



Advancements in Emissions Monitoring

Reinhold NOx/PCUG Conference
Detroit, MI
January 31, 2005

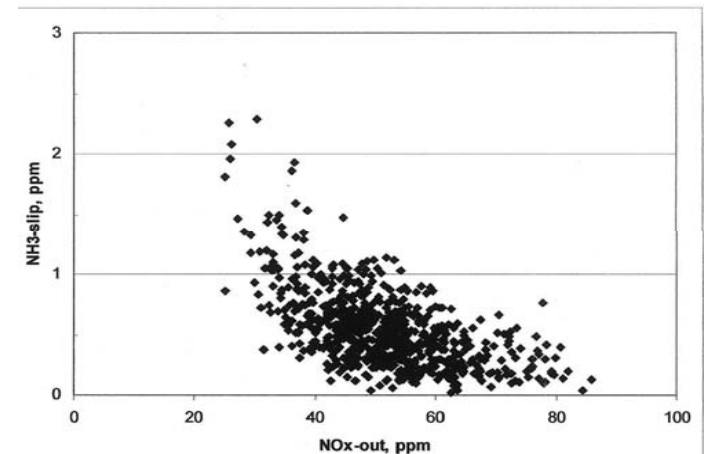
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Scope

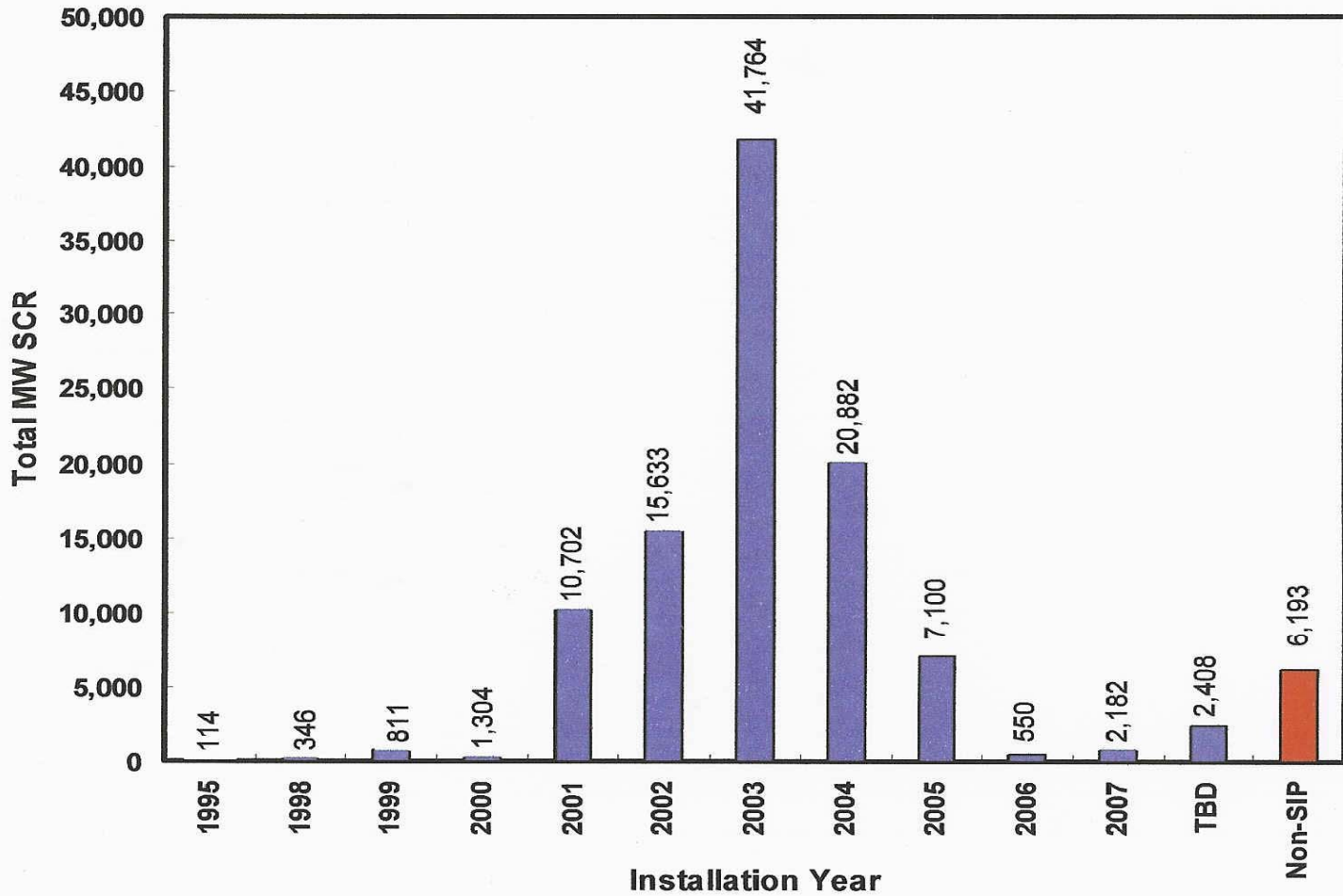
- Focus of discussions is on monitors for process control and optimization, not CEMS
 - More difficult application
 - Higher dust loadings (~5 grains/dscf)
 - Higher flue gas temperature (600 – 700 F)
- Combustion optimization (CO, CO₂, O₂, temperature)
- SNCR / SCR applications (NH₃ and SO₃)

Motivations

- More stringent NOx emission mandates for electric utility boilers has resulted in the deployment of many retrofit SCR/SNCR systems
 - SCR system applications have generated need for continuous measurement of NO, NH₃, and SO₃
 - SNCR system applications have generated need for continuous measurement of FEGT and NH₃
- Potential for improved SCR/SNCR system control
 - Maximize NOx reduction
- Minimize balance of plant impacts
 - Air heater fouling
 - Fly ash contamination
 - Plume formation



U.S. SCR Capacity



Installation Date of U.S. SCR Capacity

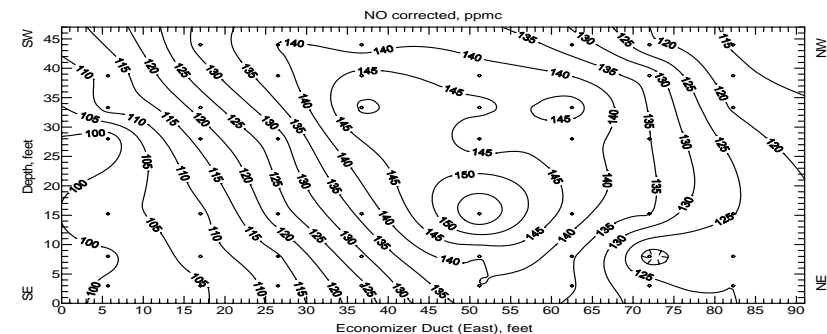
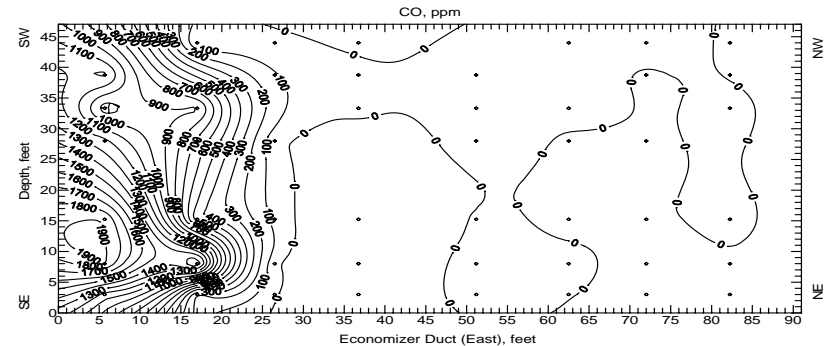
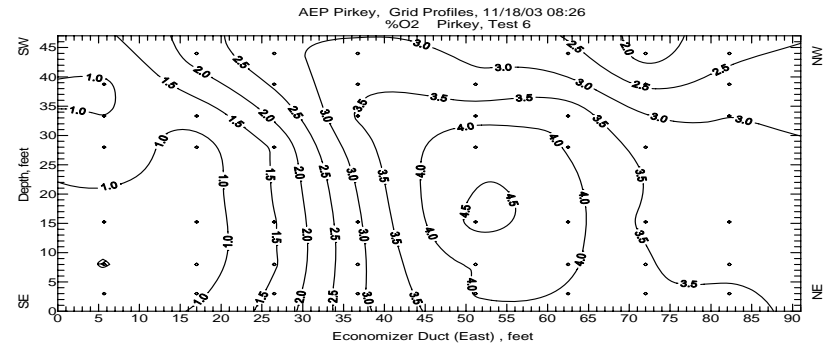
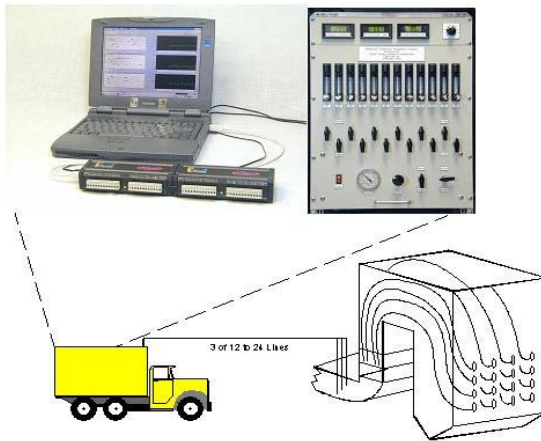
Issues

- Representativeness of sample measurement
 - Large duct cross-sectional areas
 - Stratification of species concentration
 - Air/fuel maldistributions
 - Mills/cyclones in service
 - OFA port settings
 - Burner tilts
 - Convective pass in-leakage
- Species reactivity and potential for measurement bias
- Cost and maintenance of current analyzer systems
 - Typical single point measurement or multi-probe setup
- Potential time lag between system changes and extractive measurement



Traditional Combustion Optimization and SCR/SNCR Tuning

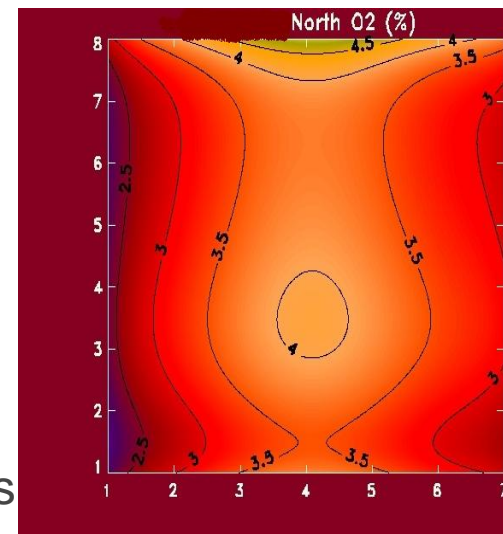
- Historical approach to tune burners or reagent injectors based on back end CO/O₂/NO profiles
- Limited benefit in that it represents point in time tuning; non-continuous feedback



Combustion Optimization

Continuous Tunable Diode Laser Technology

- ZoloBOSS – Boiler Optimization Spectroscopy Sensor
 - TDL based system with measurements achievable across furnace exit, economizer outlet, or SCR reactor inlet/outlet
 - Measures CO, CO₂, O₂, H₂O and temperature (6 lasers)
 - Multiple lines-of-sight feasible
 - Create tomographic maps of temperature and/or species concentrations
 - Currently offers up to 16 lines-of-sight
 - Status
 - Host sites available for demonstration testing
 - 500 MW wall fired design
 - 200 MW tangential split furnace
 - 880 MW tangential design furnace
 - Securing additional utility participants for funding
 - Represent first commercial utility boiler applications



Ammonia Measurement

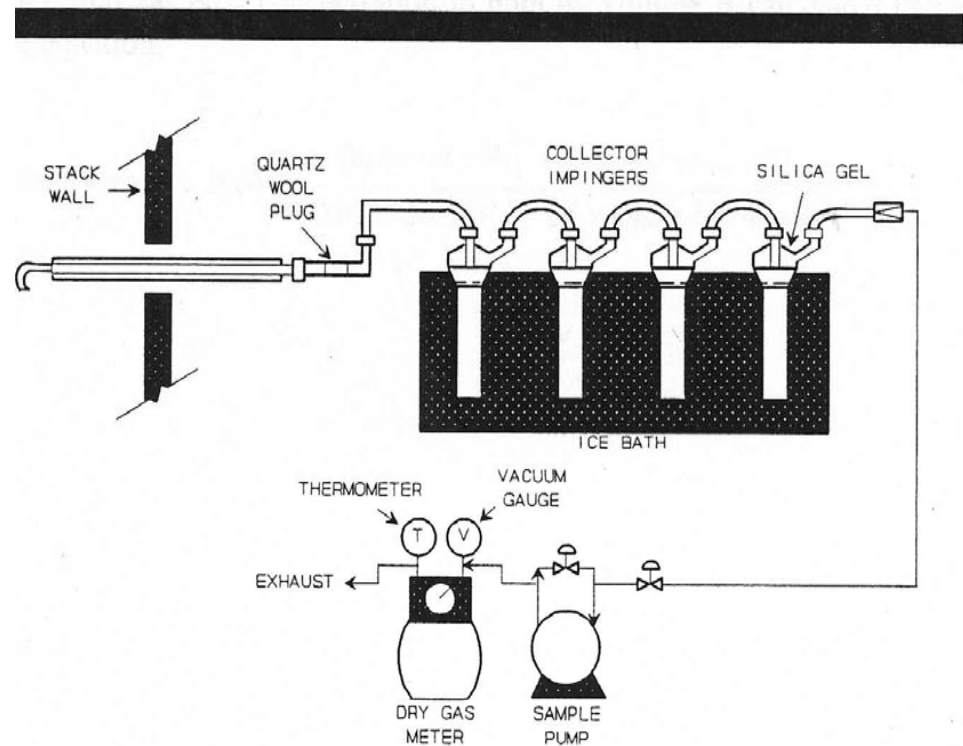
- Ammonia or urea reagents resultant in some levels of slip
- Ammonia monitors desired for more direct process control
 - Economizer outlet/air heater inlet measurement locations
 - Avoid air heater fouling/ash contamination issues
 - Single point measurements not representative
 - Capital and maintenance expense of multiple monitors
- PM_{2.5} issues prompting requirement for stack ammonia monitors in some states



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

Limitations of Wet Chemical Approach as Reference Method

- Validation of TDL techniques have relied upon wet chemical sample collection and analysis
 - Recent EPRI work has raised questions regarding precision/accuracy of wet chemistry method
 - Linear range 1.4 – 1400 ppm (10^{-4} – 0.10 M)

Standard Gas Volume	2.000	6.000	11.999	6.000	ft ³	
	56.63	169.89	339.78	169.89	liters	
Sample Collection Time	10	30	60	30	minutes	
Sample Weight	200	200	200	200	g	
Solution Concentration	1.00E-04	1.00E-04	1.00E-04	1.00E-05	moles/l	
	1.70	1.70	1.70	0.17	mg NH ₃ /liter solution	
	4.81E-04	4.81E-04	4.81E-04	4.81E-05	liters NH ₃ in sample	
Calculation of NH ₃ Conc	8.5	2.8	1.4	0.3	ppmv	

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 NH ₃ /liter	1 ppm	+/-25%	0.5 - 1.5

- Similar variability found between different laboratories
- Comparisons between different analytical techniques need to take into account associated accuracy
 - Wet chemistry accuracy found to be a function of concentration

Continuous Ammonia Measurement Issues

- Issue of getting ammonia sample to monitor typically limits measurement approach to ***in-situ* methods**
 - Potential reactions of ammonia
 - $\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O}$ $(\text{NH}_4)\text{HSO}_4$ (l) 400–500°F
 - $2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O}$ $(\text{NH}_4)_2\text{SO}_4$ (s) 400–500°F
 - $\text{NH}_3 + \text{HCl}$ NH_4Cl (s) 200–300°F
 - $\text{NH}_3 + \text{H}_2\text{O}$ (l) NH_4OH (l) $< T_{\text{DP}}$
 - Catalytic NH_3 , NO_x and ash reactions on filters $T > 600^\circ\text{F}$
- Effect of fly ash particulate in scattering optical signal
 - Analyzers currently capable of measurements on the order of ~20 feet in an open path configuration
 - Dependent upon fly ash loading and size distribution
 - Signal strength may still approach nil during sootblowing cycles

TDL Continuous Ammonia Measurement

- **TDL technology has currently achieved broadest market acceptance**
 - No interference from other gases
 - High sensitivity
 - Fast time response
 - Multi-plexing capability
 - Enables measurements at multiple locations simultaneously
 - More cost effective than single line of sight approaches

TDL Measurement Principle

- **Measure ammonia specific absorbance across line-of-sight using Beer's Law**

- $T = I / I_0 = \exp(-a c l)$

- Where:

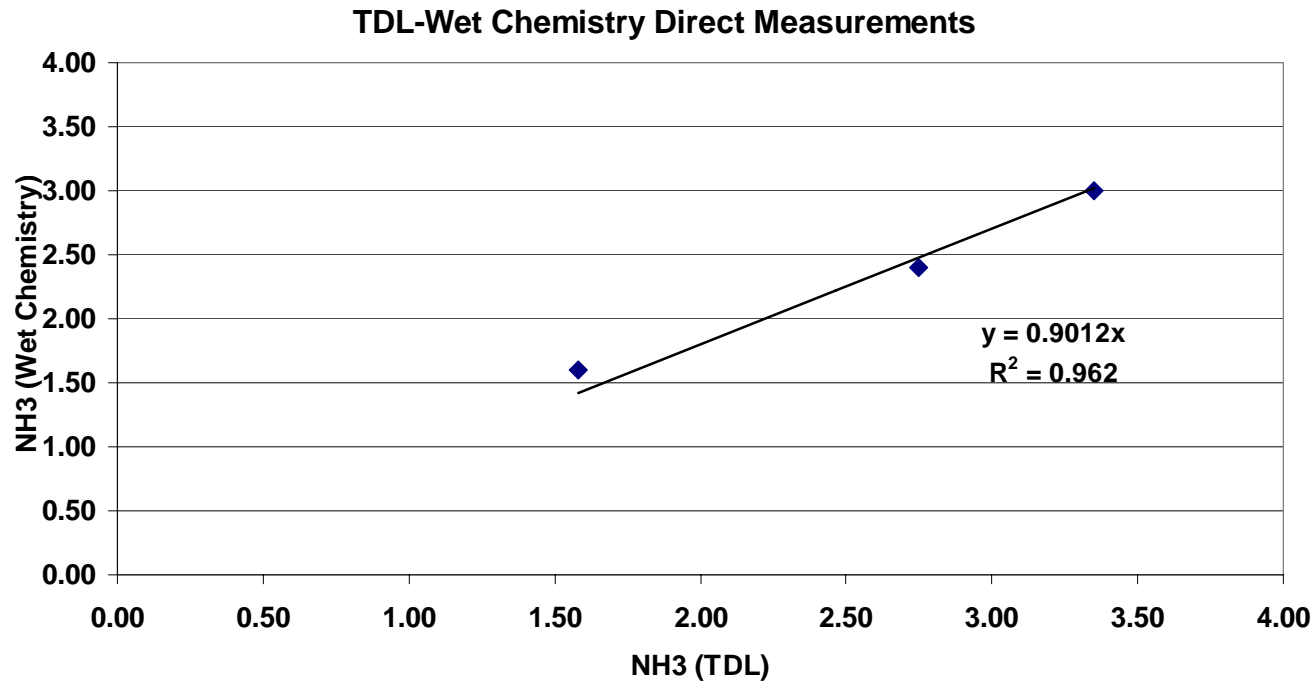
- T = transmittance of light through the gas
- I_0 = intensity of the light entering the gas
- I = intensity of the light exiting the gas
- a = molar absorption coefficient
- c = gas concentration
- l = distance the light beam travels through gas

TDL Ammonia Instruments

Manufacturer	Instrument	Technique
Analytical Specialties (NEO)*	LaserGas	Tunable diode laser, across the stack
Siemens Laser Analytics, (formerly AltOptronic)*	LDS 3000	Tunable diode laser, across the stack
Unisearch Associates*	LasIR	Tunable diode laser, across the stack
	LasIR, Fast Scan	Alternative analysis method
Industrial Automation & Instrumentation (Boreal)	InSyght	Tunable diode laser, across the stack
Opsis Inc.	LD500 Laser Diode Analyzer	Tunable diode laser, across the stack
Sick Maihak Inc.	GM700	Tunable diode laser, single probe

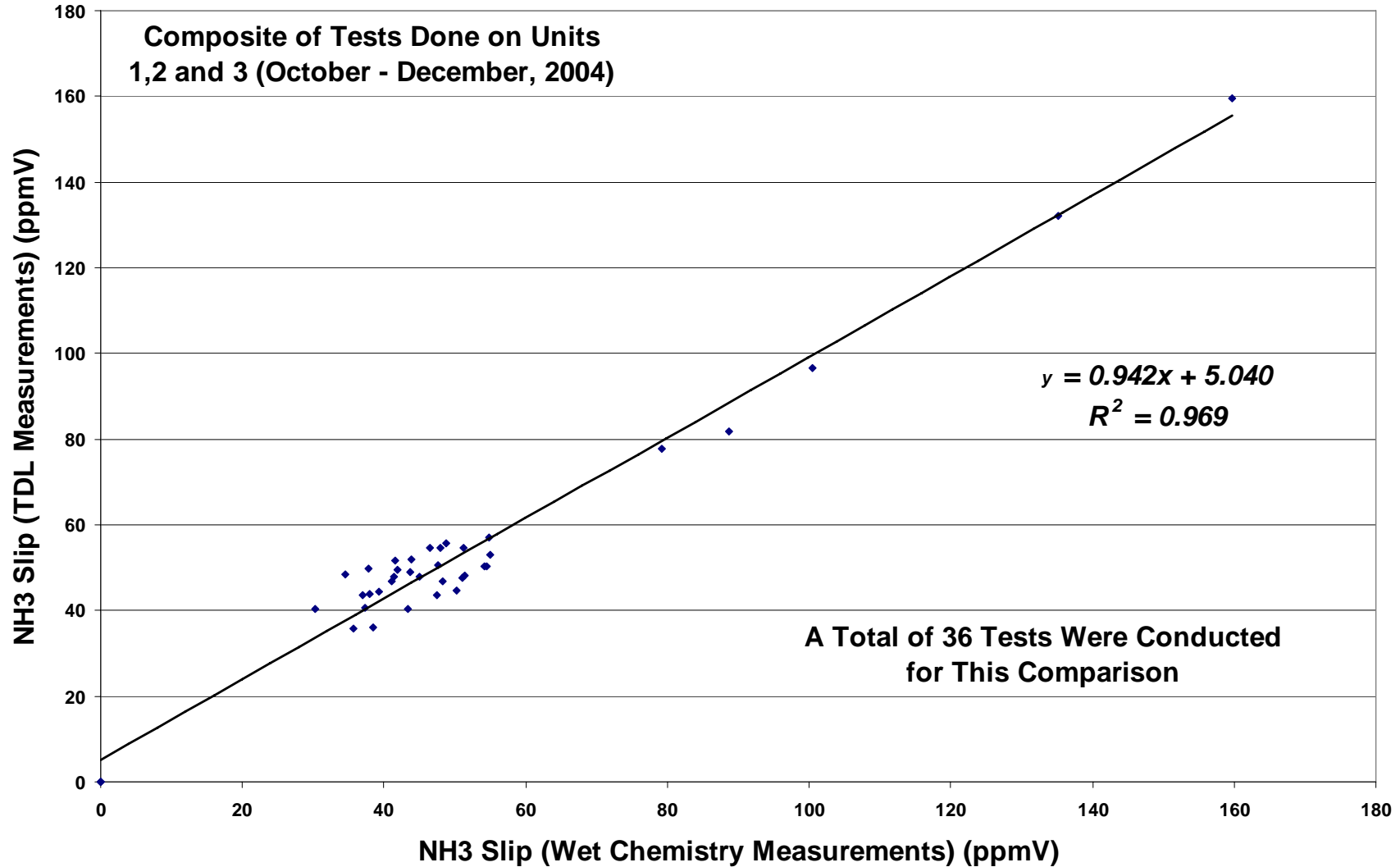
*Installed in utility boiler systems.

Comparison of TDL Results Utility Boiler Measurements at Same Port



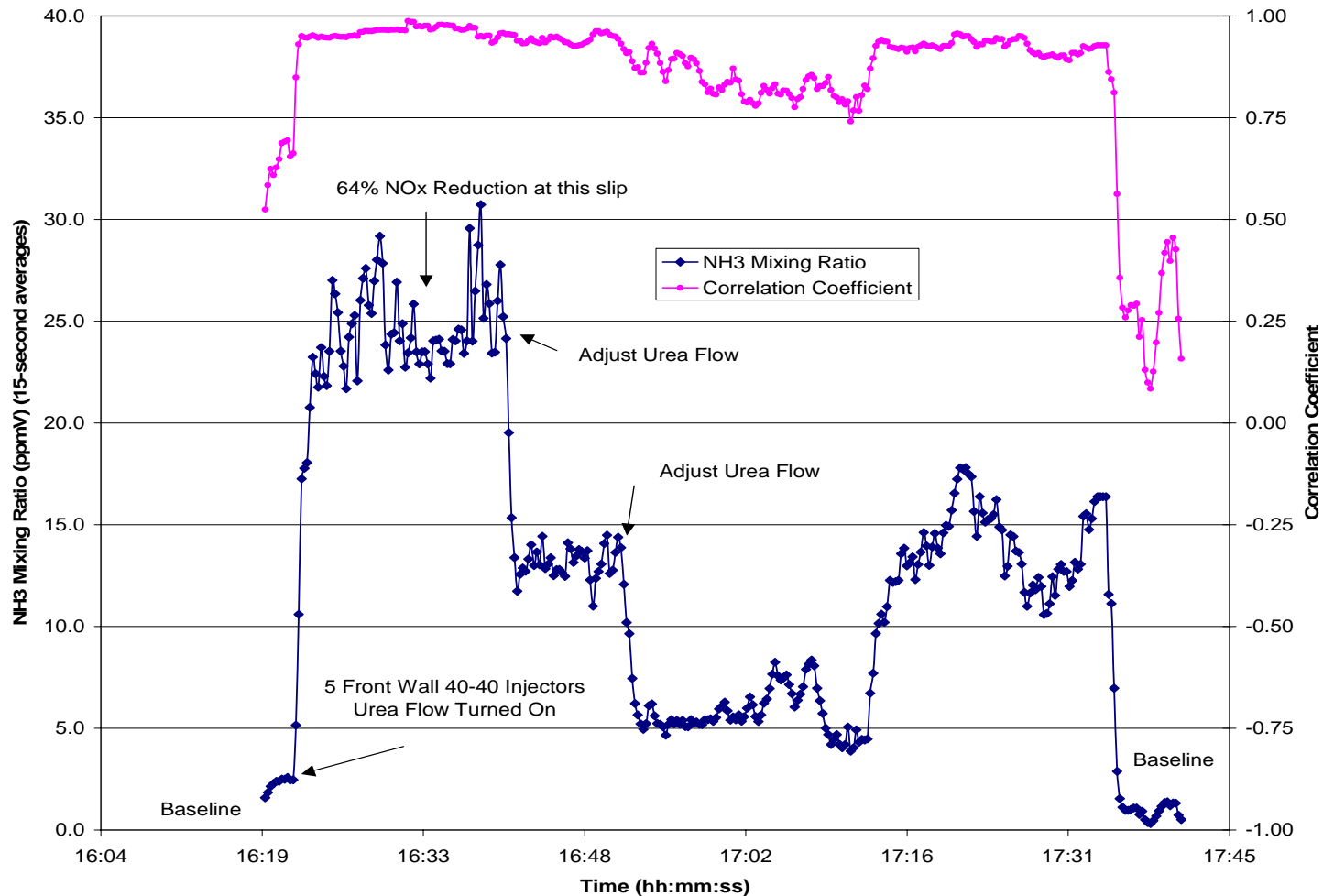
- 20 minute TDL measurement followed by 20 minute wet chemistry
- Average deviation between TDL and wet chemistry of 7.4%
 - Based on range of average ammonia slip values between 1.58 ppm and 3.35 ppm
- Range of TDL measured ammonia slip values of +/- 36% about the mean

Assessment of Dynamic Range



SNCR Tuning Based on Ammonia Slip

Tuned SNCR performance to < 5 ppm within 90 minutes with portable probe

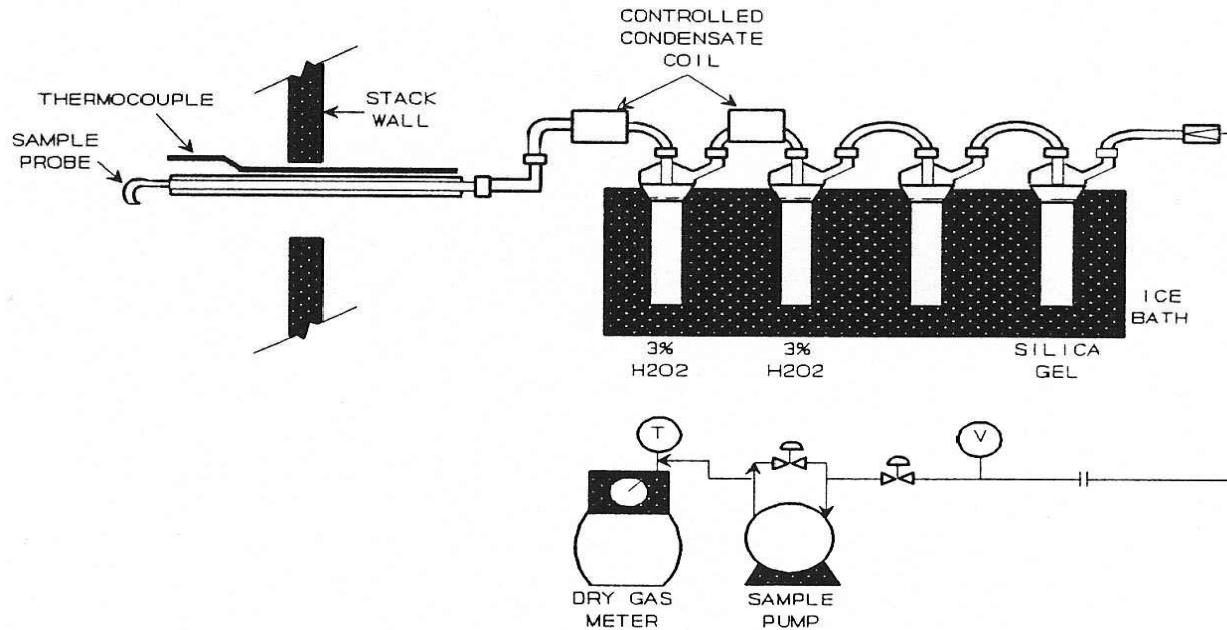


Motivation for Continuous SO₃ Measurements

- Installed SCR systems oxidize portion of SO₂ to SO₃
- SO₃ can form H₂SO₄ 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 SO₃ measurements are difficult
 - single point batch samples
 - Prone to error if appropriate sample temperature not maintained
 - long turnaround times for analysis
 - expensive



SO₃ Controlled Condensate Sampling Schematic



Sample Train for Determination of Sulfur Oxides by EPA Controlled Condensate Method

SO₃ Sampling Issues

- Issue of getting SO₃ sample to monitor typically limits measurement approach to ***in-situ methods***
 - Potential reactions of SO₃

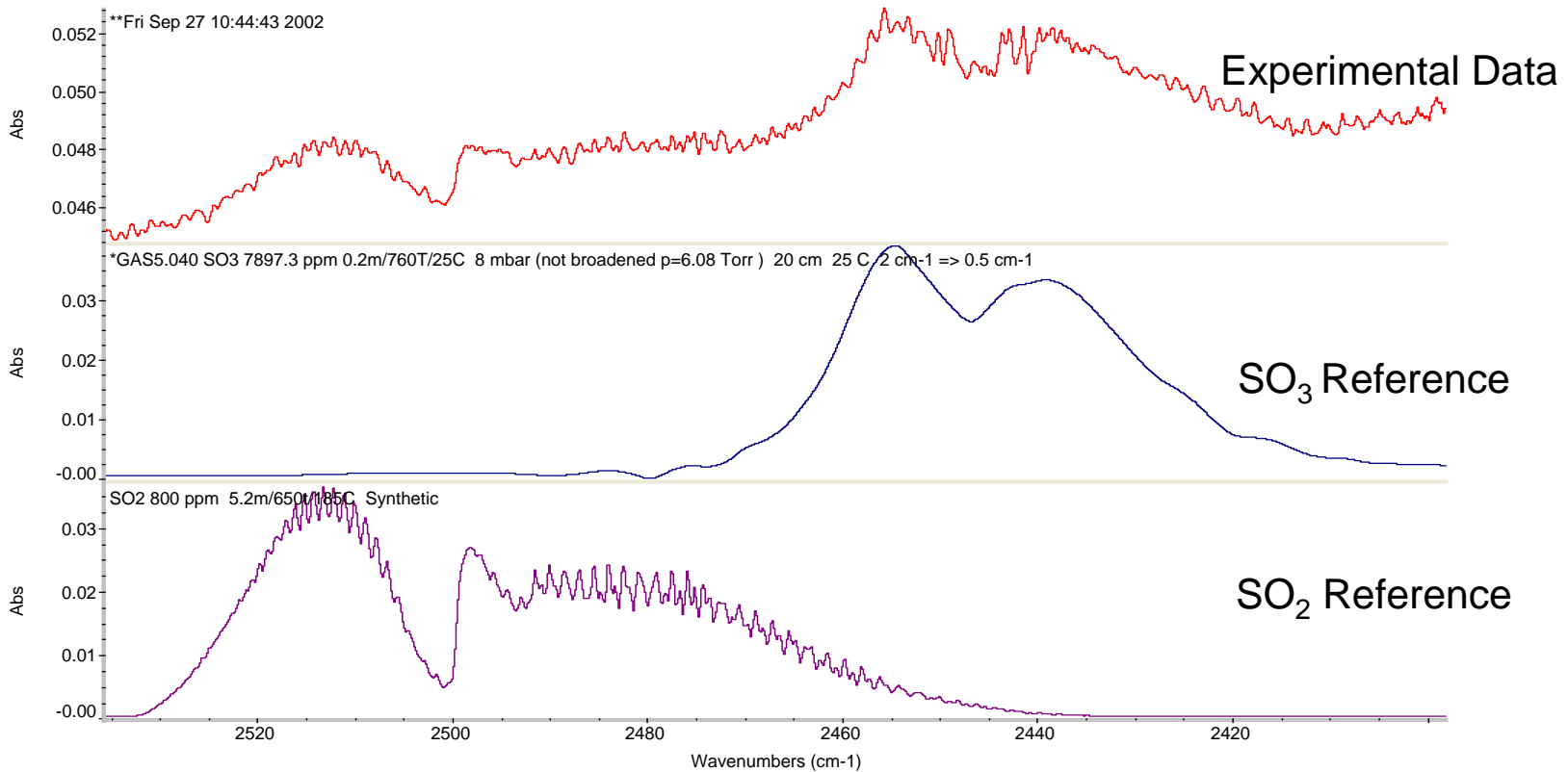
• SO ₃ + H ₂ O	H ₂ SO ₄	Acid dewpoint
• SO ₃ + CaO	CaSO ₄	< 2000°F
• NH ₃ + SO ₃ + H ₂ O	(NH ₄)HSO ₄ (l)	400–500°F
• 2NH ₃ + SO ₃ + H ₂ O	(NH ₄) ₂ SO ₄ (s)	400–500°F
 - Sample stream temperature needs to be maintained above highest reaction temperature
 - Reactions with fly ash constituents necessitate minimization of sample stream contact with filtration media

FTIR SO₃ Measurements

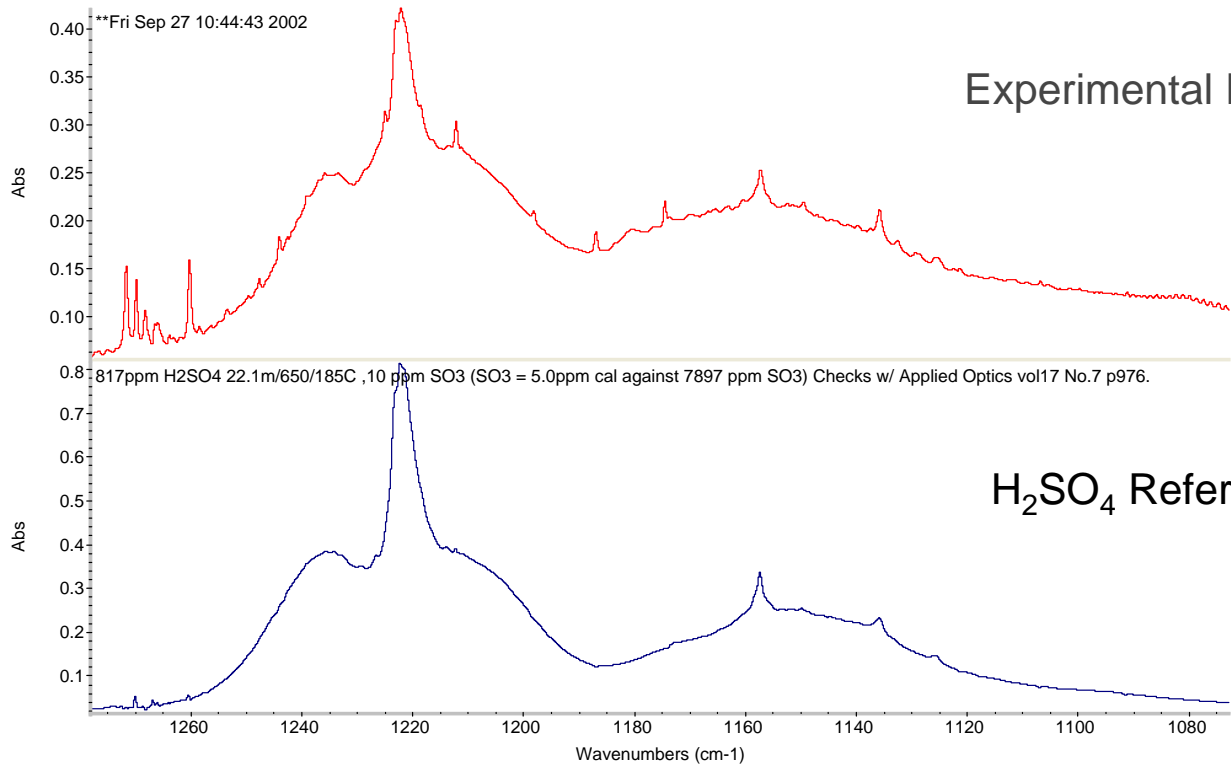
- FTIR has been developed for use in incinerators
 - Instrument operated uninterrupted at incinerators for more than three months at a time
 - Reported extractive FTIR measurements of SO₃ and H₂SO₄ at a coal-fired power plant
 - Extractive measurements proved difficult because of the sample line conditioning required
- To eliminate extractive sampling combining FTIR with EPRI/UCR phase discrimination probe
 - Provides in-situ path lengths
 - Designed for dust attenuation
 - Enables line-of-sight measurements in duct
- SO₃ has strong absorption characteristics in the IR
 - Demonstration planned for first quarter of 2005



Experimental FTIR Spectrum for SO₂ & SO₃



Experimental FTIR Spectrum for H₂SO₄



Approach

- Designing probe for single port access
- Necessitates high temperature retro reflector
 - Transparent to optical wavelengths of interest
- Long path lengths to achieve target 1 ppm detection limits
 - Phase discrimination probe to minimize ash attenuation of beam strength



NOx Measurements

- NOx comprised of NO + NO₂
- NOx formation completed prior to upper furnace
 - At flue gas temperatures > 300°F ~95% - 98% of NOx present as NO with balance NO₂ in coal fired boilers
 - As flue gas cools out of the stack, NO is oxidized to NO₂
 - At high concentrations NO₂ forms a brown plume
 - NO₂ is water soluble and forms HNO₃ (acid aerosol)
- Extractive multi-point sampling typically used for combustion optimization
- Current systems applied to SCR control require high maintenance

Potential NO Measurement Approach

- Tunable diode laser
 - NO has low molar absorptivity
 - Requires longer path length
 - Tradeoff with signal power attenuation from fly ash
- Benefits
 - In situ measurement
 - Quick response time
 - Multiplexing capability of TDL would enable multiple path measurements with single monitor
 - Reduced maintenance relative to current monitoring approach

Summary

- TDL monitors being demonstrated that provide continuous information for optimization of boiler performance (CO, CO₂, O₂, H₂O, Temperature)
 - Assessing detection limits
 - Determining the number of lines of sight required for generation of tomographic maps with adequate resolution
- In-situ measurements eliminate potential biases due to interfering reactions
- TDL also being demonstrated for continuous multi-path measurements of ammonia
 - Accuracy and dynamic range validated
 - Differences in vendor instruments
- FTIR being demonstrated for continuous single path measurement of SO₃