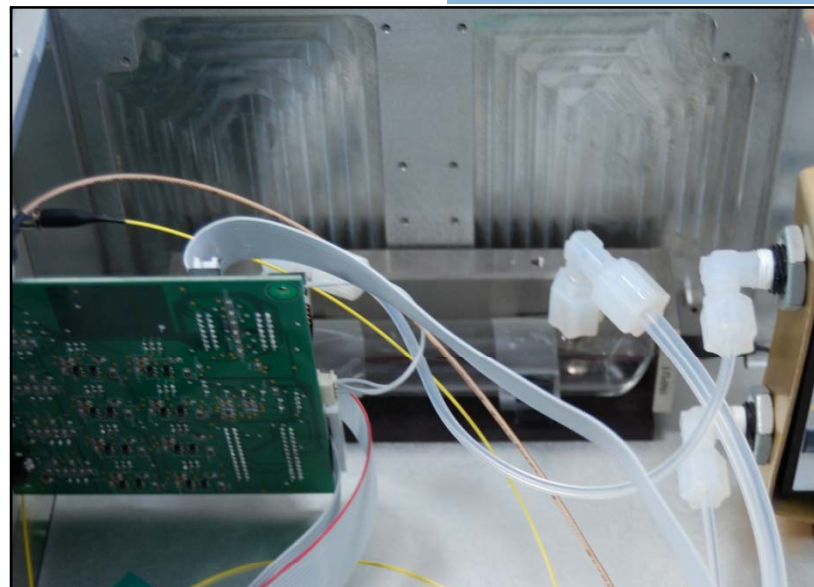
- Anti-reflective coating added to optics window to limit optical noise
- Pushing the analyzer detection limit, typically measuring nearly zero amount of HCl in stack flue gas
- Zero drift issue that required a software change
- Original bench alignment of flow-through cell introduced optical noise. Changed to cell integrated with optical bench to eliminate
- Wet stacks may require heated optics windows



Tunable Diode Laser Audit Method

Flow-Through Audit Cell

- **Dynamic spiking audit**
- **HCl application with 1 - 1 ½ minute response time with 15 foot calibration cylinder distance**
- **Short recovery time**
- **Temperature correction factor used to account to difference between flow through cell and flue gas temperatures**





Brick Manufacturer - HCl Application

Process HCl Measurement for Brick Manufacturer in Georgia

- ***Application Summary***

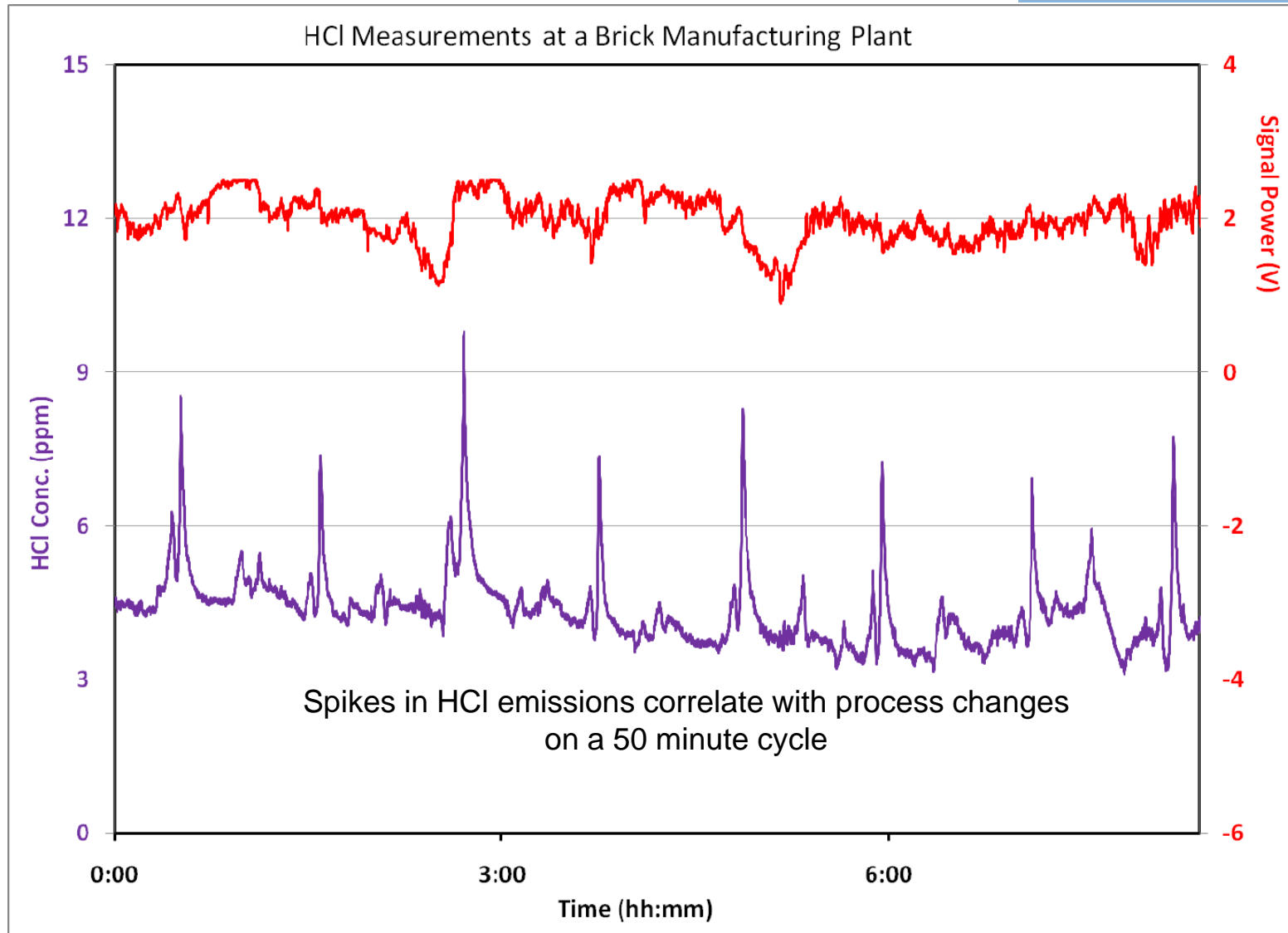
- **Process control measurement**
- **Ammonia injection into process for brick coloring. SO₂ also present**
- **5 ¾ foot detection path with dual pass optics for 11 ½ foot effective detection path**
- **70 foot stack elevation of optics**
- **Constant process background of 4 ppm HCl with spike up to 10 ppm**
- **Blower ports left open to draw ambient air past windows**
- **Permanent installation and operation since January 2011**

- ***Lessons Learned***

- **Initial installation issues with ammonia bisulfate coating windows in 20 minutes. Change to heated optics windows allows for two week operation before cleaning windows**
- **HCl spikes track with opening of kiln door every 50 minutes**
- **Since background level is present, auto background subtraction can't be used**



Brick Manufacturer - HCl Application



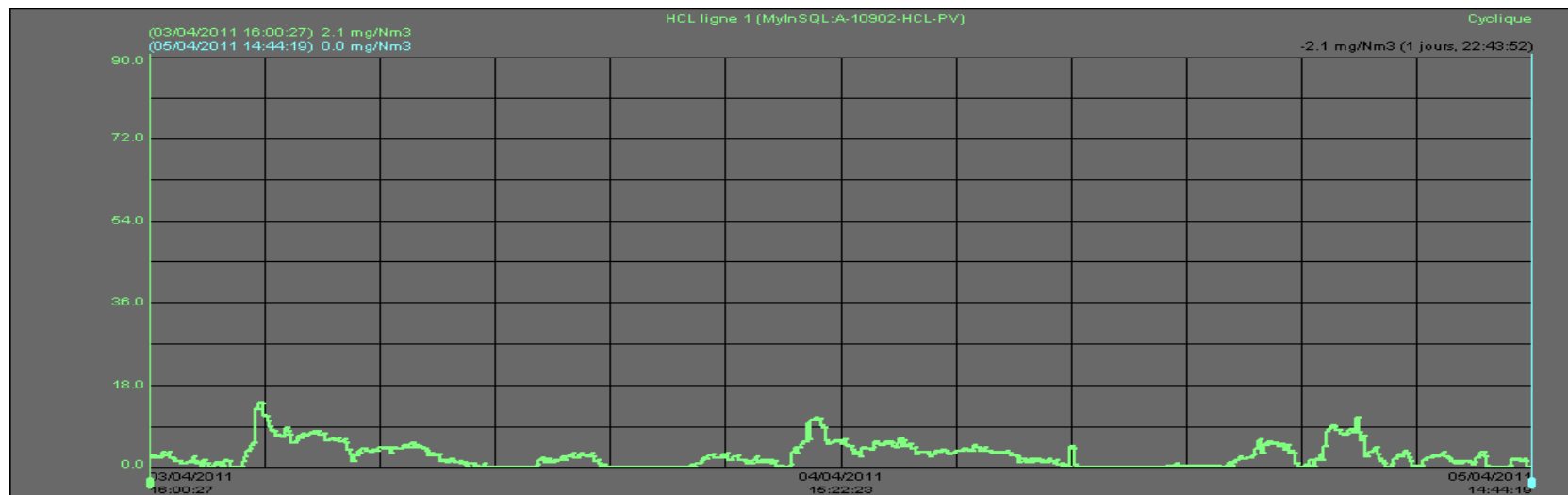


Additional Applications

Incinerator HCl Measurement - Grenoble, France

- **Operating for 8 years**

LasIR HCl Measurements in an Incinerator Flue Gas Mg/m^3





Additional Applications

Digester Gas H₂S Measurement - Denver, CO

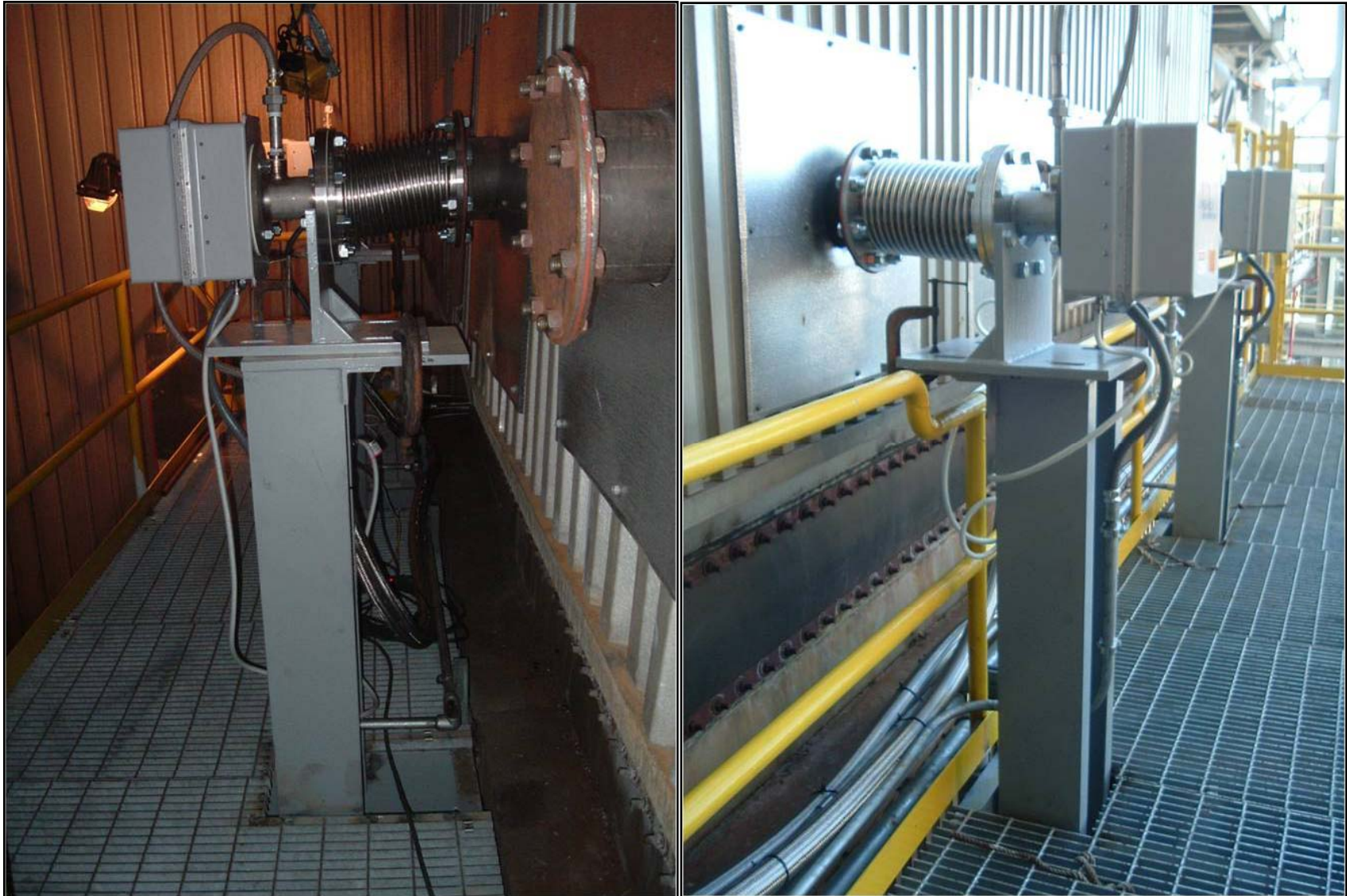
- **Application Summary**
 - **Measurement of H₂S in methane (digester gas)**
 - **Original system utilized in-situ analyzer configuration - multiple year operation**
 - **Original extractive system with a 12 meter path length, being replaced with extractive system - pairing TDL with and extractive Harriot multi-pass cell with effective path length of 0.8 meters**
 - **Dual range with 0-600 ppm low range and 0-3000 ppm high range**
 - **Class 1, Div 2 application**
 - **35% moisture**

**Applicability to Utility HCl Applications*

- **WFGD Stack Moisture**
 - **Full or dilution extractive sampling can be utilized**
 - **Extractive cell can be operated at reduced pressure**

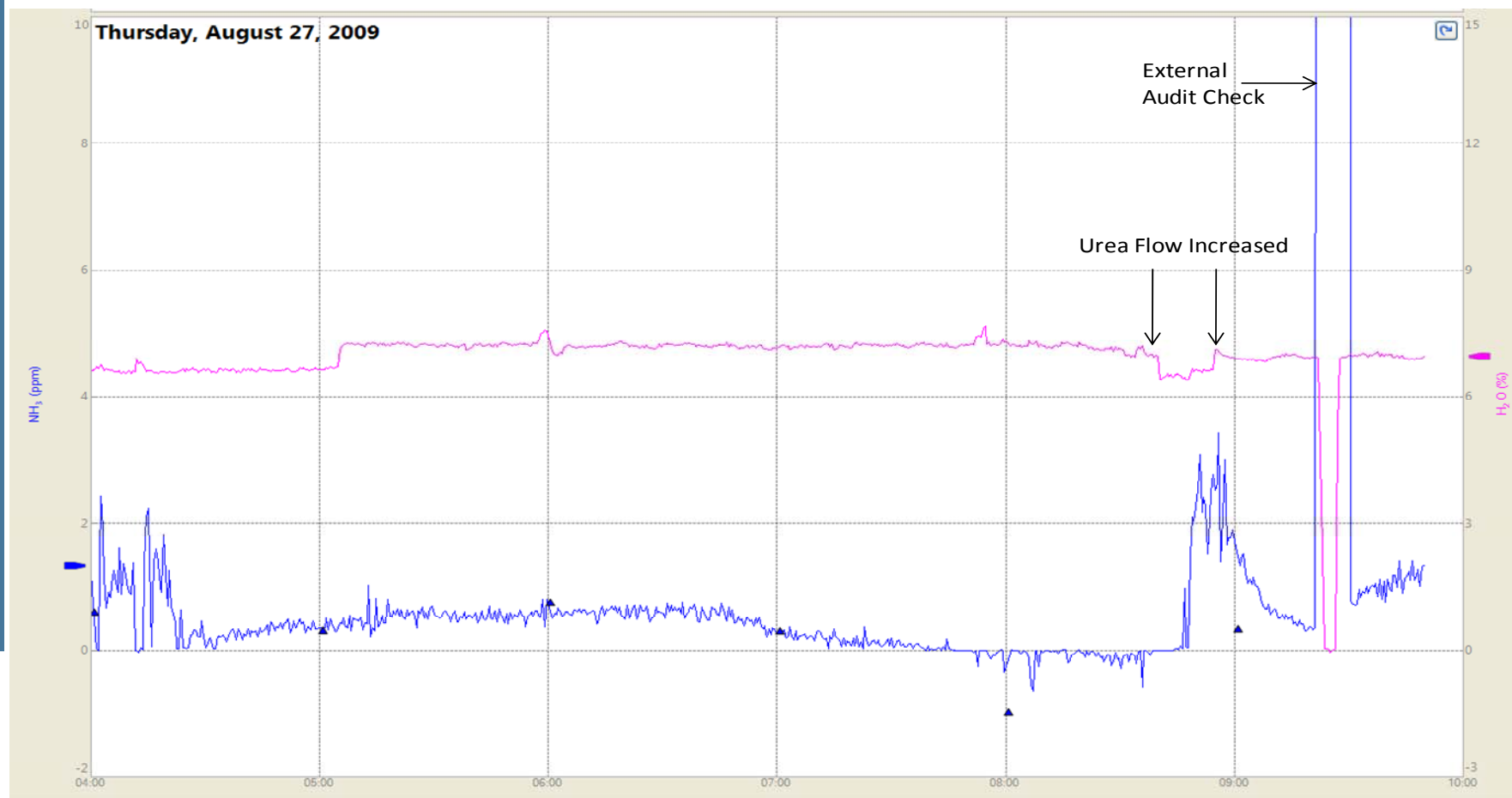


Coal Fired Boiler- SNCR Ammonia Slip Application





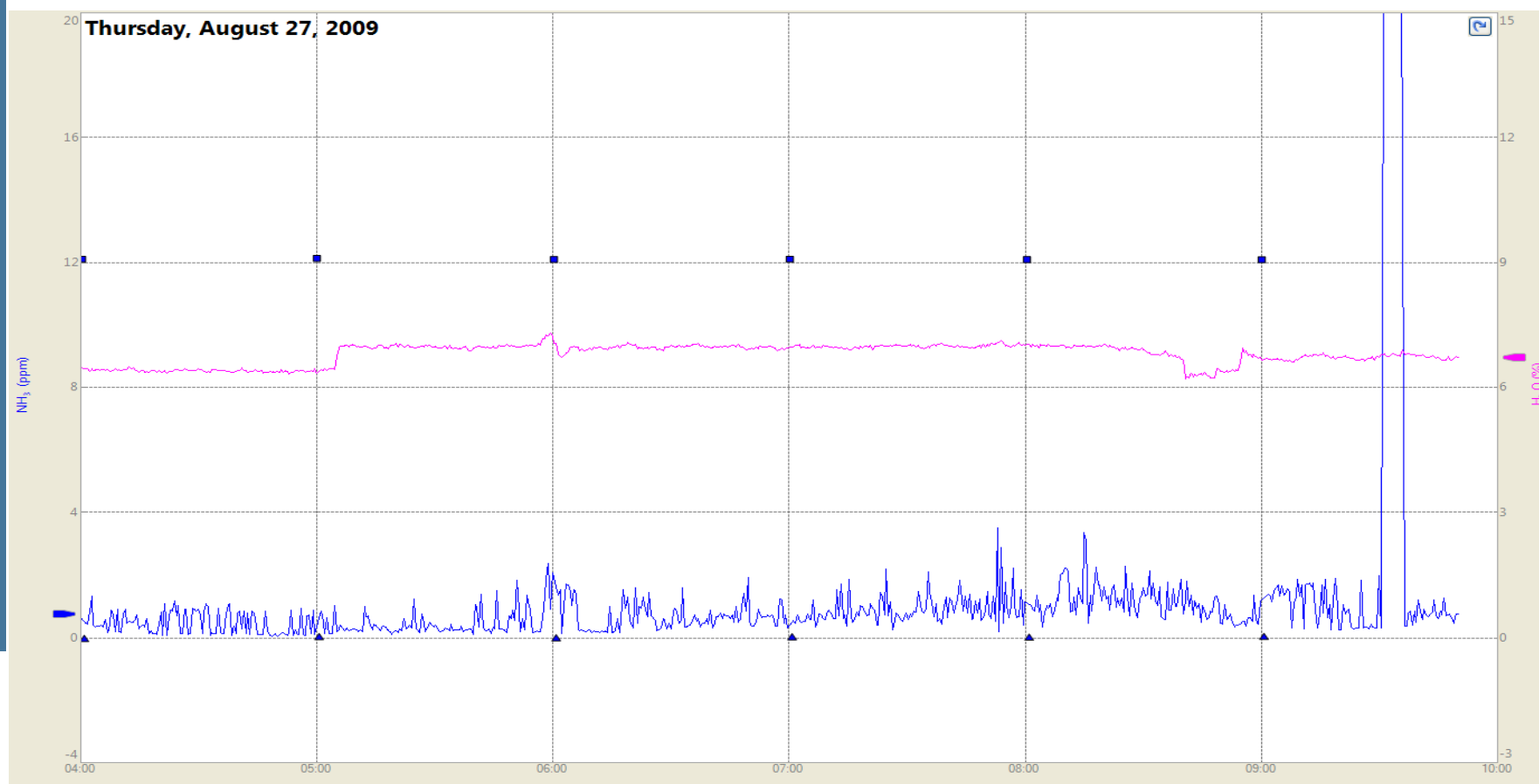
Coal Fired Boiler- SNCR Ammonia Slip Application



Unit 1, TDL Channel 1 Ammonia Slip Measurement



Coal Fired Boiler- SNCR Ammonia Slip Application

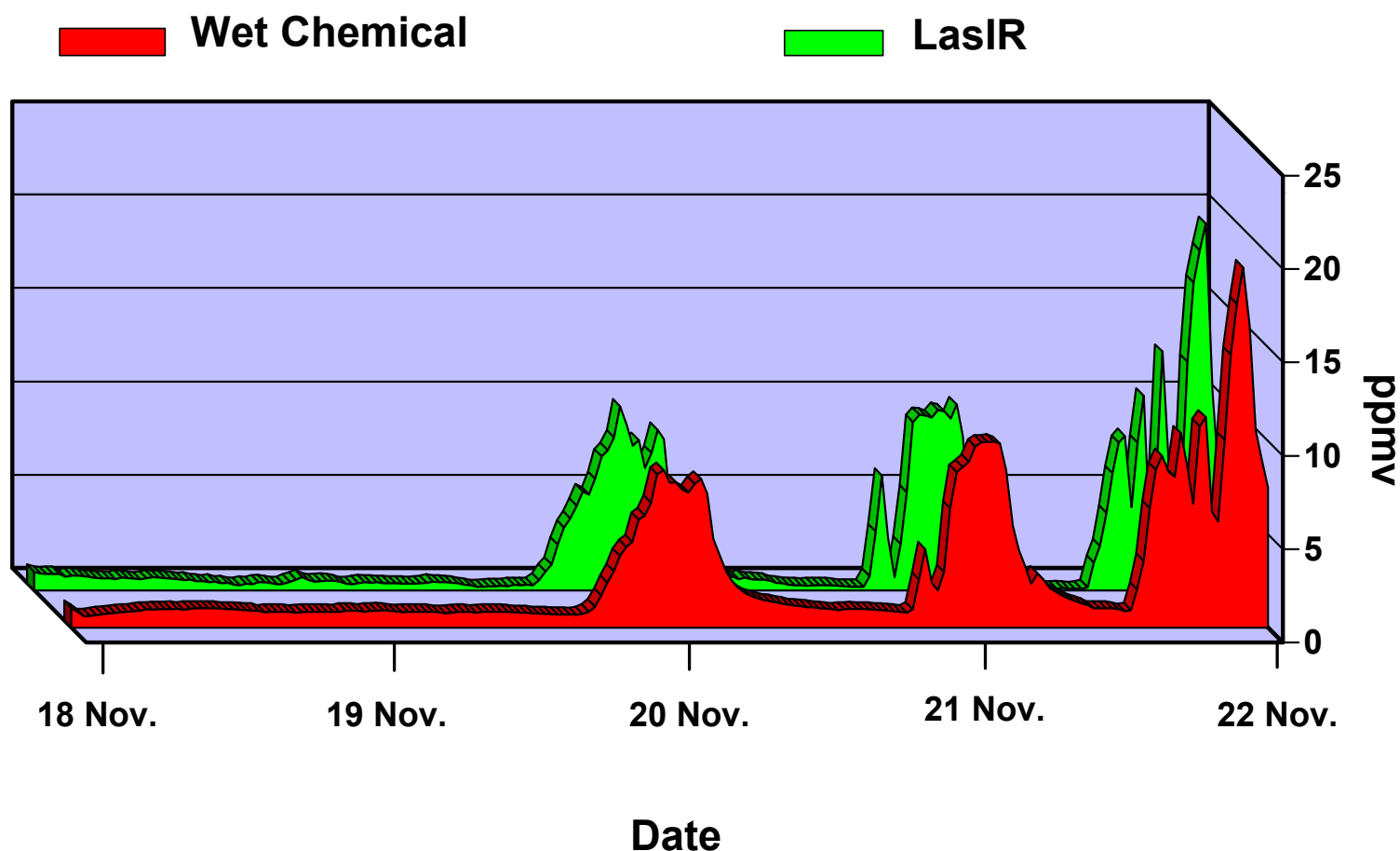


Unit 1, TDL Channel 2 Ammonia Slip Measurement



Aluminum Smelter - HF Application

HF Stack Measurements taken at an Aluminium Smelter





Summary

- **Fast response**
- **Wide dynamic range**
 - **Capable of both low and high range measurements**
- **Does not require calibration or use of calibration gas for audit verification**
- **No analyzer drift**
- **Monitoring of multiple paths with one analyzer**

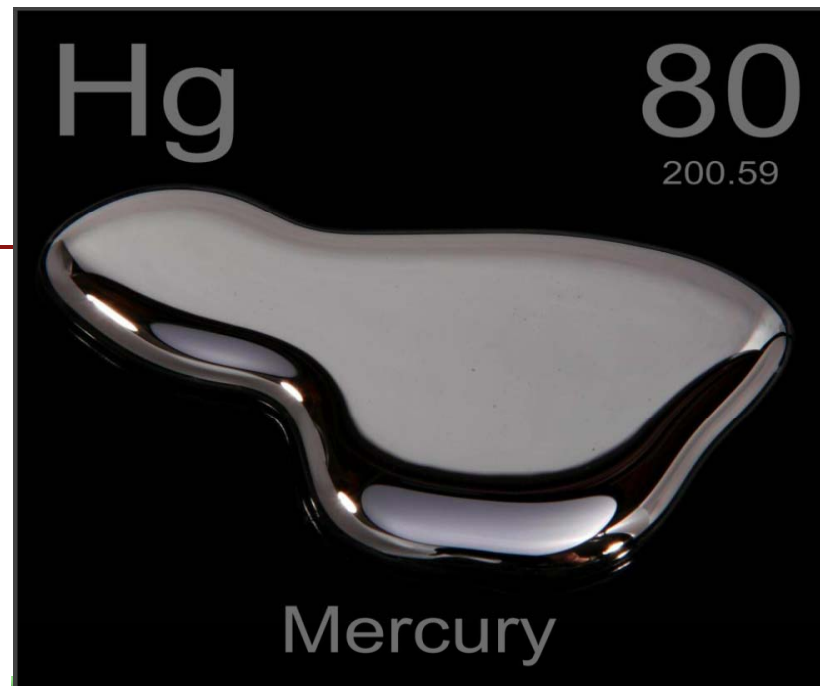


Mercury Monitoring Technologies and Detection Principles

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Mercury Fountain by Alexander Calder
Joan Miro Museum in Barcelona, Spain
Copyright ©2008 Theodore W. Gray



Mercury Monitoring Technologies & Detection Principles

Regulations, where do we stand?

- Since vacating the Clean Air Mercury Rule (CAMR), the implementation of mercury monitoring has primarily fallen on the state and local regulators.
- The EPA often uses Consent Decrees to mandate mercury monitoring.
- Cement MACT requires plants to monitor mercury emissions in kiln exhaust.
- More industry monitoring on the horizon.
 - Mercury and Air Toxics (MATS) Rule



Mercury Monitoring Technologies & Detection Principles

- Detection Technologies
 - Continuous Monitoring
Cold Vapor Atomic Fluorescence
Example: Thermo Freedom Mercury Series
 - Continuous Batch Measurement
Pre-Concentration on Gold Filter, Thermal Desorption, Atomic Fluorescence
Example: Tekran Series 3300
 - Long Term Batch Measurement
Sorbent Trap or Appendix K
Example: Apex Instruments



Mercury Monitoring Technologies & Detection Principles



- Dilution based measurement
- Inertial Filter Sample Conditioning
 - Conversion at the Stack
- Direct Measurement CVAF
 - High sensitivity
- True real-time monitoring
 - Modular design
 - iSeries platform



Mercury Monitoring Technologies & Detection Principles



Model 3330 Inertial Probe



Model 3320 Sample Conditioner



Model 2537A AF Analyzer



Model 3310 Calibration Unit



Mercury Monitoring Technologies & Detection Principles

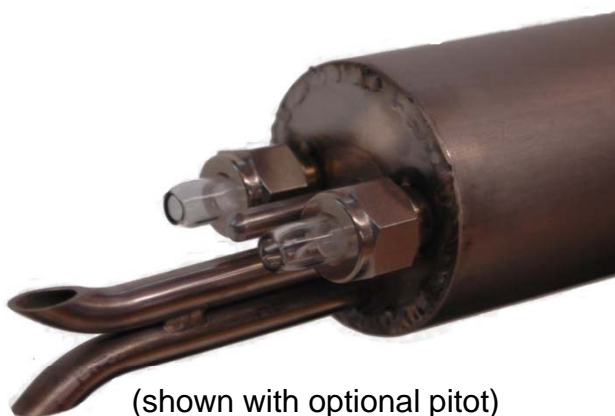
Principles of Operation

- Mercury in sample gas is pre-concentrated onto (pat'd) pure gold cartridge
- Adsorbed mercury is thermally desorbed
- Detected by atomic fluorescence detector
- Two cartridges are used to alternately sample and desorb allowing continuous operation
 - No gaps in data stream



Mercury Monitoring Technologies & Detection Principles

HGP Dual Trap Sampling Probe



(shown with optional pitot)



Configuration:

- Heated Sample Probe –Dual Probe Heaters
 - Length (4,6,9,12ft Standard)
 - Material –C276 Hastelloy or 316 SS
- Enclosure – Insulated SS Junction Box
 - Trap Sizes – 10mm Large Standard
 - Optional 6mm Small Trap Adapter
 - Paired trap holders
 - Pitot Tube – Optional S Type Pitot



Mercury Monitoring Technologies & Detection Principles

Sorbent Trap



Configuration:

- Section 1: Sample Collection Section
- Section 2: Breakthrough Indicator Section
- Section 3: Vapor-Spike Section to Measure Recovery



Method Comparison

Detection Method	Advantages	Disadvantages
Continuous Monitoring	<ul style="list-style-type: none">▪ True real time feedback for process control.	<ul style="list-style-type: none">▪ Large upfront investment costs▪ Maintenance intensive system▪ NIST traceable calibration gases/sources issue▪ Consumable chlorine gas for mercuric chloride generator
Continuous Batch Measurement	<ul style="list-style-type: none">▪ Lower detection levels possible due to time integration of sample.	<ul style="list-style-type: none">▪ Large upfront investment costs▪ Maintenance intensive system▪ NIST traceable calibration gases/sources issue
Long Term Batch Measurement	<ul style="list-style-type: none">▪ Lesser initial investment for system startup.	<ul style="list-style-type: none">▪ Labor intensive process requiring post installation maintenance and analysis costs▪ Must climb stack on daily/weekly basis for sample collection▪ Glass trap breakage - loss of data▪ Sample breakthrough - loss of data▪ Chain of custody sample issues



Particulate Matter Monitoring Technologies and Detection Principles

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PM CEMS

Why are PM CEMS Important?

- **Opacity correlates poorly to PM emissions**
 - **PM CEMs can address the shortfalls of continuous opacity monitors (COMs)**
 - **With the onset of continuously decreasing limits of SO₂ and the concern of SO₃ from SCR installations, wet scrubbers have proven to be a highly efficient means of reducing SO₂, SO₃ and fine particulates; however a wet gas effluent is a result. This result is in the form of wet particulate and water droplets.**
 - **The Mercury and Air Toxic Standards (MATS) sets new standards for PM as a surrogate for non-Mercury metals.**

Where are PM CEMS Being Installed?

- **Proposed Boiler MACT applications (Industrial and Utility)**
- **Scrubbed stack PM monitoring**
- **New coal-fired power plant permits**
- **EPA consent decrees**



PM CEMS

40CFR60 Appendix B Performance Specification 11

- **The purpose of PS-11 is to establish the initial installation and performance procedures required for the evaluating the acceptability of a PM CEMS.**
- **PS-11 applies to any PM CEMS that is required by Title 40 of the Code of Federal Regulations (CFR) to install and operate a PM CEMS.**
- **PS-11 requires a site to perform initial installation and calibration procedures that confirm the acceptability of the PM CEMS.**
- **A site specific correlation of the PM CEMS must be developed to establish response against manual gravimetric reference method measurements including Method 5 and 5I and Method 17.**

PS-11 provides:

- **Guidelines for selecting a PM CEMS**
- **Installation location guidance**
- **Procedures for certifying a PM CEM**
- **Minimum performance limits**
- **Example calculations**



PM CEMS

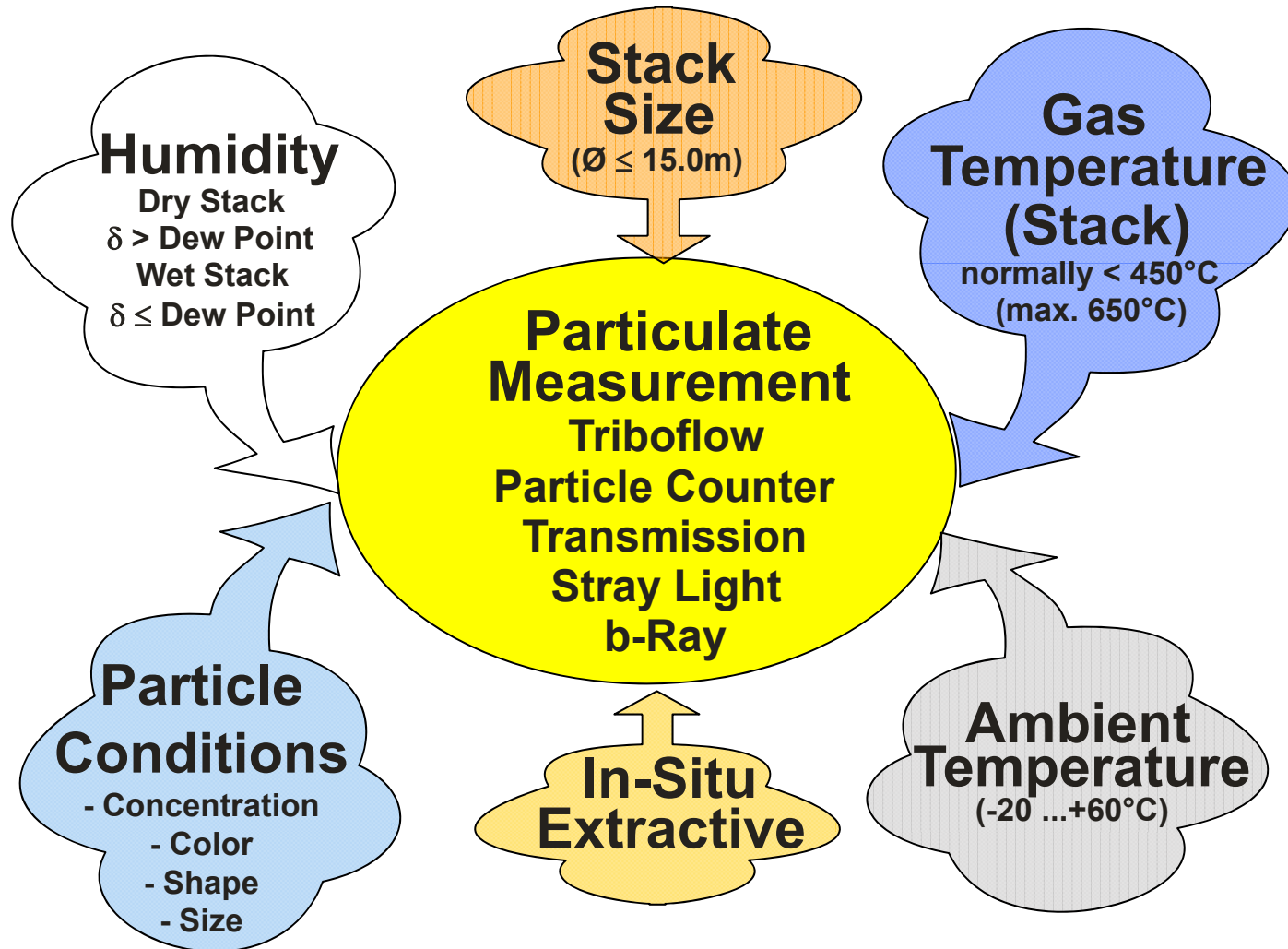
Principal Technologies used

- **Light Scattering**
 - Can measure very low dust levels.
 - Some practical problems.
- **Beta Attenuation**
 - Uses continuous paper tape filter.
 - Dust particles adhering to the filter absorb beta-particles emitted by radioactive source. This absorption gives a measure of dust density.
- **Probe Electrification (Triboelectric)**
 - Sensitive
 - High accuracy
 - Requires compensation for flow, temperature, etc.



PM CEMS

Design Considerations and Selection Parameters





Mass Emissions Monitoring Technologies and Detection Principles

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Stack Flow Measurement

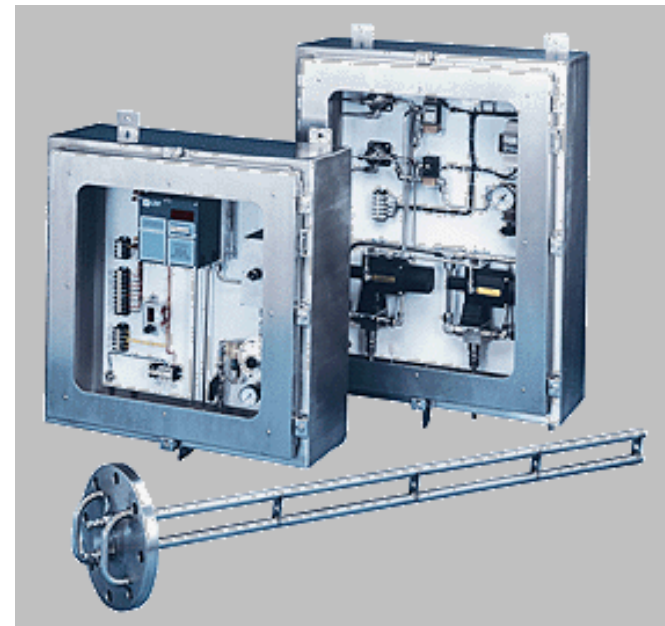
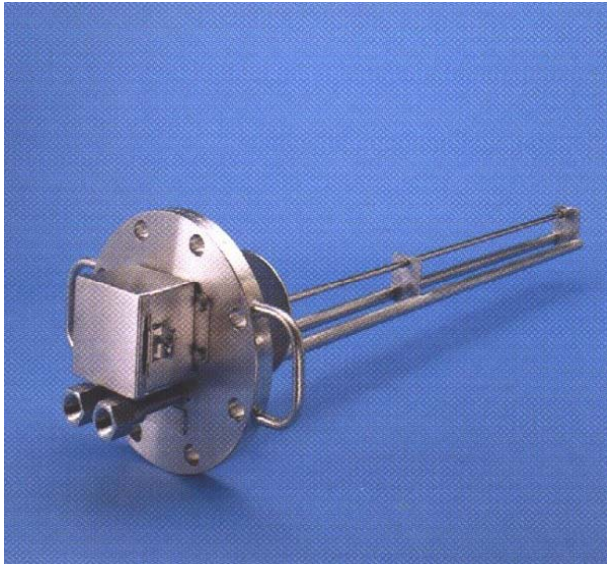
Stack Flow Measurement Techniques

Used for mass emissions reporting requirements (lbs/hr, tons/year, etc)

- **DIFFERENTIAL PRESSURE**
 - S Type Pitot
 - Averaging Pitot – Annubar
 - Accuracy Limited At Low Flow
- **UTRASONIC**
 - Requires Electronic Cal Check
- **THERMAL SENSING**
 - Requires Electronic Cal Check
- **OPTICAL**



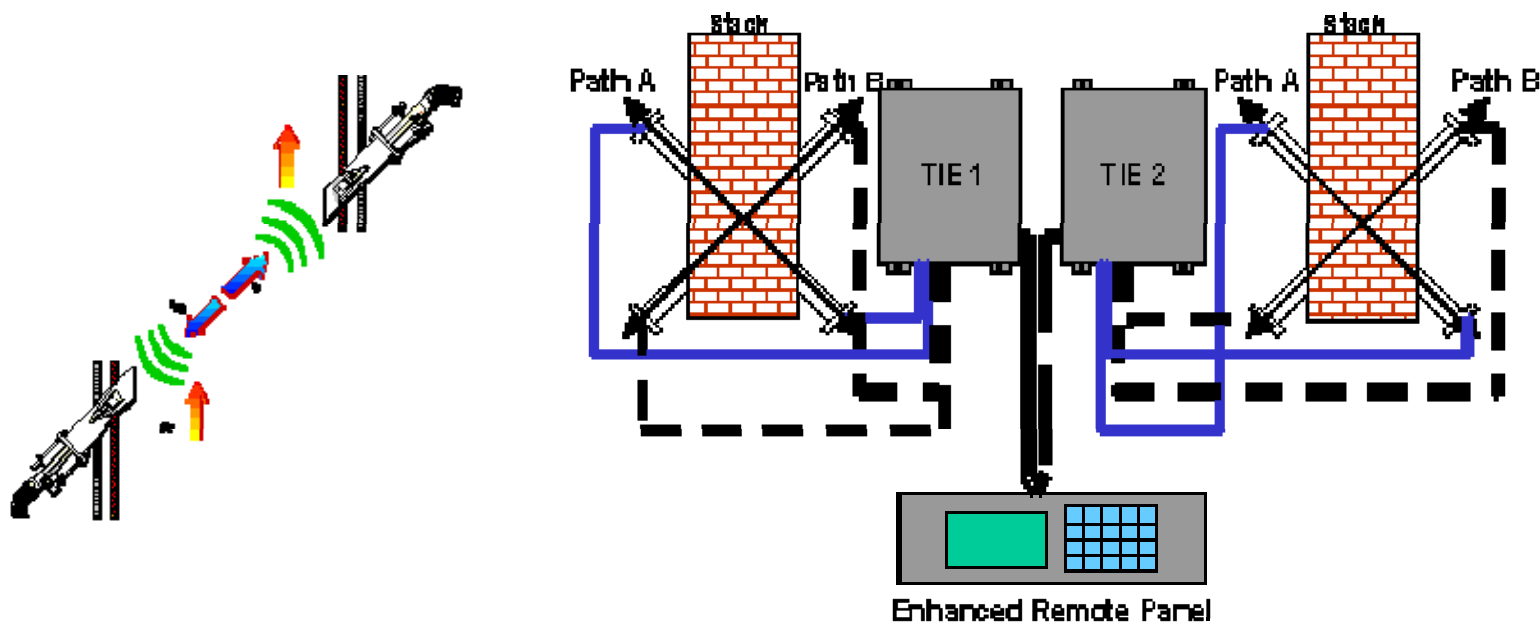
Stack Flow Measurement



Averaging Pitot Flow – Differential Pressure



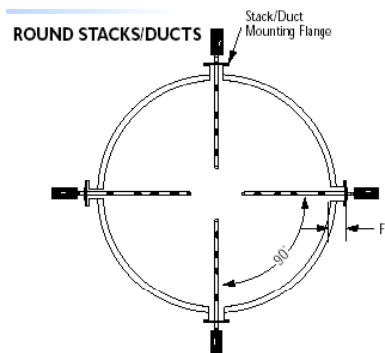
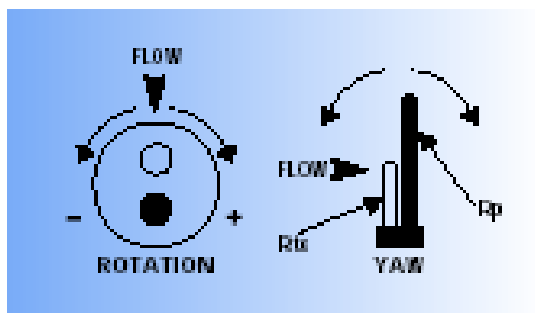
Stack Flow Measurement



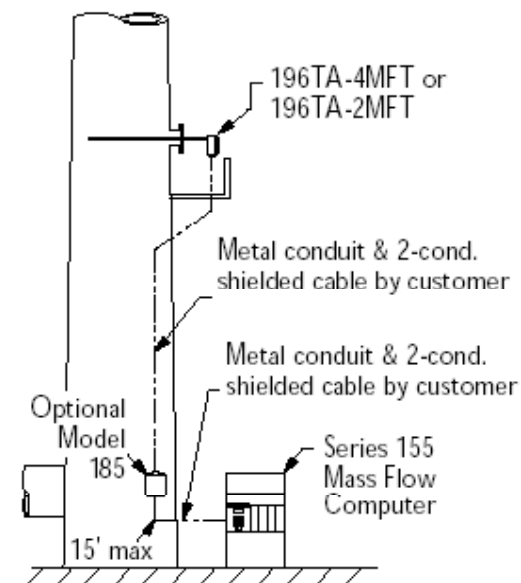
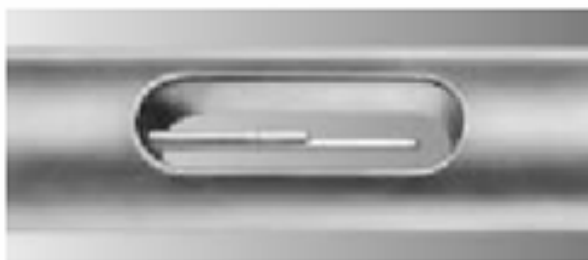
Ultrasonic Flow - Acoustic



Stack Flow Measurement



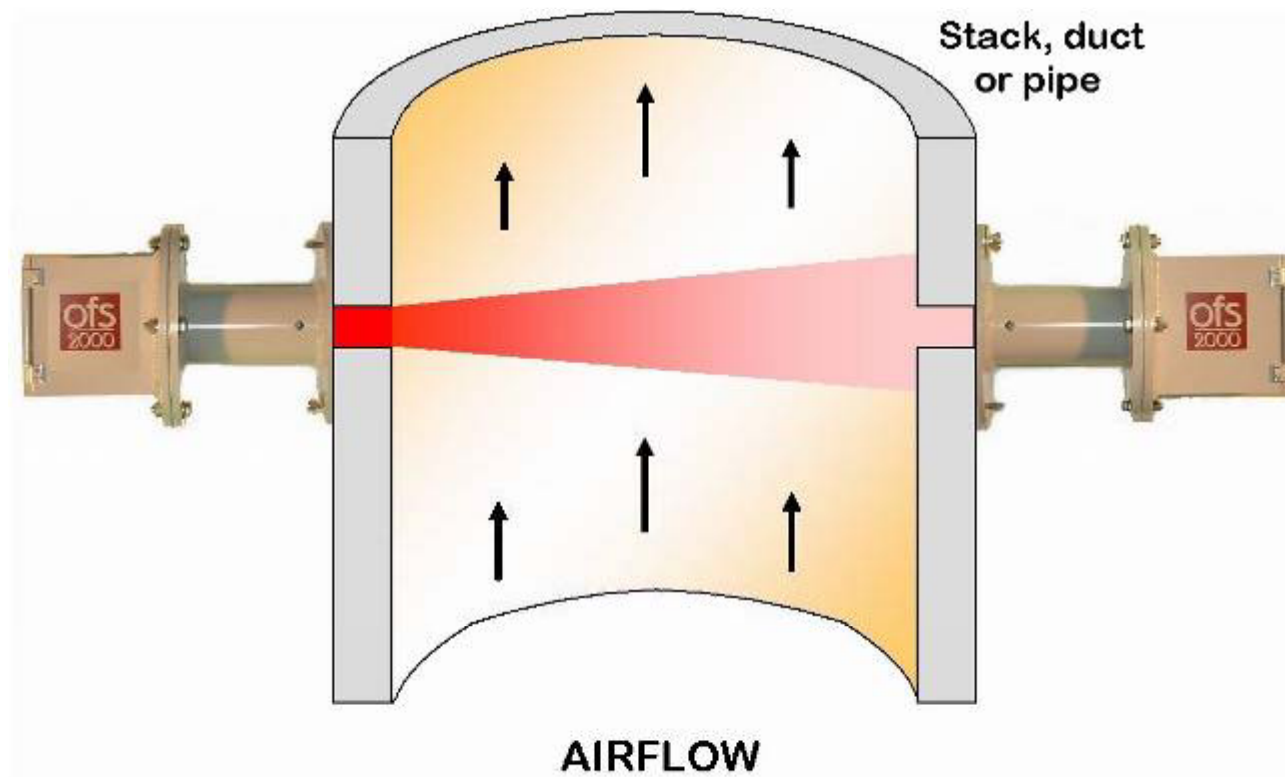
Category # 1: Half Span, Single-End Support



Thermal Sensing



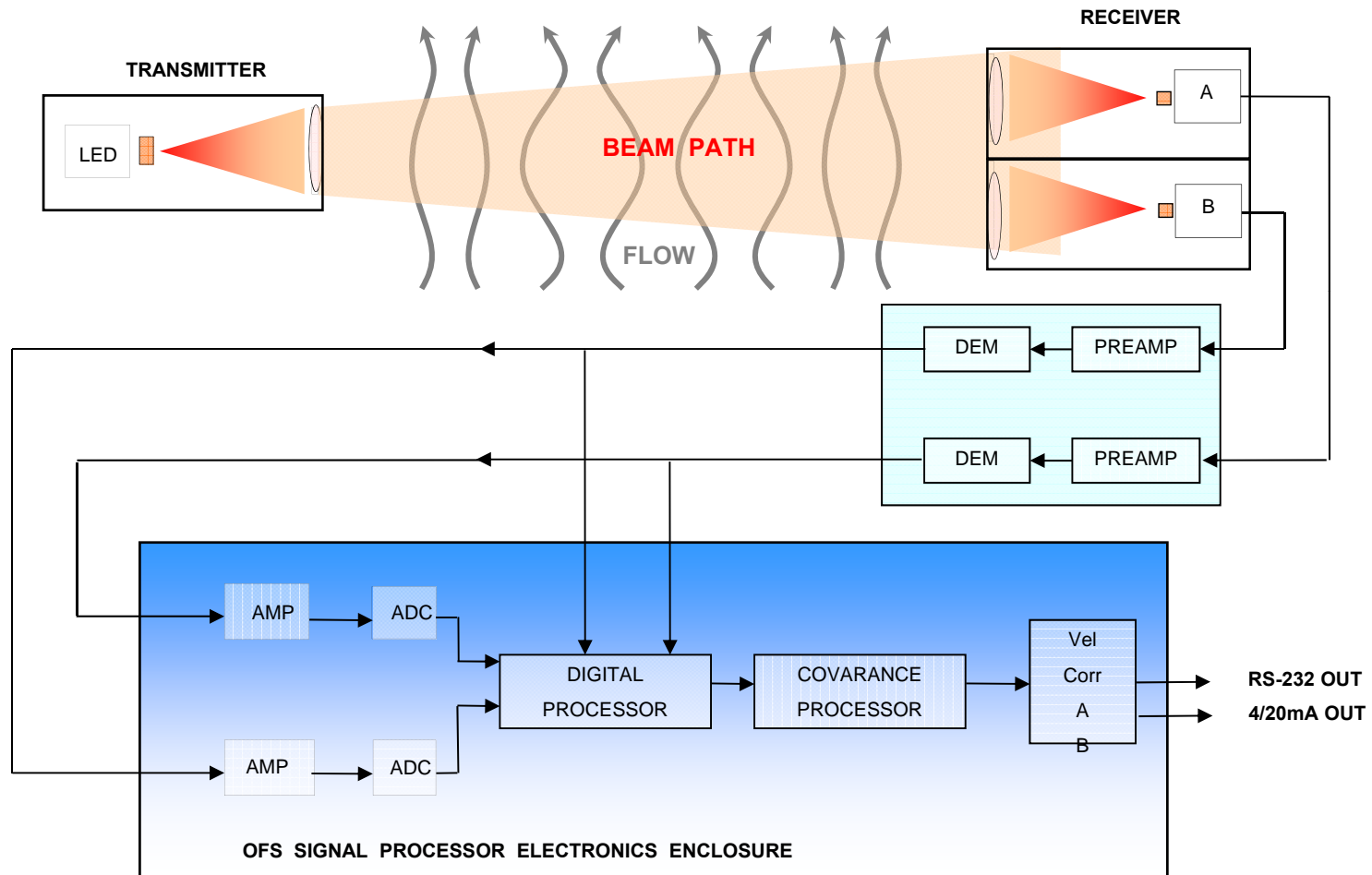
Stack Flow Measurement



Optical Flow Sensor



Stack Flow Measurement



Optical Flow Sensor



Questions?



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