Reinhold Environmental Ltd.

2010 NOx-Combustion Round Table & Expo Presentation

February 8 & 9, 2010   Chattanooga, TN

Workshop 20
Status of NH_3, SO_3, and NO_x Measurements in Coal-Fired Boilers

Reinhold NOx-Combustion Roundtable

Chattanooga, TN

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Presentation Overview

- Measurement drivers
- Characteristics of measurement location for process control applications
- In situ versus extractive
- NH_3, SO_3, and NOx measurements
  - Measurement methods
  - Issues encountered
  - Approaches taken to address issues
  - Application case studies
- Summary

NH_3, SO_3, and NOx Measurement Drivers

- NOx reduction mandates at Federal, State, and local regulatory levels
  - Necessitated broad based deployment of post combustion SCR and SNCR systems for NOx control
  - NH_3 slip measurements needed for:
    - Process optimization with direct reagent feed rate control
    - Minimizing balance of plant impacts
    - Retention of fly ash sales
    - Compliance with ammonia permit limitations
- SCR catalyst oxidizes portion of SO_2 to SO_3
  - SO_3 mitigation technologies implemented on site specific basis
  - Incorporation of scrubbers will likely increase SO_3 issues due to increased use of higher sulfur coals at scrubbed plants
  - SO_3 measurements needed for process control
- SCR inlet/outlet NOx measurements often used for reagent feed rate control
  - NOx measurements in fly ash laden flue gas maintenance intensive
- For NH_3 instances of compliance monitoring requirements are starting to occur

Measurement Location Characteristics

Process Control Applications

- Direct species measurement in flue gas stream between economizer exit / air heater inlet
  - Fly ash particles present vs. CEM measurements downstream of ESP
  - Higher flue gas temperature (i.e. 650 +/- 100 F) than typical CEM measurements at stack
- Measurement uses typically span three levels of complexity
  - Alarm signal to operators if target level exceeded
  - Representative ‘average’ flue gas measurement used for global reagent feed rate control
  - Spatially resolved measurements used for localized optimization of individual or groups of reagent injectors
- Less rigorous QA/QC and documentation requirements than compliance level measurements
- Implementation typically based on potential cost/benefit
  - Limited I&C budgets for maintenance

In Situ vs. Extractive Measurement

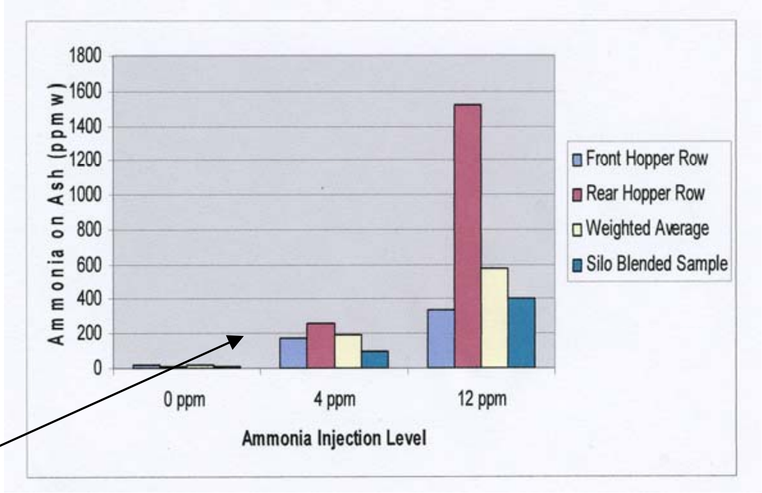
- Complications associated with economizer outlet measurement location
  - Representativeness of measurement due to non homogeneous flue gas
  - Reactivity of species
  - Fly ash requires filtration and/or purge air
- Issue of getting reactive species to monitor favors ***in-situ* methods**
  - Typically dealing with trace level concentrations
  - SO_3 / NH_3 reactive with potential reactions including:
    - $SO_3 + H_2O \longrightarrow H_2SO_4$ Acid dewpoint
    - $SO_3 + CaO_{(s)} \longrightarrow CaSO_{4\ (s)}$ < 2000°F
    - $NH_3 + SO_3 + H_2O \longrightarrow (NH_4)HSO_{4\ (l)}$ 400–500°F
    - $2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_{4\ (s)}$ 400–500°F
  - Sample stream temperature needs to be maintained above highest reaction temperature
  - Potential impacts of sample stream contact with filtration media
    - Catalytic NH_3, NO_x and ash reactions on filters T > 600°F
- In situ measurements provide potential benefits over extractive approach
  - Limited measurement bias
  - Faster system response
  - Line of sight measurements more representative relative to single point

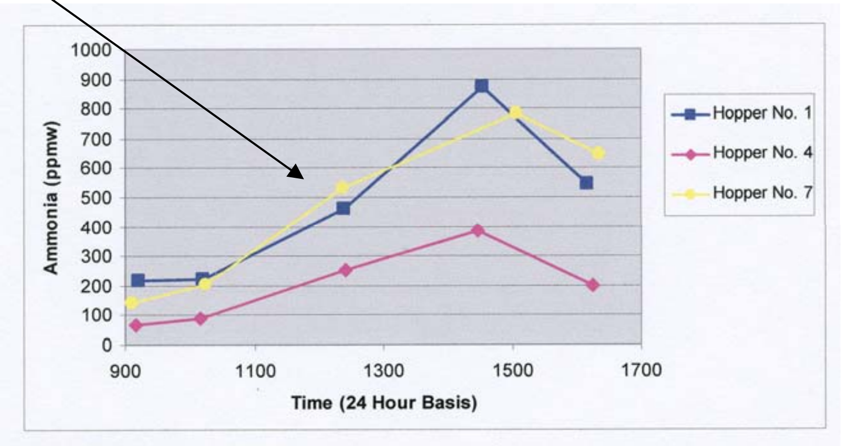
Ammonia Measurement Approaches

- Extractive batch sampling
  - ESP fly ash samples
  - Wet chemistry with ion specific electrode (ISE)
- Extractive continuous sampling
  - NOx differential with and without NH_3 oxidation
- In situ continuous sampling
  - Tunable diode laser
  - FTIR

Ammonia Measurement
Fly Ash Batch Method

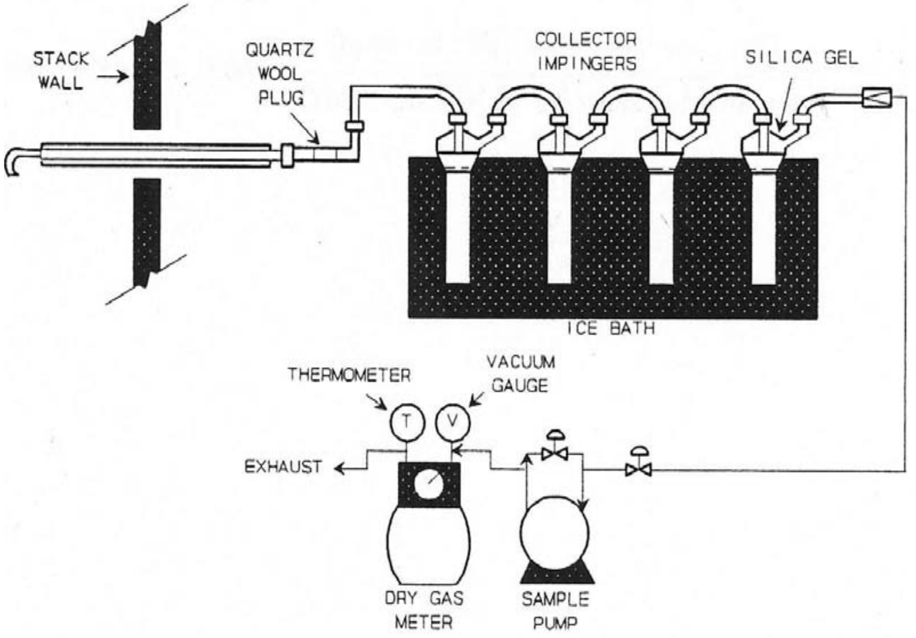
- Popular method for trending relative NH_3 slip over time
  - Requires ash sample be collected at same location under similar operating conditions
    - Represents a time averaged sample
    - Spatial and temporal variation of measurements within ESP documented
  - Ammonia reported relative to weight of fly ash sample (ppm_w)
- Typical ammonia on ash levels < 50 ppm_w
  - Measured values site specific
  - Fly ash conditioning with SO_3 on PRB or lignite fired boilers can impact ammonia retention





Ammonia Measurement
Historical Wet Chemistry Batch Method

- Typically requires one hour sample collection for < 1 ppm detection limit
- Calibrate with standard NH_4Cl solutions of known concentration
  - Calibration curve non-linear at low ammonia levels
- Need to temperature equilibrate samples with standards prior to analysis for best accuracy
  - Use gas sensing ion specific electrode
  - Results not immediately available
- Relatively high cost ($20,000/week for outside contractor with onsite analysis)
  - Time averaged sample
  - Limited process information



Ammonia sampling probe/train arrangement

Ammonia Measurement
Historical Wet Chemistry Batch Method

Potential measurement issues with wet chemistry

- Glass or quartz lined probes optimum
  - Stainless steel measurement probes can create sampling bias at flue gas temperatures in excess of 750 F
    - $2NH_3 + 5/2O_2 \xrightarrow{\text{Hot SS}} 2NO + 3H_2O$
- Analysis variability
  - Calibration standards analyzed with same equipment by four different operators

Sample Solution Concentration (moles/l)	**Flue Gas Conc**	**Std. Dev.**	**NH3 Conc Range**	
10^{-4} moles NH_3/liter	10 ppm	+/-7%	8.6 - 11.4	
10^{-5} moles NH3/liter	1 ppm	+/-25%	0.5 - 1.5	

  - Similar variability found between different laboratories
    - Wet chemistry accuracy found to be a function of concentration

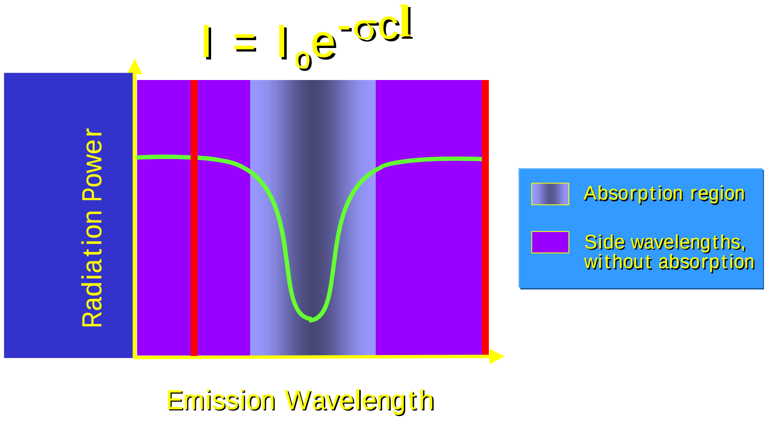
Ammonia Measurement
NOx Differential Continuous Extractive Method

- Method measures NOx with and without NH_3 oxidized to NO
- Predominant applications on GT HRSG with SCR
  - Low NOx and NH_3 levels
    - 2 ppm NH_3 / 2 ppm NOx implies 2 ppm differential against 4 ppm combined measurement of NH_3 + NOx
    - Subtracting small number from another small number
- Coal fired boilers represent significantly higher background NOx measurement (0.07 lb/MBtu NOx ~ 50 ppm_v)
  - 2 ppm NH_3 / 50 ppm NOx implies 2 ppm differential against 52 ppm combined measurement of NH_3 + NOx
  - Subtracting small number from a large background number limits accuracy of NH_3 measurement
  - Also have difficulty in transporting reactive NH_3 species in sample lines with other reactive species (i.e. SO_3)

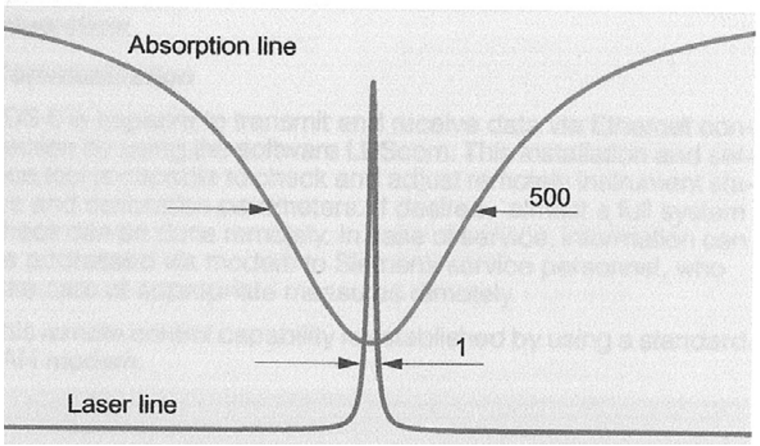
Ammonia Measurement
Tunable Diode Laser (TDL) Continuous Method

- Measure absorbance across line-of-sight using Beer's Law
  - $T = I / I_o = \exp^{(-\sigma\ c\ l)}$
    - Where:
      - T = transmittance of light through the gas
      - I_o = intensity of the light entering the gas
      - I = intensity of the light exiting the gas
      - σ = molar absorption coefficient
      - c = gas concentration
      - l = distance the light beam travels through gas
- Limited interference from other gases
- High sensitivity
- Fast time response

Scanning of Near-IR radiation across a single absorption feature



Unisearch Associates Inc



Ammonia Measurement
EPRI Monitor Evaluation Approach

Three Step General Approach

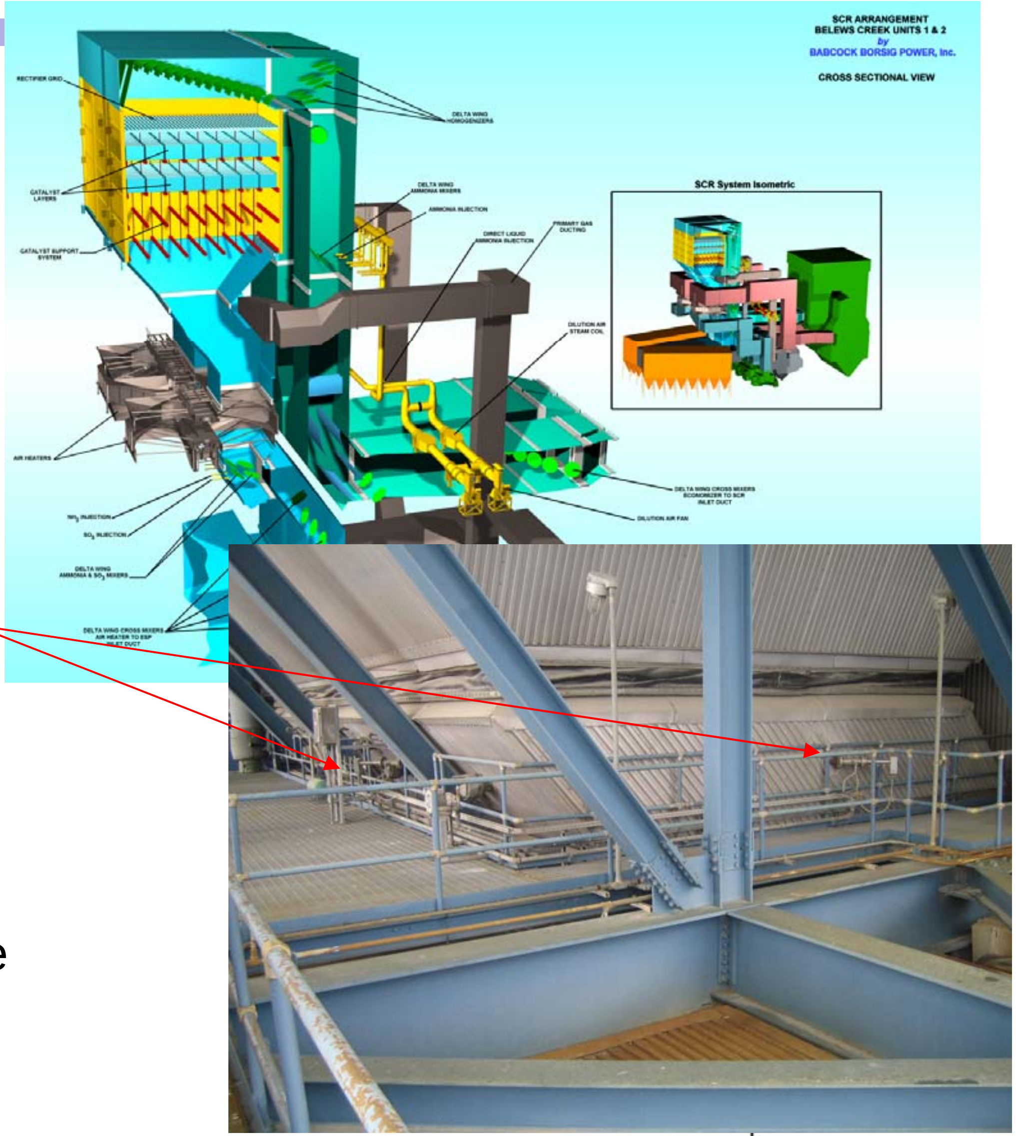
1. Laboratory Assessment
   - Establish accuracy, detection limits, and possible interferences
     - Test over range of target gas concentrations and cell conditions
       - Vary temperature, moisture, background gas composition
2. Single Path Field Demonstration
   - Establish operability and reliability characteristics
     - Test over range of path lengths with particulate laden flue gas
     - Assess alignment and signal to noise ratio over time and operating conditions
     - Assess maintenance requirements
3. Cost Benefit Application Demonstration
   - Structured test with end use of data stream
     (i.e. process control, operator advisory, etc.)
   - Document implementation specification, capital and installation costs, benefits from end use

Ammonia Measurement
TDL Measurement Status

- Lab evaluations indicate TDL ammonia monitors tested work well under controlled conditions
- Application to coal-fired boilers introduce complications
  - Optical measurement issues
    - Port installation and alignment
      - Laser signal implications
    - Variable fly ash in flue gas
      - Soot blowing cycles
      - Laser beam attenuation and variable S/N
    - Long path lengths (reduced power and maintenance of alignment)
  - Current uses
    - Non-spatially resolved measurements for alarm or data trending
    - Spatially resolved measurements for open loop monitoring/control
    - Closed loop process control and/or optimization

Ammonia TDL Case Study ‘A’
NEO LaserGas Series I Application

- 1200 MW B&W opposed wall design
  - Babcock Power Delta Wing ammonia injection system
    - NH_3/NOx RMS < 2%
- NEO LaserGas Series I
  - Installed at SCR reactor exit as part of 2003 retrofit
  - Line of sight cuts across corner of each reactor exit
    - Nominal 15-foot path length
    - Just downstream of expansion joint
    - Reduced flue gas velocity and particle mass flux
  - Alignment maintained over load range
  - Only required annual preventive maintenance to date
  - Favorable comparison of NEO data to ammonia on ash data



Ammonia TDL Case Study ‘B’ Siemens LDS 6 Application

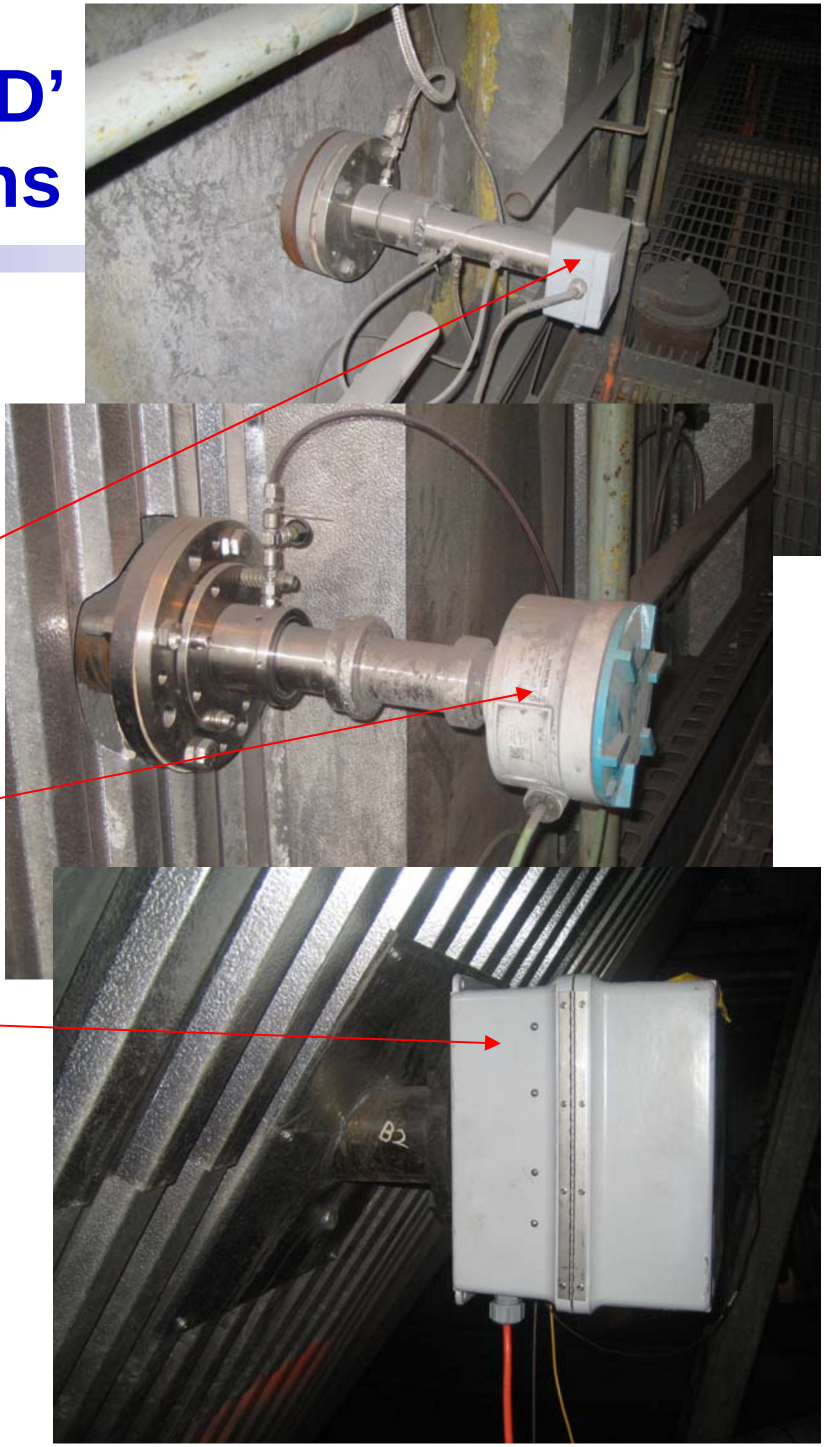
- 140 MW tangential design unit
  - SOFA/SNCR NOx Control
  - Hot side ESP
    - Eliminates particle impacts
- Siemens LDS 6 two channel NH_3 monitor
  - Nominal 18-foot path length
    - Used flange alignment tool during port installation
    - Alignment maintained over load range
  - Wet chemistry comparison conducted after initial installation
  - Only requires annual preventive maintenance to date
- Reduce reagent flow during load transients to minimize slip
  - Ammonia alarm set at levels > 6 ppm

Ammonia TDL Case Study ‘C’ Unisearch LasIR Application

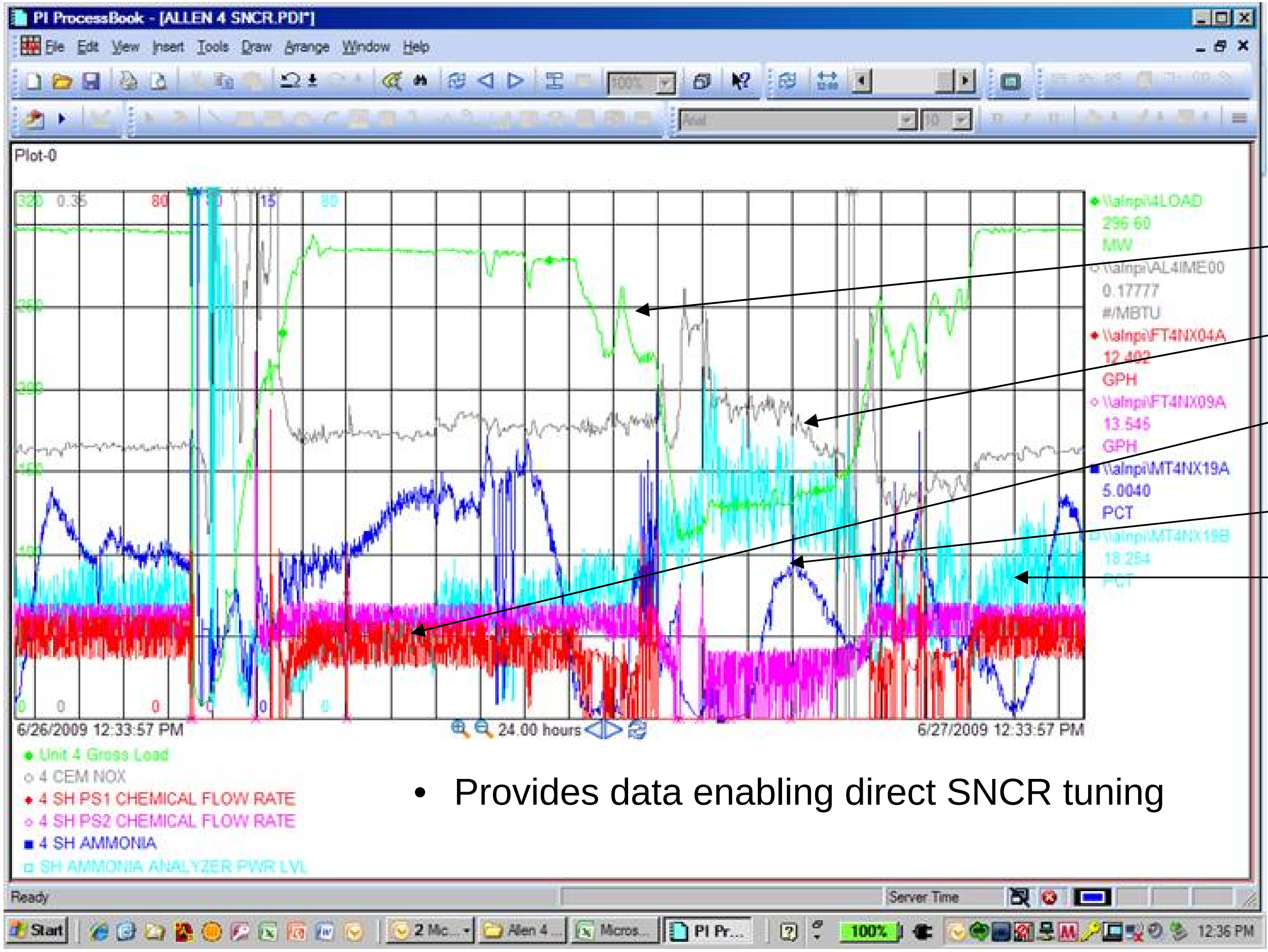
- 200 MW cyclone design unit
  - OFA / RRI / SNCR
  - FGR fans removed
- Unisearch SM-410 four channel monitor
  - Nominal 13-foot path length at economizer outlet
  - 0 to 20 ppm span
  - CEMTEK and TAI Engineering installation
    - Hard mount off duct
    - Flexible connection to port
    - Blower used for purge air

Ammonia TDL Case Study ‘D’ Multiple Monitor Applications

- Tangential design units
  - Single and twin furnace arrangements
  - Nominal 20 foot path length at economizer outlets
    - Duct expansion/contraction over load range
- Unit 1 & 3 – NEO LaserGas Series I monitors installed
  - Never reportedly worked
- Unit 2 – Siemens LDS 6 two channel system installed
  - Never reportedly worked
  - Siemens claimed too high dust loading
- Unit 4 – Unisearch LasIR
  - Four channel monitor with one path installed on SH and RH boiler
  - Initial difficulties encountered with signal strength
  - Installed shields and increased detector size with viable measurements obtained



Ammonia TDL Case Study ‘D’
Unisearch LasIR and Unit DCS Data



Load

CEM NOx

Urea Flow Rate

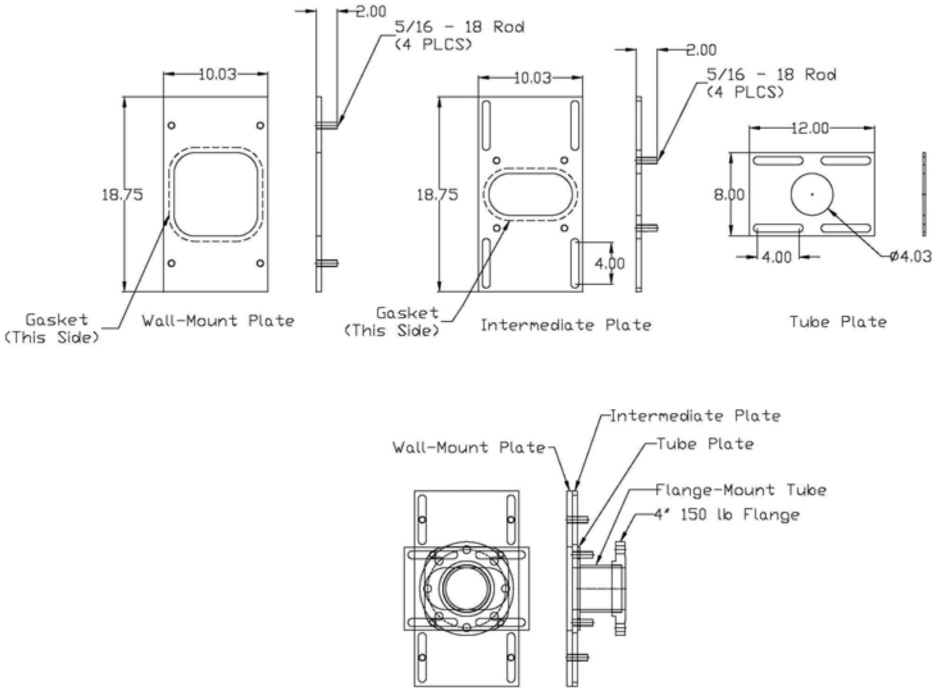
Ammonia Slip

TDL Power Level

- Provides data enabling direct SNCR tuning

Ammonia Measurement Cross Duct Port Alignment

- Vendor specifications of +/- 2 degree port alignment
- Installation procedures and port alignment can vary significantly from site to site
  - – No adjustment capability
    - Significant issue as typically installed during an outage
    - Limited installation 'windows'
  - – Need for more standardized installation approach
    - Ideally would provide ability to accommodate changes in duct flexture between ambient and normal operating conditions



Ammonia Measurement
Single Port Probe Measurements

- Viable for locations with limited physical access on both sides of duct
- Requires monostatic TDL monitor with transmission and detector on one side
  - Testing longevity of reflector and maintenance of optics cleanliness
  - Assessing detection limits over nominal 4 meter path length
- Probe provides permanent measurement path alignment
- Less representative than full cross duct path measurement

Motivation for Continuous SO_3 Measurements

- Installed SCR systems oxidize portion of SO_2 to SO_3
- SO_3 can form H_2SO_4 or ABS that can condense on surfaces and cause corrosion, or be emitted and form blue plume
- Alkaline additives expensive
  - no means to continuously optimize use
- Accurate SO_3 measurements are difficult
  - single point batch samples
    - Prone to error if appropriate sample temperature not maintained
  - long turnaround times for analysis
  - expensive

SO_3 Measurement Approaches

- Extractive batch sampling
  - Controlled condensate (further discussion)
- Extractive continuous sampling
  - Unaware of any proven or reliable approaches
- In situ indirect batch sampling
  - ABS Breen probe
- In situ continuous sampling
  - FTIR (further discussion)
  - UV-DOAS
  - Mid-infrared TDL

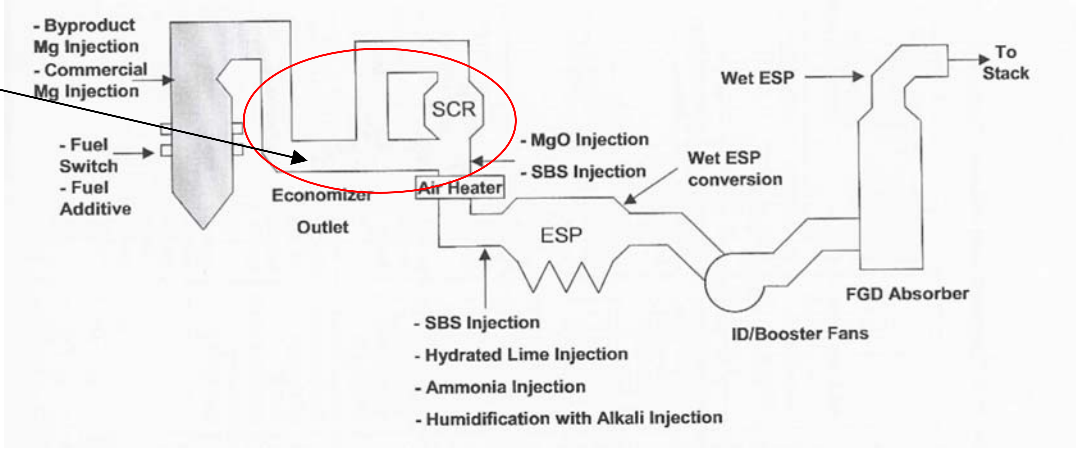
Continuous SO_3 Measurements Measurement Locations

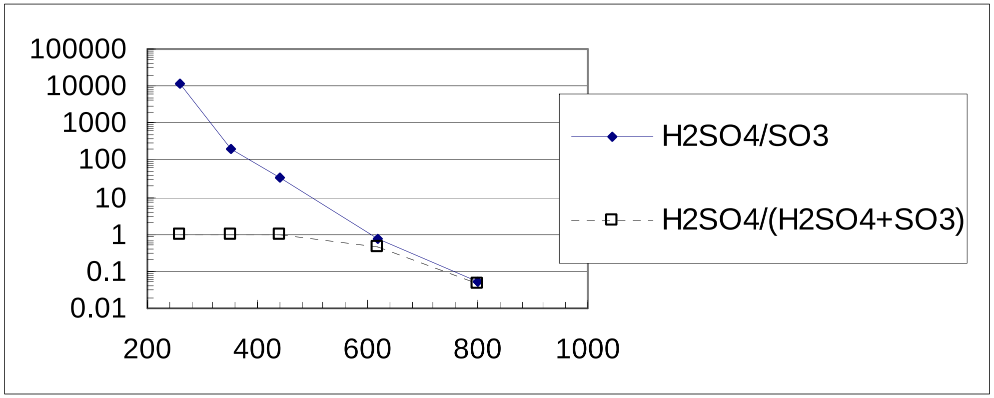
Measurement Issue

- $SO_3 + H_2O \longrightarrow H_2SO_4$
- Equilibrium concentrations changing between 800 – 400 F
  - As a result measurement locations upstream of air heater need to measure both species

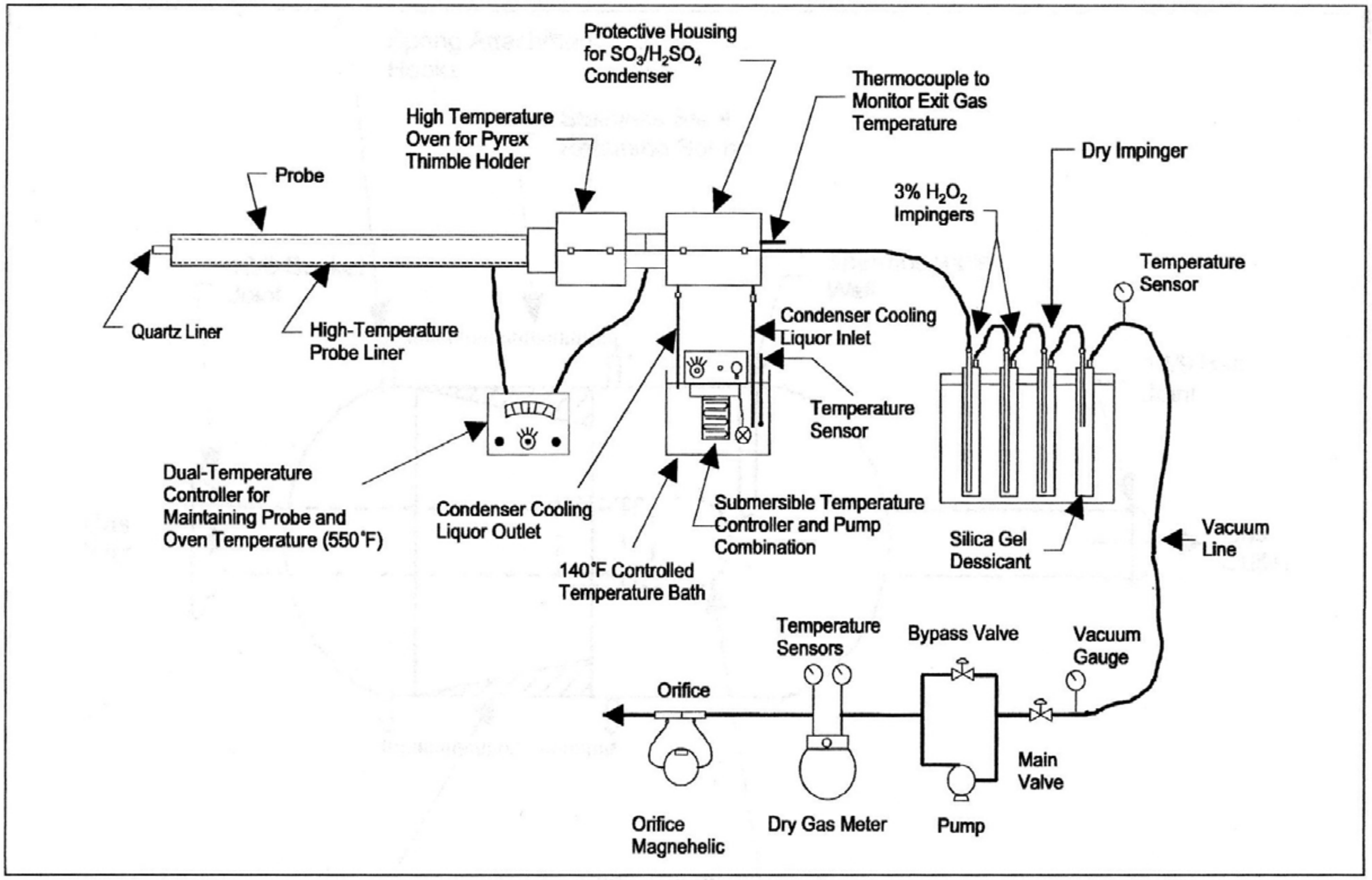
Solution – Measurement approach needs to monitor both species (i.e. SO_3 and H_2SO_4)

- FTIR focus of recent EPRI evaluations
- FTIR tests at Plant Crist Mercury Research Center
- Dual detector approach implemented





SO_3 Measurement Controlled Condensate

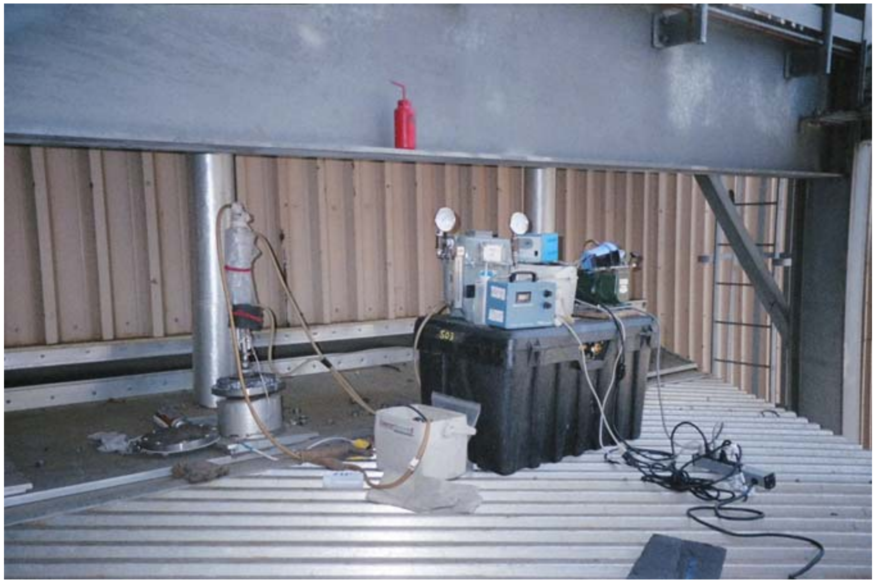


SO_3 Measurement
Controlled Condensate

- Single point measurements
  - SO_4 solid trapped in probe filter
  - SO_3 aerosol condensed in coil
  - SO_2 gas collected in H_2O_2 solution
- Nominal 30 minute sample collection period
  - 20 samples over 12-hour test day with 2-person crew
  - Nominal $2,500 per day testing cost plus mobilization, travel, shipping, equipment rental, and sample analysis (~ $50/sample)
    - Overall testing cost of $15k - $25k for 3 test days on site with travel / setup / tear down / sample analysis
- Question of temporal and spatial variance within duct
- Potential for sample bias
  - Alkaline ash on filter can react with SO_3

SO_3 Measurement
Controlled Condensate

Date	SO_3 Avg (ppm)	SO_3 Avg (ppmc)	Variance (%)
8/23 (10 samples)	33.5	36.6	12.0%
8/24 (26 samples)	30.6	34.2	9.7%
8/25 (20 samples)	29.1	32.0	10.5%



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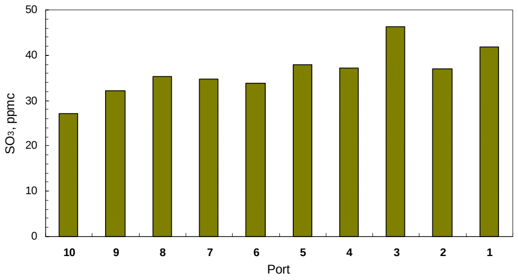

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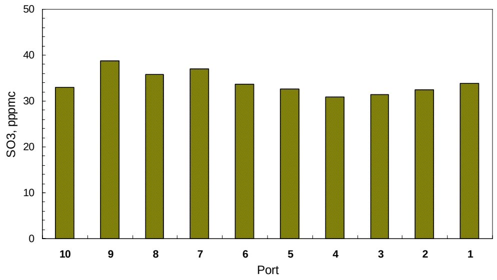

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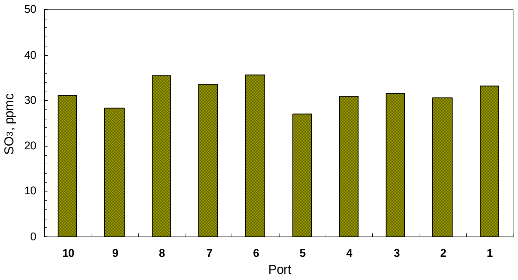
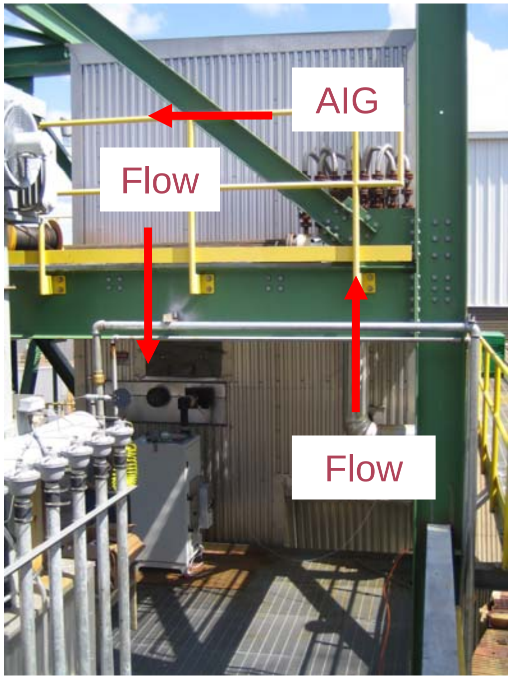


Continuous SO_3 Measurement FTIR Configuration at MRC

- Testing over both open and shielded line of sight paths
  - Nominal 2 meter duct depth
  - Retro doubles path length
  - Sealed measurement path
- Special windows required for FTIR application
  - Minimize absorbance over wavelength range of interest
  - Purge air line to keep window clean
  - Corner cube to reflect beam

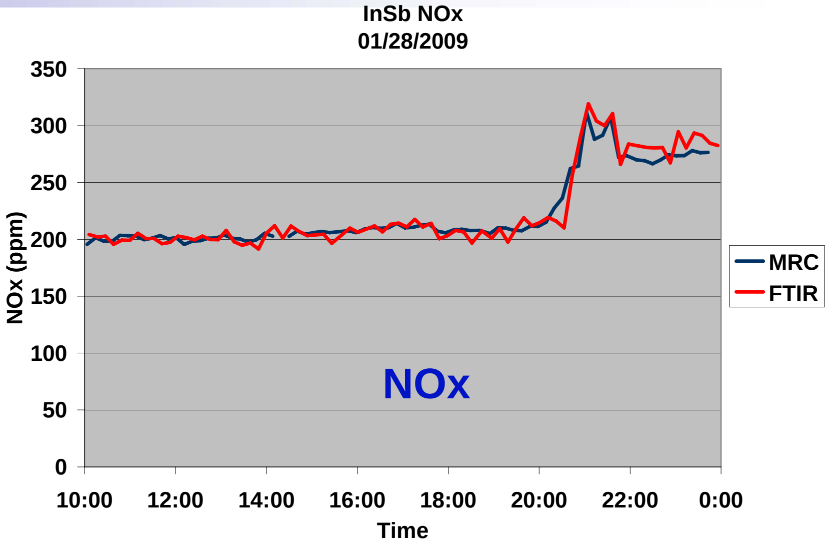
SCR Inlet

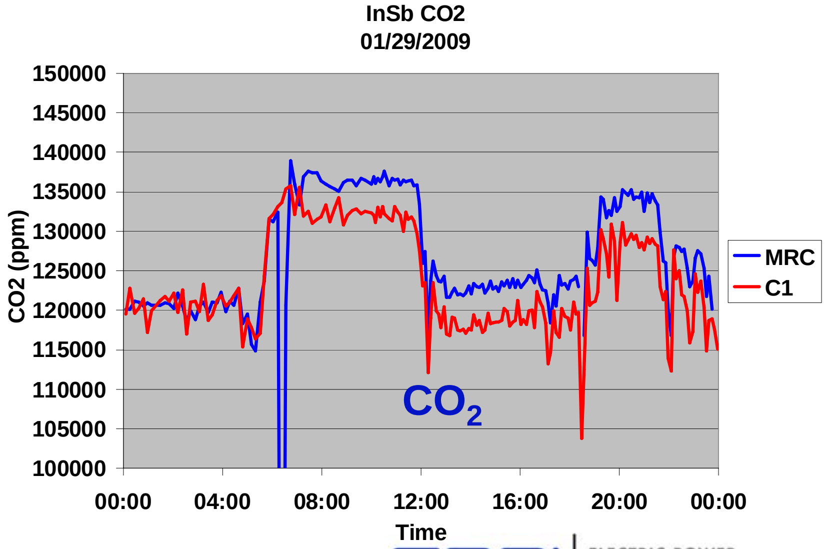


Retro Housing

Continuous SO_3 Measurement FTIR

- Fourier Transform Infrared (FTIR)
  - Multiple species measurements targeted
    - Nitrogen species: NO, NO_2, NH_3
    - Sulfur species: SO_2, SO_3, H_2SO_4
    - Combustion species: CO, CO_2
    - Halogens: Cl and Br
- Application at MRC
  - Enables reference measurements
  - Vary SO_3 or NH_3 concentration
- Initial tests not able to attain target detection limit of 1 ppm for SO_3
  - Future efforts focused on increasing signal strength
  - Determine if 1 ppm SO_3 detection limit achievable

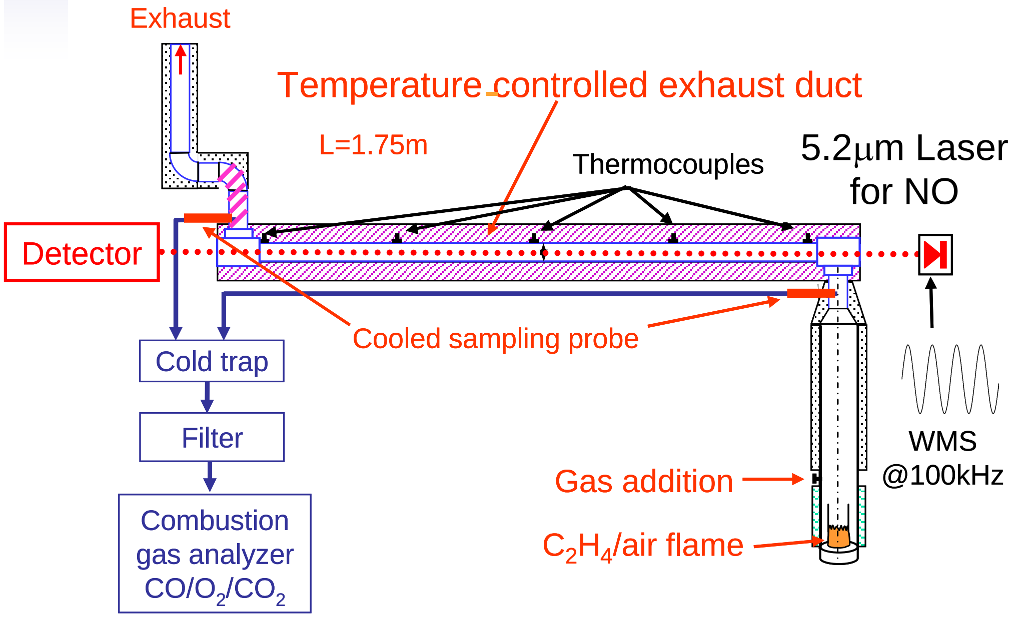


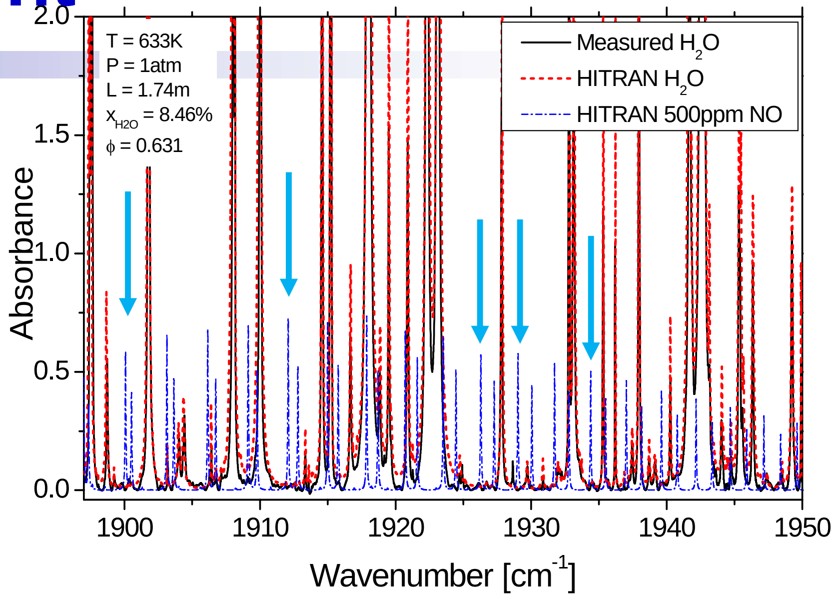


Continuous NO Measurement

- NOx = NO + NO_2
  - NO_2 measured by reducing it to NO
  - $NO_2 \xrightarrow[\text{SS > 1350 F}]{} NO + \frac{1}{2} O_2$
  - At flue gas temperatures upstream of air heater NOx predominantly present as NO (e.g. 95% - 98%)
- Chemiluminescent approach most prevalent
  - $NO + O_3 \xrightarrow{} NO_2 + O_2$
  - $NO + O_3 \xrightarrow{} NO_2^* + O_2$
  - $NO_2^* \xrightarrow{} h_\nu + NO_2$
- Measurement applications in high dust environments have necessitated increased maintenance
- Exploring alternate optical method using mid-IR TDL

Continuous NO Measurement





Water absorption spectrum measured at 700F
Shows potential windows for NO detection

- Novel new QC laser enables laser absorption detection of NO at high T
- Narrow spectral resolution of laser allows detection of NO between H_2O lines
- Predicted H_2O windows validated with laboratory measurements

Next step: Measurements in coal combustion gases to confirm optimum window for sensitive NO detection and determine real-world performance

Summary

Ammonia Measurement

- TDL monitor accuracy of ~ 0.50 ppm over 15 foot path length
- Mixed results with field experience
  - Inconsistent installation practices
    - Poor signal due to alignment difficulties
    - Extended path length and/or particle loading beyond monitor capabilities
  - Successful application characteristics
    - Alignment issues addressed
      - Port locations not subject to duct expansion/contraction
      - Larger detector
      - Monitor installed off duct with line of sight maintained over load range
    - Flue gas particle loading
      - Use of shields with purge air to limit particle obscuration
      - Low velocity measurement location
      - Downstream of hot side ESP
- Current focus on process control applications but consideration of potential compliance monitoring requirements needed

Summary

SO_3 Measurement

- FTIR provides multiple species measurement for flue gas measurement applications between economizer outlet and air heater inlet
- Field application with in situ measurements requires upgraded IR source to boost signal strength
- Field tests to assess ability to obtain ~ 1 ppm detection limits over 4 meter path length

NO Measurement

- Lab tests have demonstrated viability of mid-IR TDL measurement of NO in combustion flue gas
- Field testing has confirmed ability to make measurements in field
- Need to assess signal to noise and detection limits in field with thermal electric cooler vs. liquid N_2
- Integrate laser onto measurement probe