Monitoring and Control of Alkali Volatilization and Batch Carryover for Minimization of Particulate Emissions and Crown Refractory Corrosion in Glass Melting Furnaces

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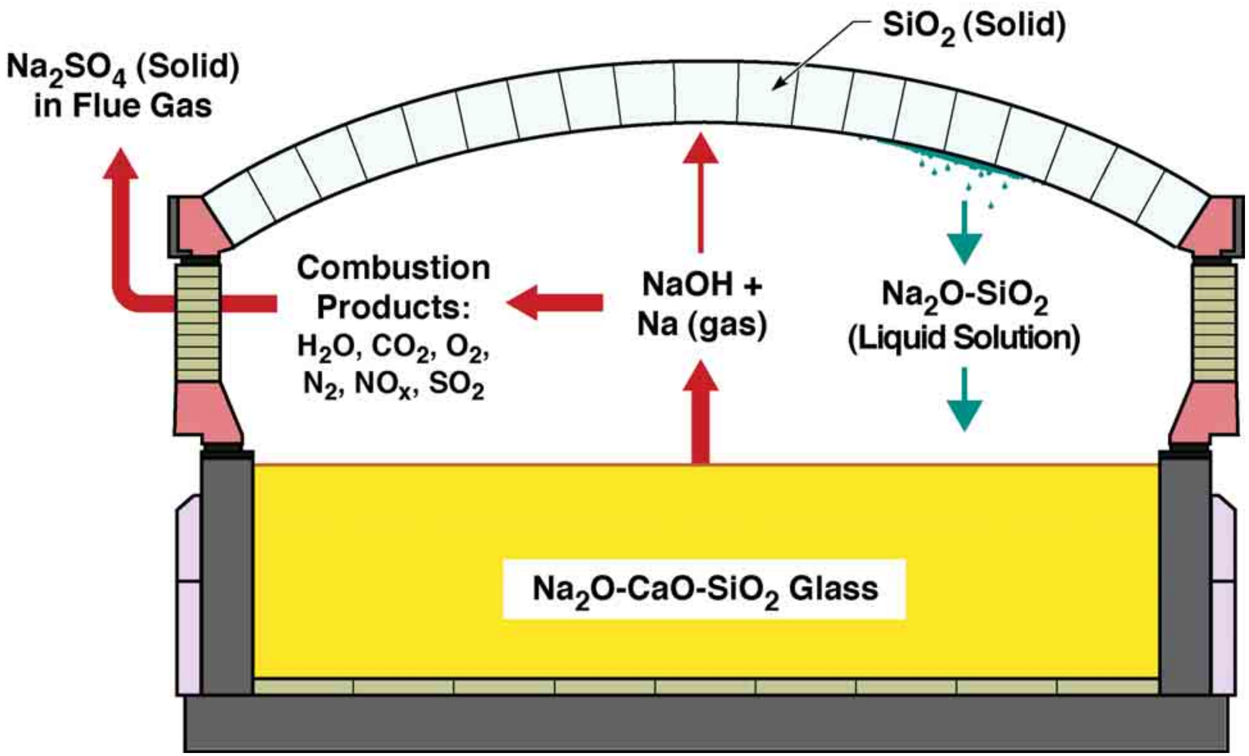
DOE Materials, Glass and Sensors Portfolio and Project Review
June 2004

Introduction

- Many glass furnaces are oxygen/natural gas fueled
- Typical raw materials (batch) for container glass
  - Sand (SiO_2)
  - Soda ash (Na_2CO_3)
  - Limestone ($CaCO_3$)
  - Salt cake (Na_2SO_4)
  - Recycled glass
  - K, Al, Mg, Fe, Ti, etc.
- Inorganics can enter the combustion space
  - Volatilization
  - Batch carryover
- Problems with inorganics
  - Crown and superstructure corrosion
  - Particulate matter emissions

Example

Crown corrosion more problematic in oxy-fuel furnaces



Background

- **Volatilization depends on**
  - Temperature of the furnace
  - Velocity of gases across the melt
  - Composition of gases above the melt
  - Diffusion in the melt
  - Mass transfer at the melt/gas interface
- **Batch carryover depends on**
  - Composition of the batch
  - Particle size of the batch
  - Velocity across the batch
- **Simultaneous optimization is difficult – especially in oxy-fuel furnaces**

Reactive volatilization sample reactions

- $Na_2O\ (l) \Leftrightarrow 2\ Na\ (g) + \frac{1}{2}\ O_2\ (g)$
- $Na_2O\ (l) + H_2O\ (g) \Leftrightarrow 2NaOH\ (g)$
- $Na_2O\ (l) + CO\ (g) \Leftrightarrow Na\ (g) + CO_2\ (g)$

Motivation

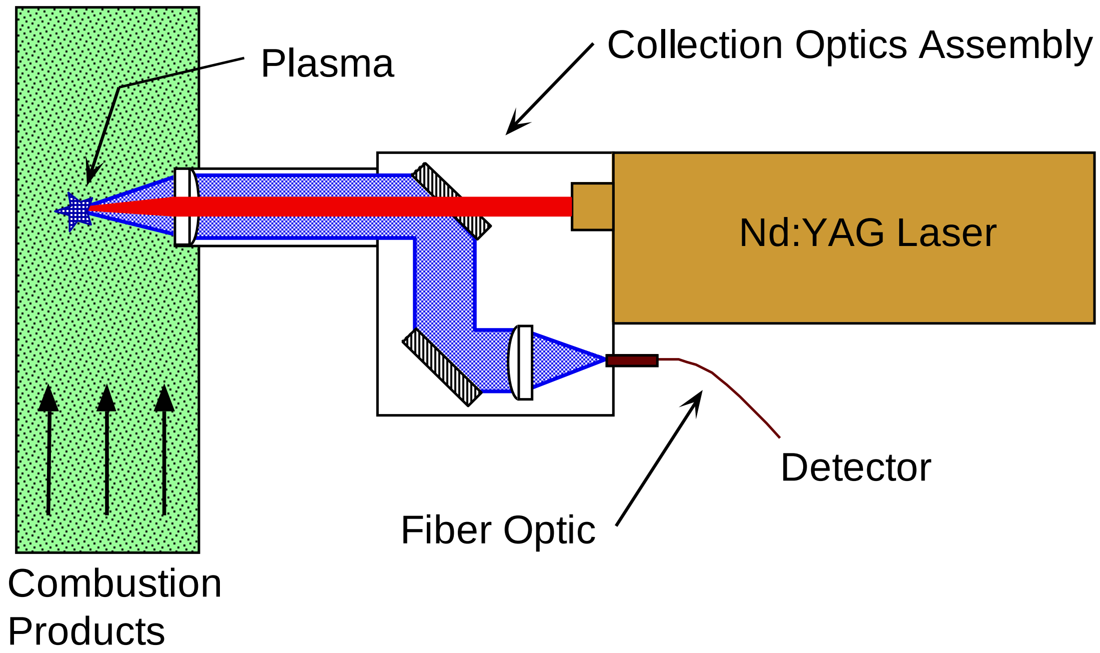
- Oxy-fuel furnaces relatively new so not understood
- Methods outdated for analyzing volatilization and carryover
  - Collection on cooled targets
  - Extractive sampling
- Difficult to correlate with changes in furnace conditions

- In-situ technique would allow more thorough study

Objectives

- Use laser-induced breakdown spectroscopy (LIBS) to examine Na, K, Ca, Mg, Si, and Al *in-situ* in the flue of an operating glass furnace
- Use gas analysis to determine furnace stoichiometry
- Determine effect of furnace operating conditions on volatilization and batch carryover
  - Temperature
  - Stoichiometry
  - Pressure

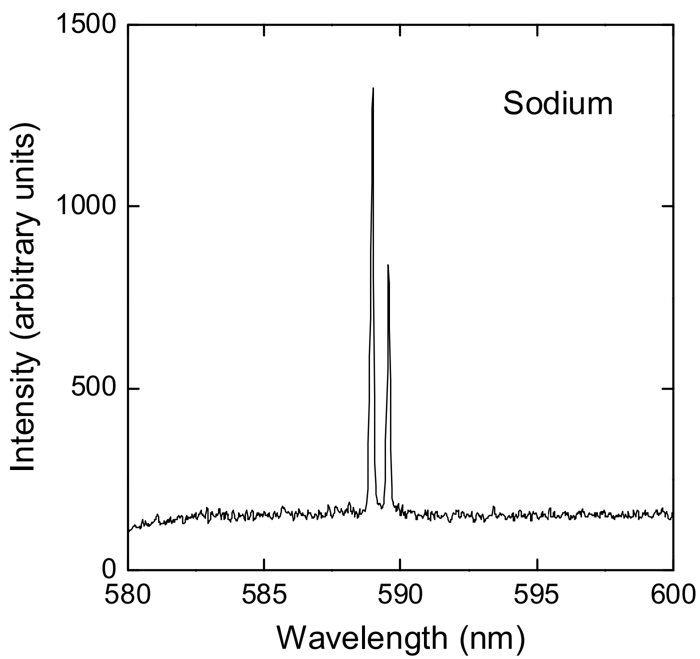
LIBS

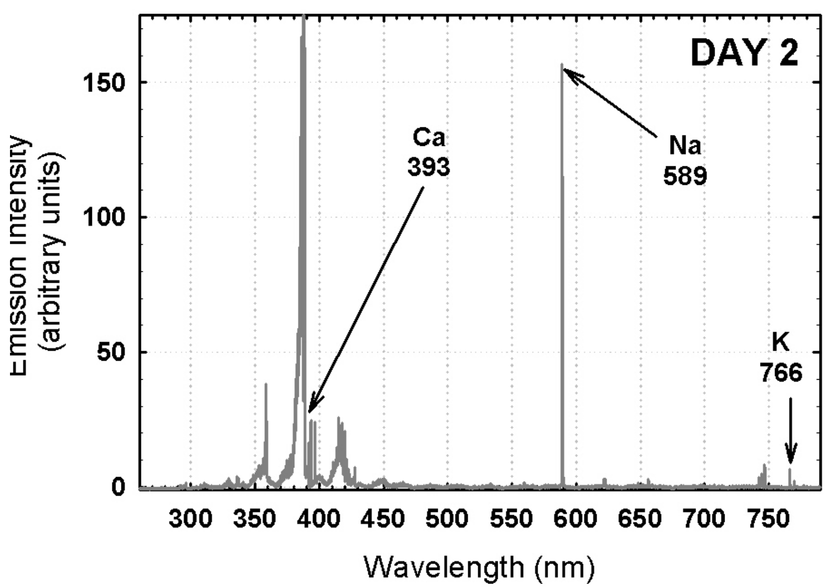


- Particles + gases
- ND:Yag Laser
  - 400 mJ, 5 Hz
- 1064 nm, 10 ns
- Delay time 10 μs or 20 μs
- Gate width 50 μs

Two LIBS detection schemes

- Linear spectrometer
  - Single shots at 5 Hz
  - Narrow spectral windows
    - 20 nm at 0.05 nm resolution
  - Can see Ca & Al, Si & Mg, Na, or K depending on window
- Echelle spectrometer
  - 1600, 800, or 500 shot averages
  - Broadband
    - 300 nm – 900 nm
    - Resolution 0.1 nm at 400 nm
  - Multiple elements



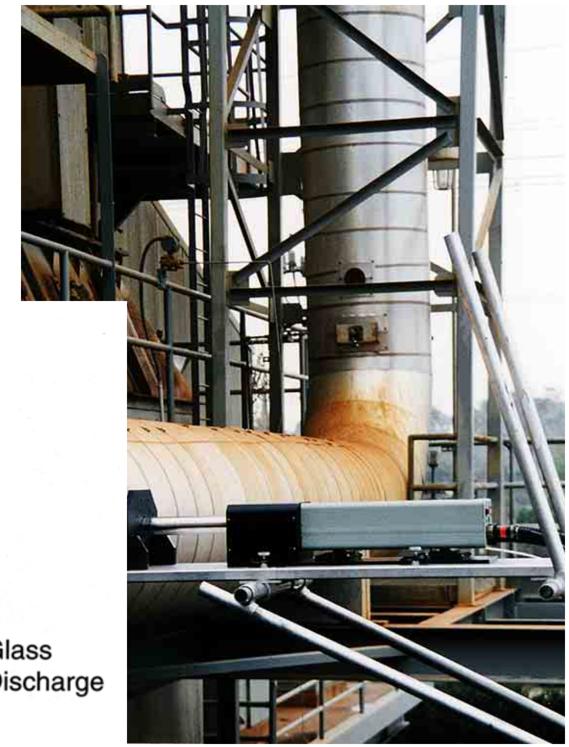


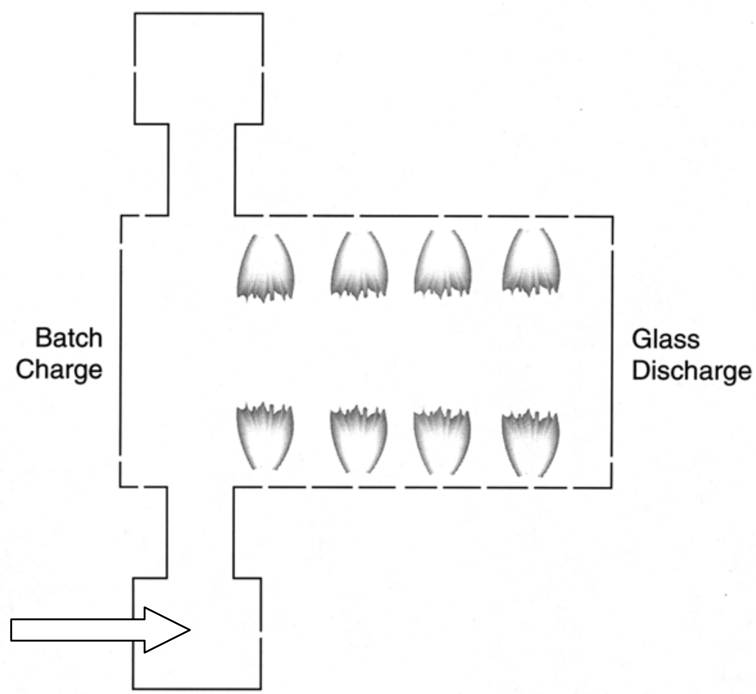
LIBS has been applied in two areas of a container glass furnace

- **Exhaust duct**
  - **Dilution ~2.5-3.5**
  - **Low temperature**
    - **620 K – 720 K (650 º F - 840 º F)**
  - **High velocity**
    - **29 m/s (95 ft/s)**

- **Vertical flue**
  - **Little dilution**
  - **High temperature**
    - **1450 K (2150 º F)**
  - **Low velocity**
    - **0.5 m/s (1.6 ft/s)**

Gallo Glass Company
Tank #1





Field Tests to Date

Date	Pull Rate (t/day)	O/G	Heat Release Rate (MW)	% Boost	
Dec 2001	430	2.16	15.2	14.6	Exhaust
June 2002	336 435	2.12	12.0 14.9	13.2	Vertical Flue
May 2003	322 405	1.98 - 2.18	11.3 - 13.9	13.7 - 15.6	Vertical Flue
June 2004	325 270 375	2.00 - 2.13	13.1 - 14.8	12.6 - 14.6	Both

(40-50 MMBtu/hr)

Highlights of Previous Findings

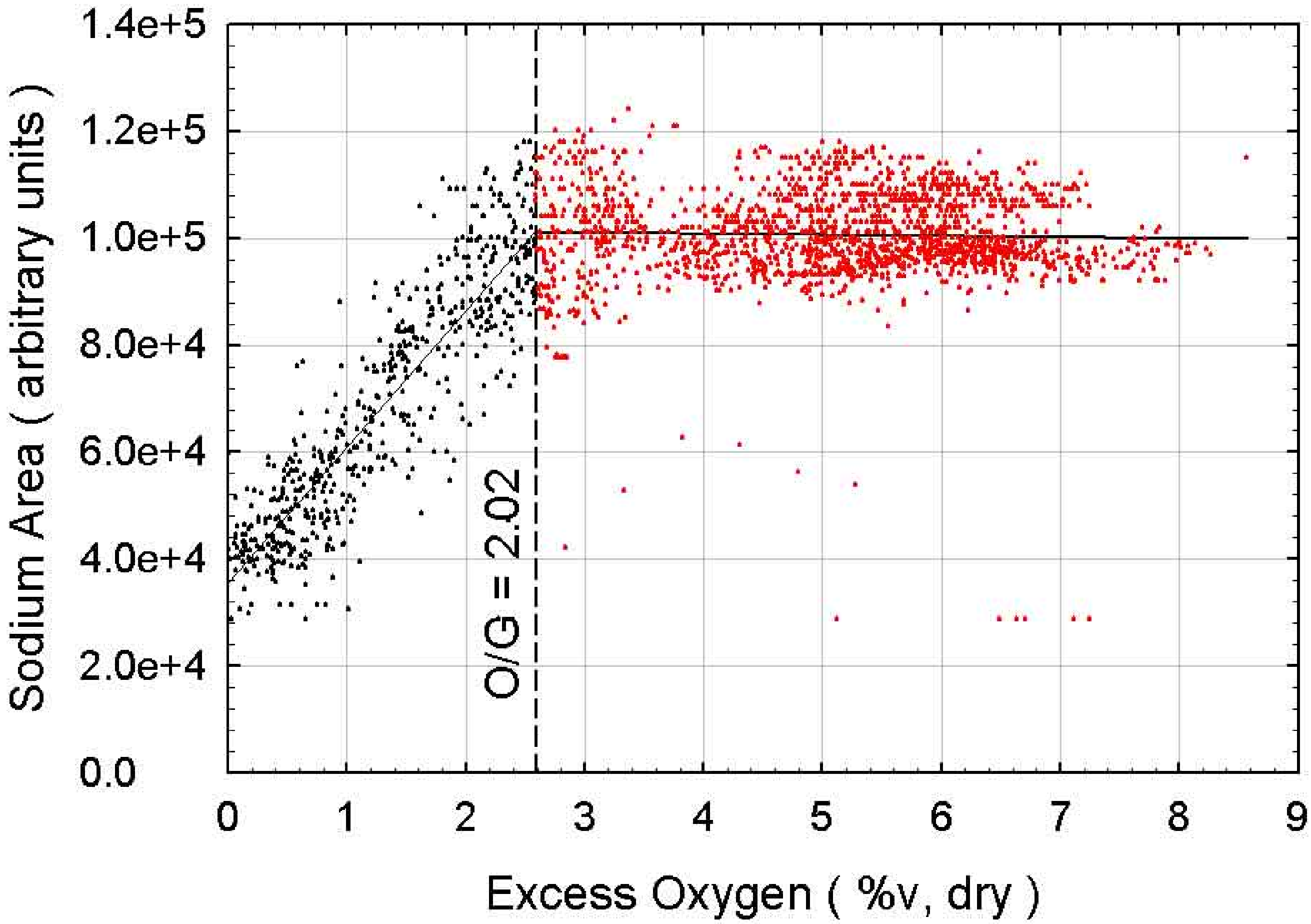
- Combustion products depend on O_2/NG
- Ambient temperature affects in-leakage and NO
- Rich conditions alter SO_2 release

- Sodium correlates with potassium
- Other metals do not correlate with alkali but intercorrelate
- Alkali release depends on temperature & maybe stoichiometry
- Rich conditions may affect alkali release

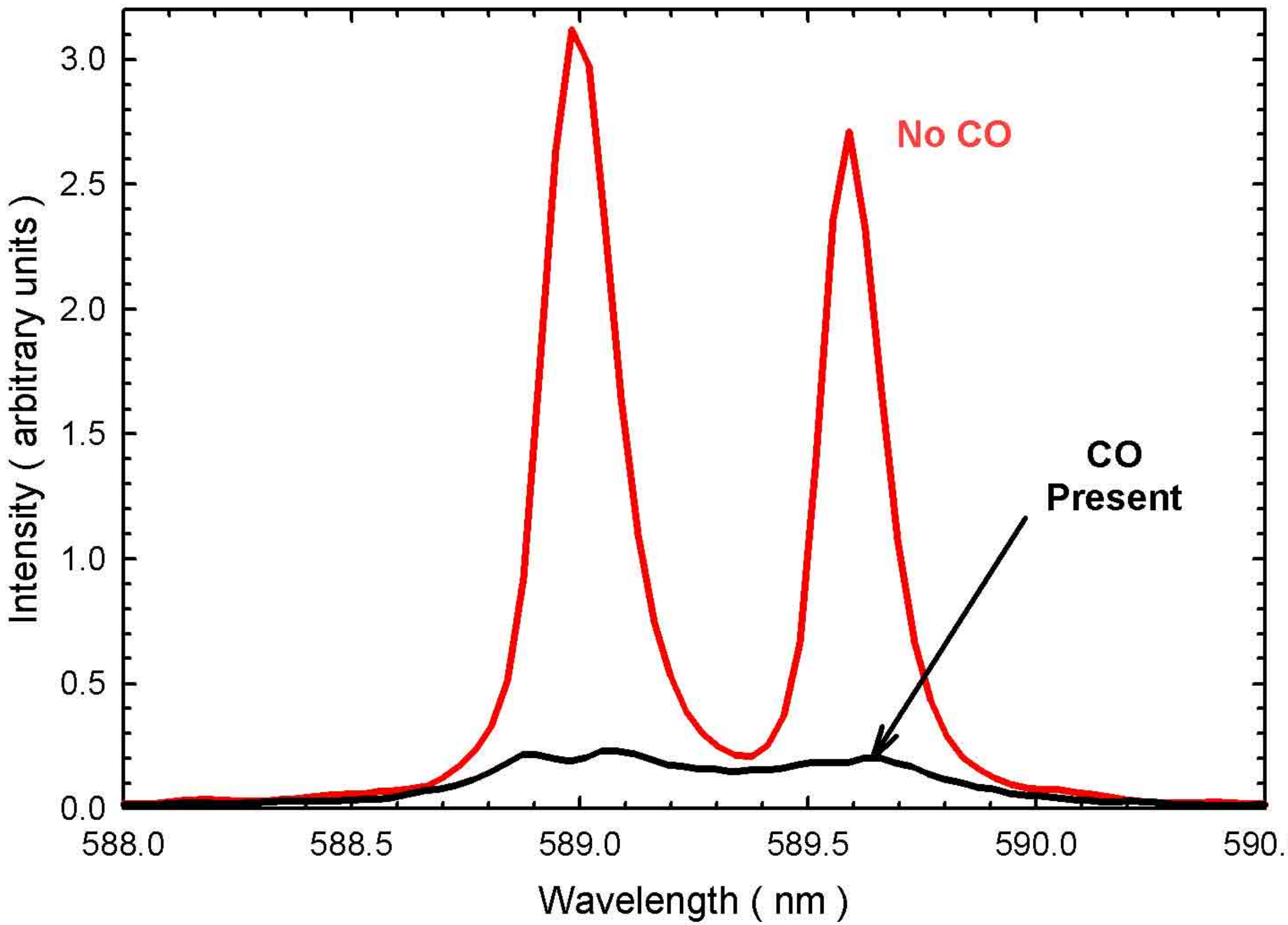
- Batch particles
  - can be detected
  - size distributions can be calculated
  - depend on pressure

FY04 Results

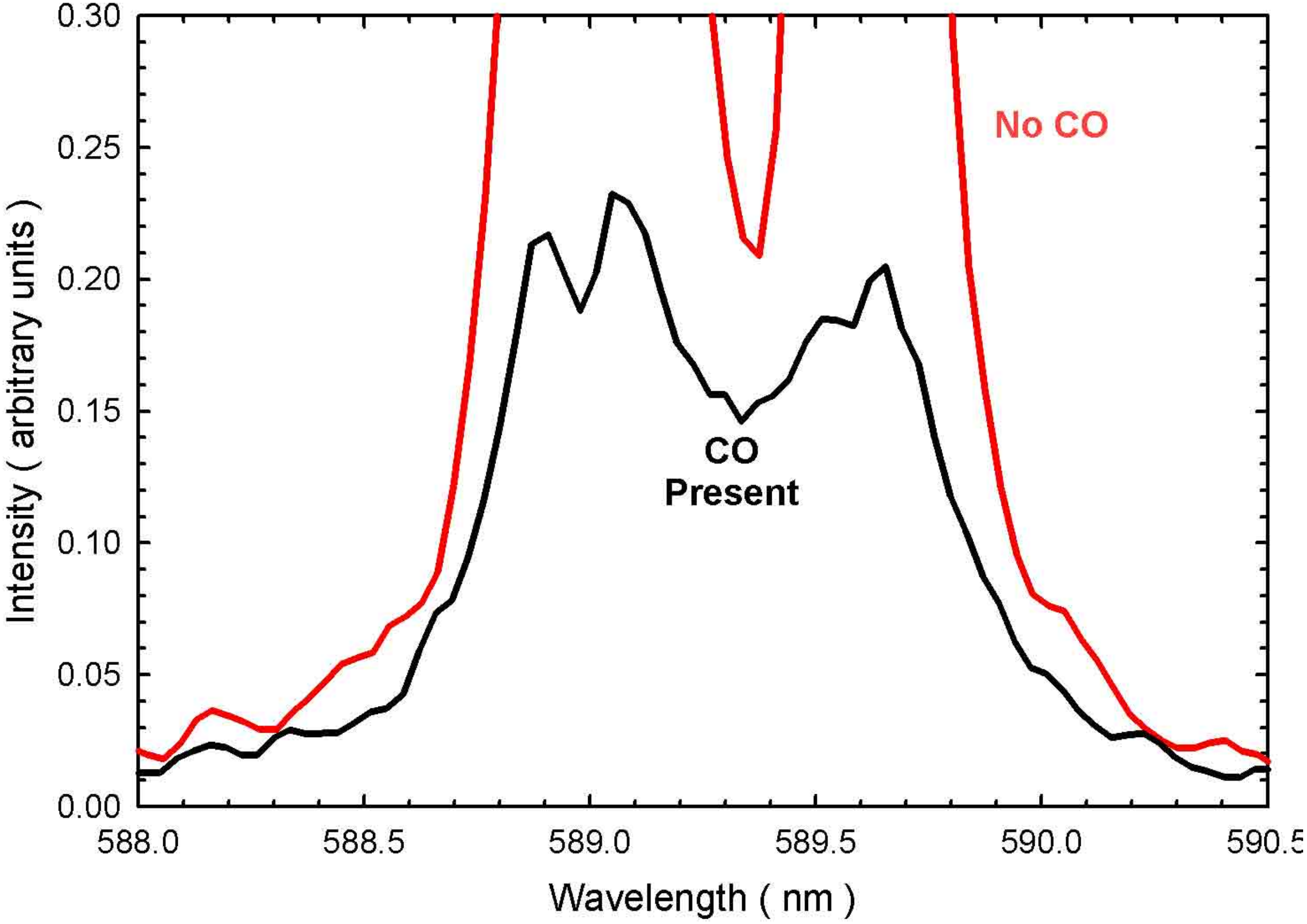
FY03 mystery solved



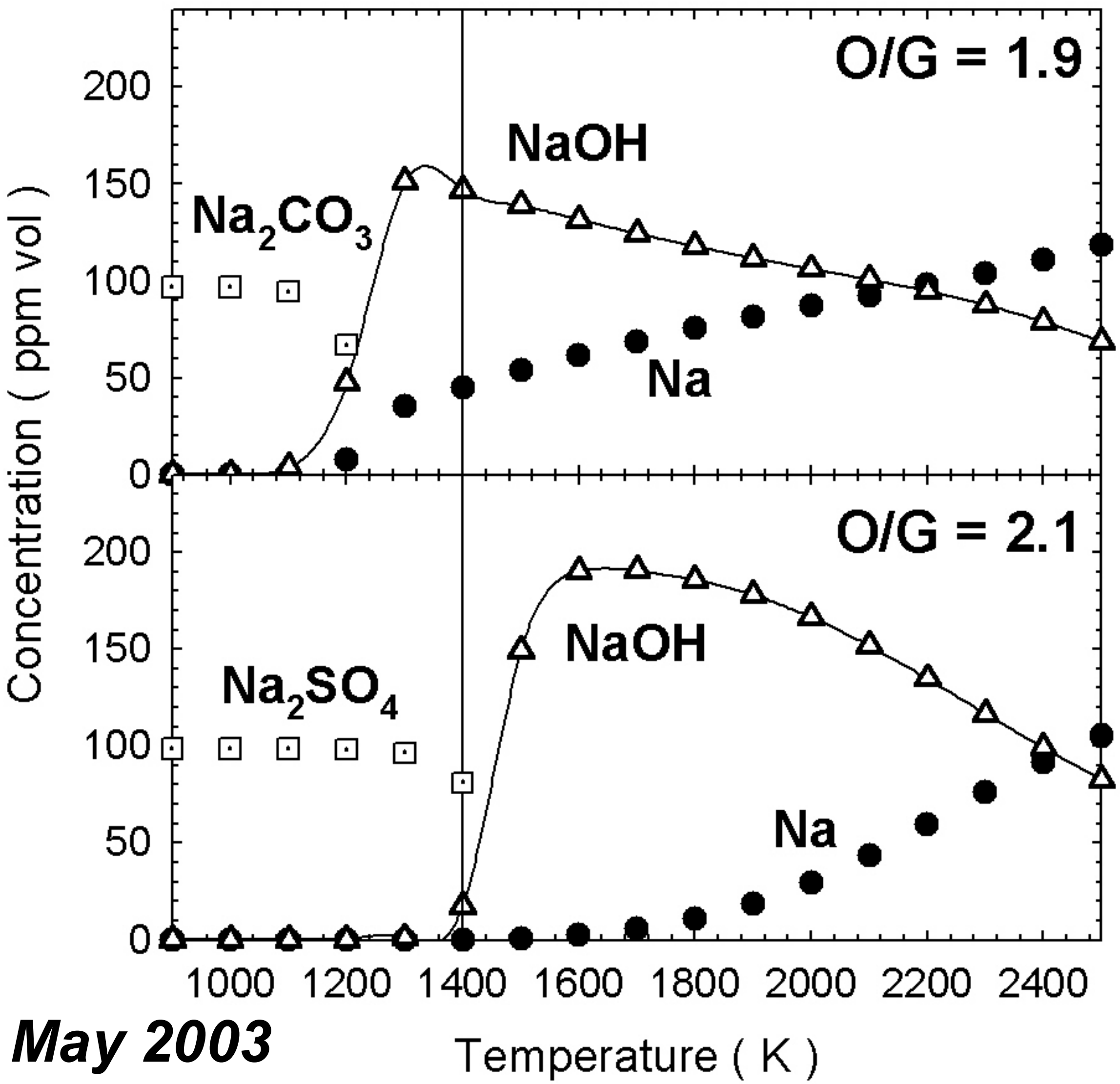
Spectra in presence and absence of CO



Na atoms absorb signal when CO is present



Equilibrium shows Na when fuel-rich

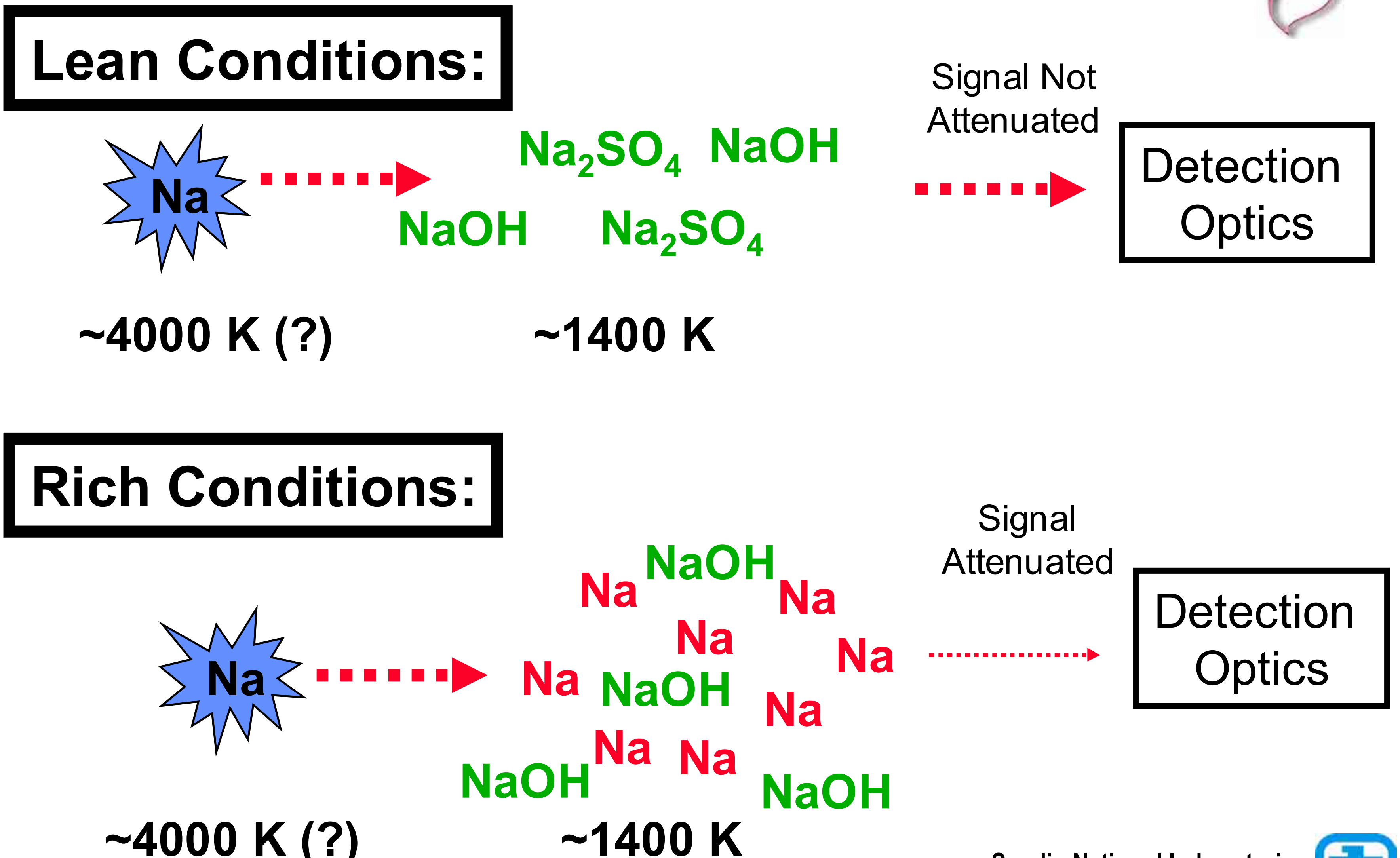


Rich (CO Present)

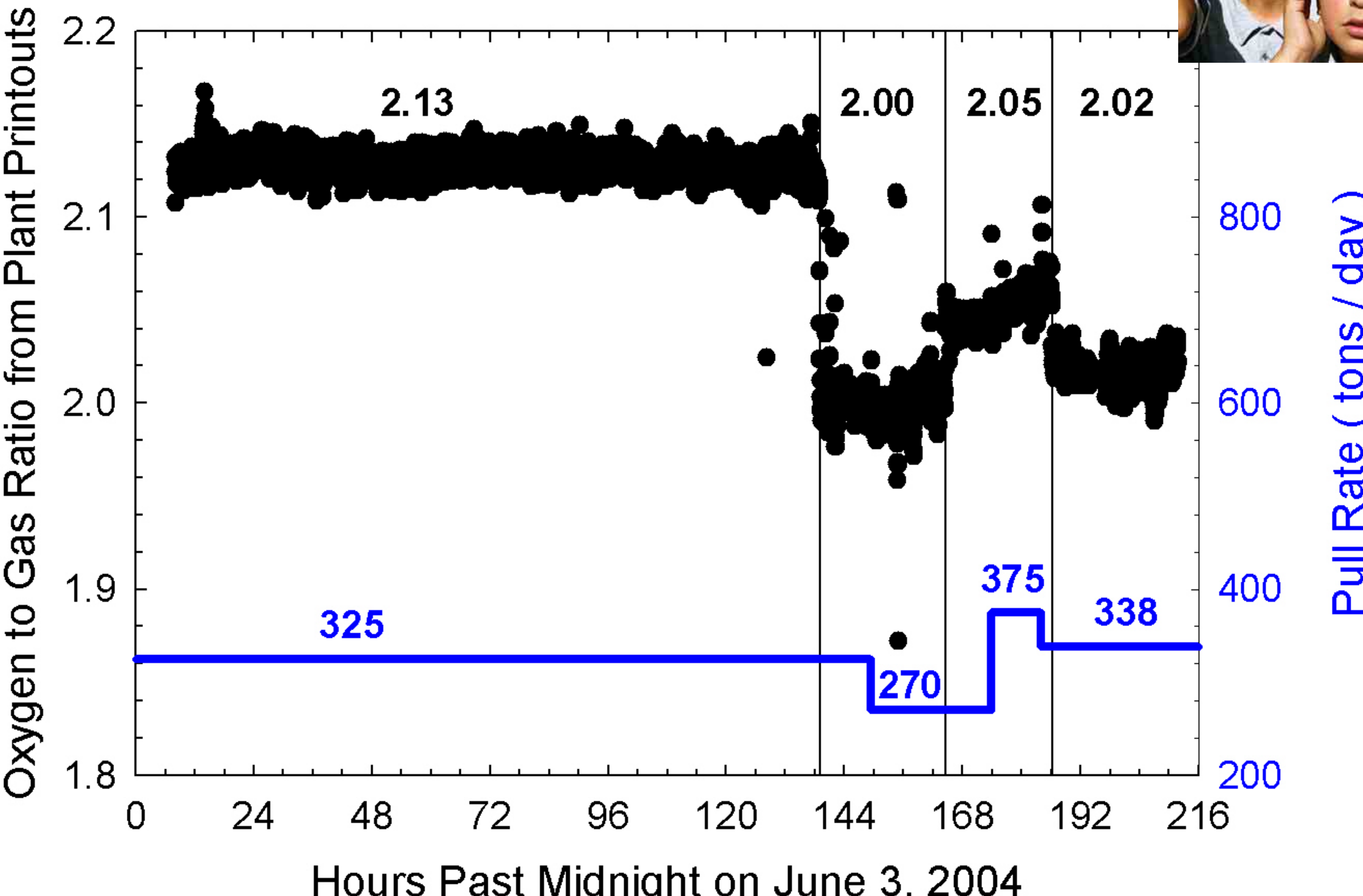
Lean (No CO)

May 2003

Scenario in glass furnace



June 2004 tests



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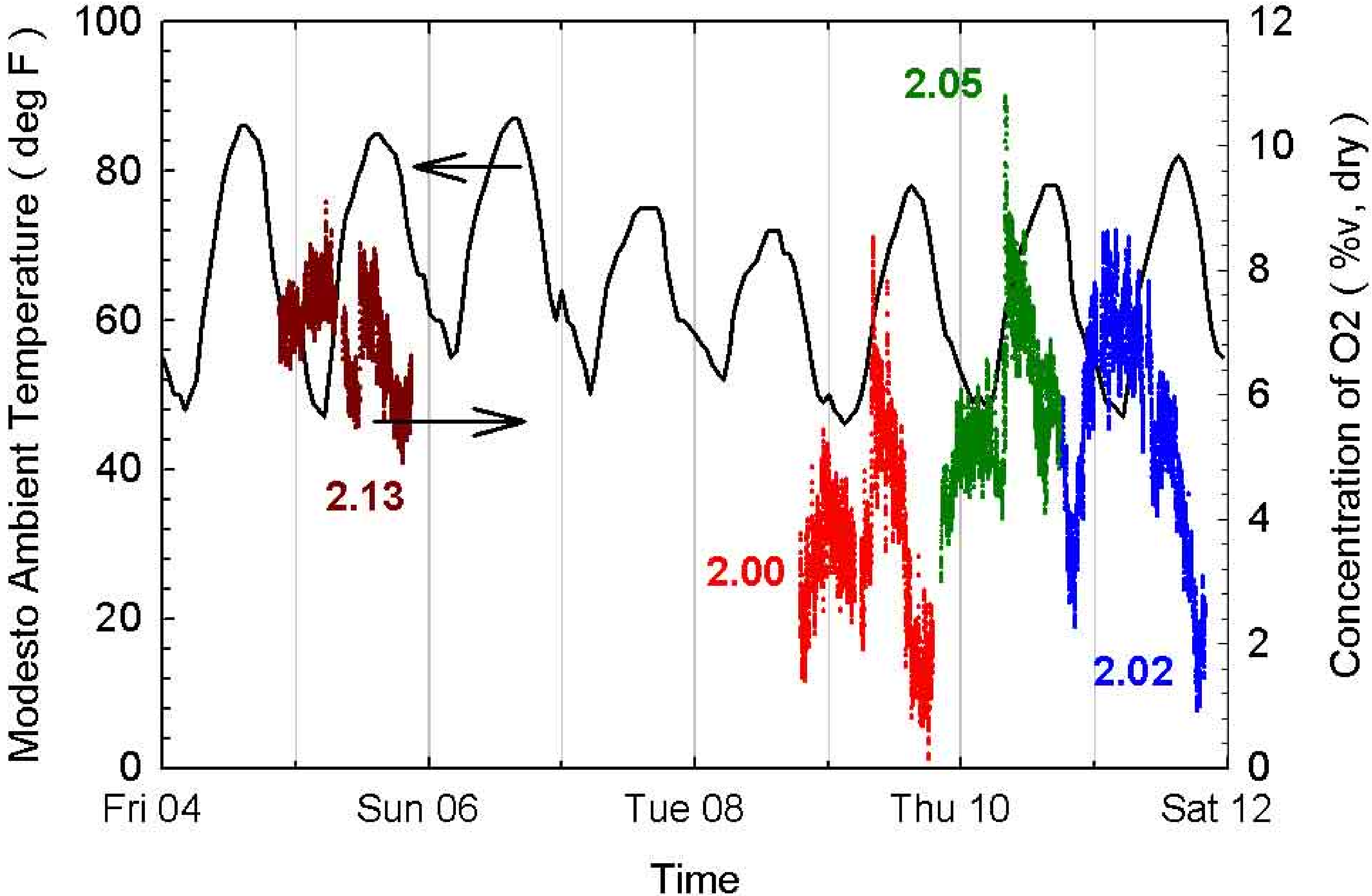
Ambient T still affects inleakage



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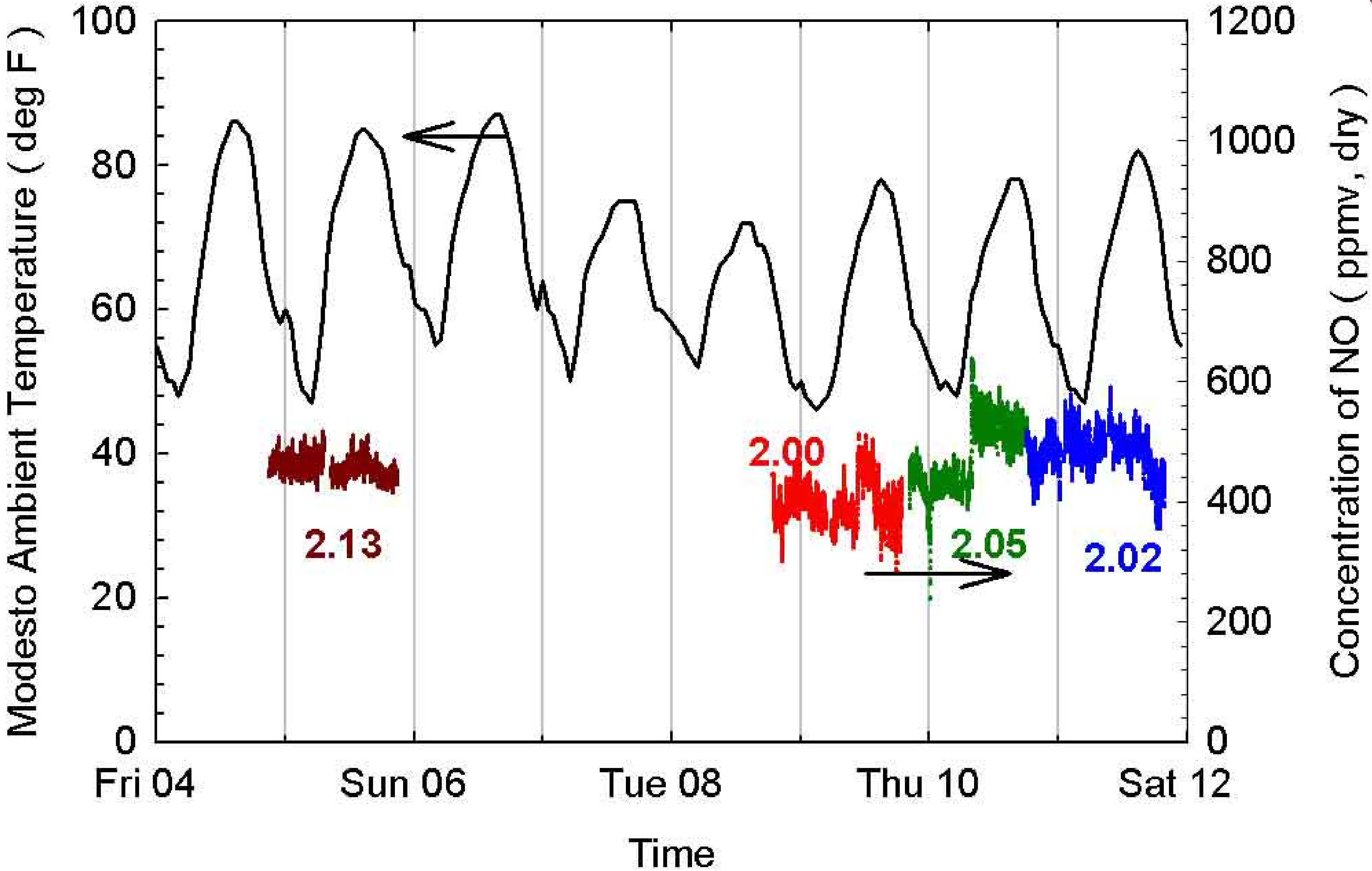
NO also affected by inleakage



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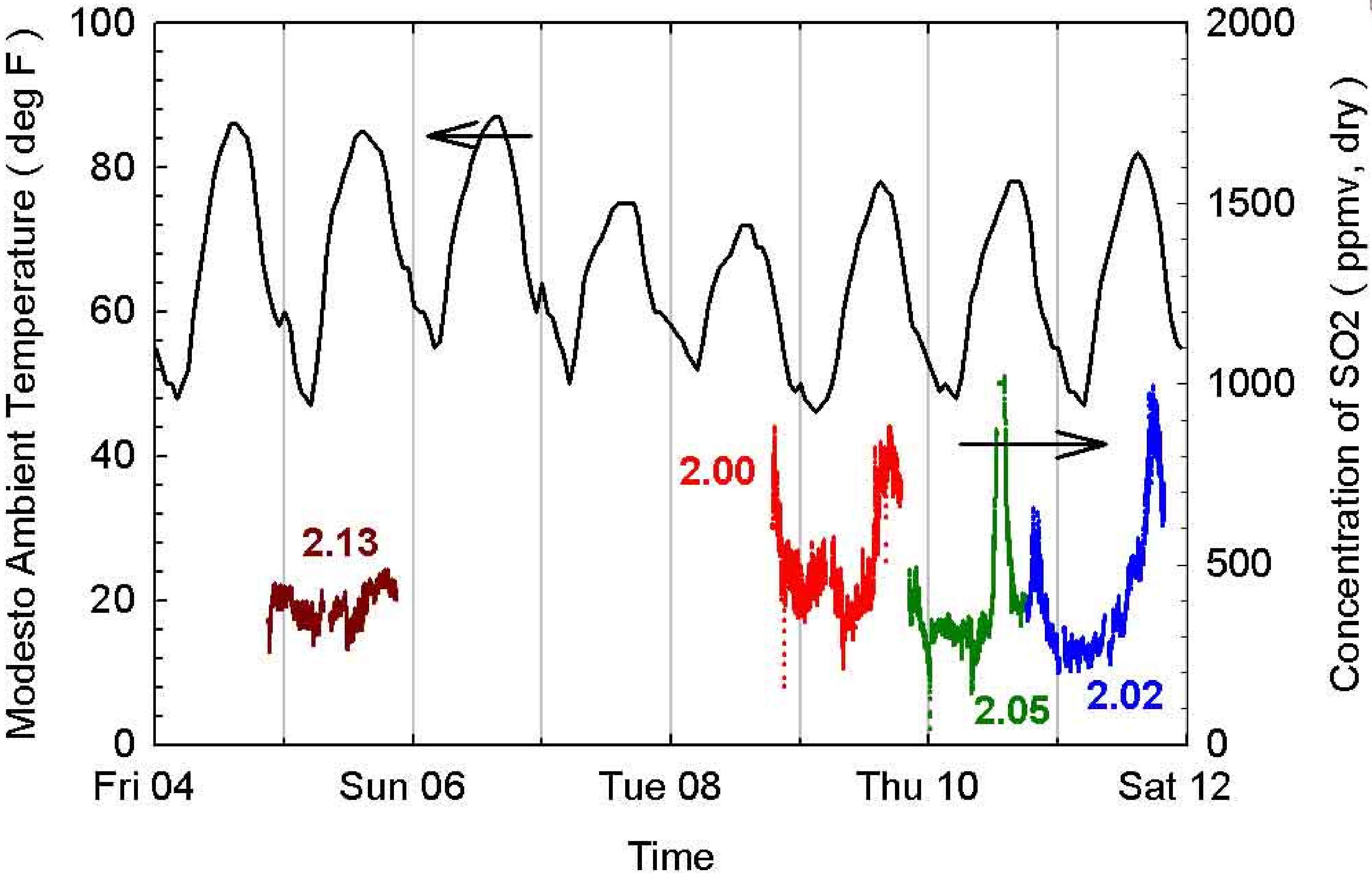
Rich conditions still alter SO_2 release



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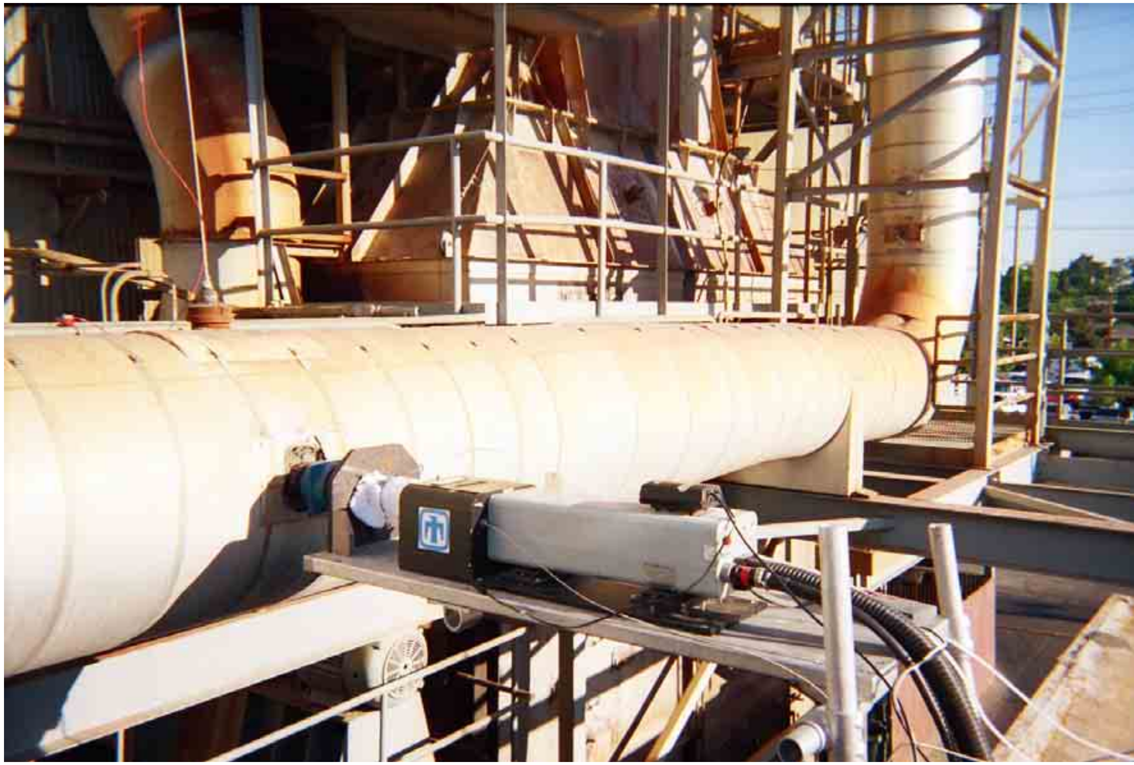
June 2004 Field Test Objectives

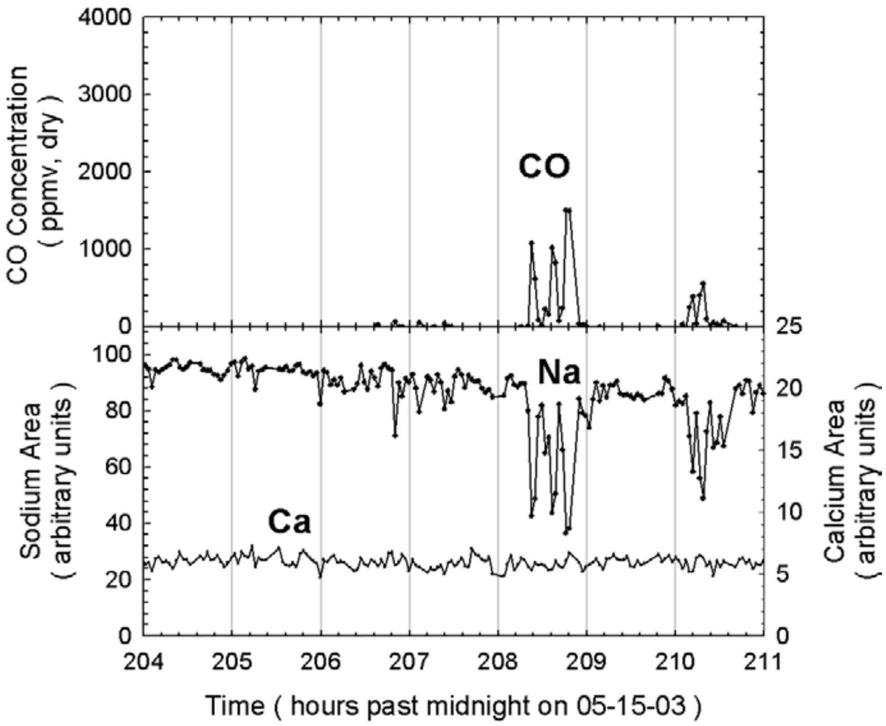
1. Measure Na at a cooler location to avoid interference
2. Quantify and determine source of air inleakage
3. Examine effect of furnace pressure on batch particles
4. Expand energy analysis to include inleakage



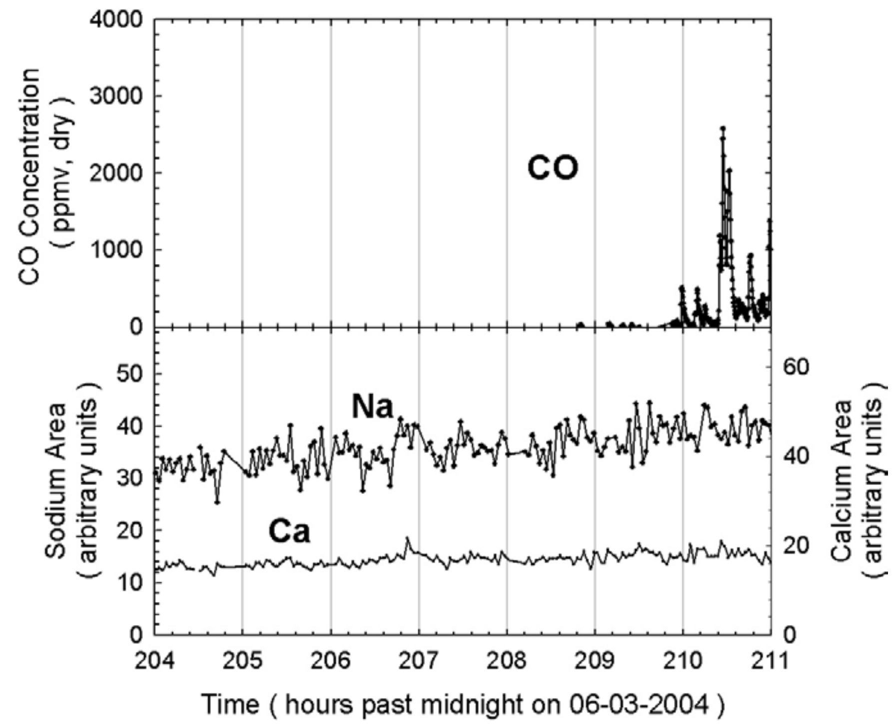
1. Measure Na at a cooler location to avoid interference

Upstairs Na signal not affected by CO

May 2003 – Vertical Flue
~1400 K (2100 °F)

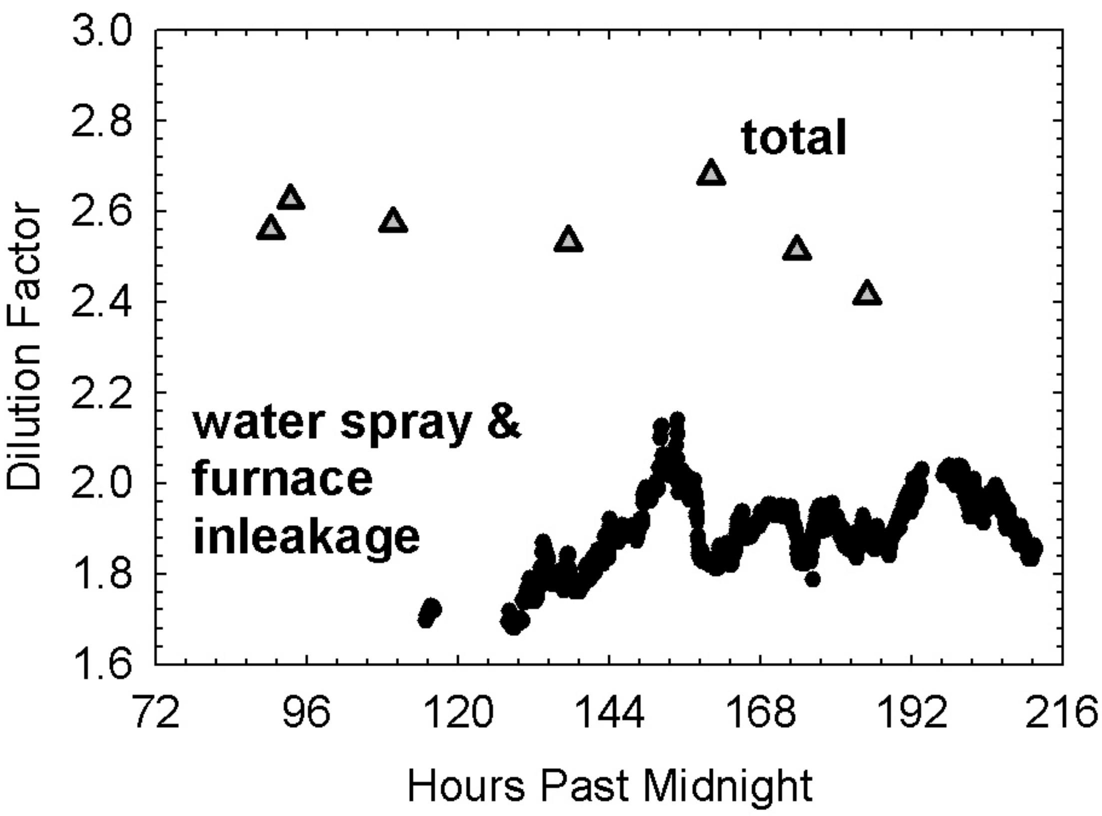


June 2004 – Exhaust Duct
~700 K (900 °F)

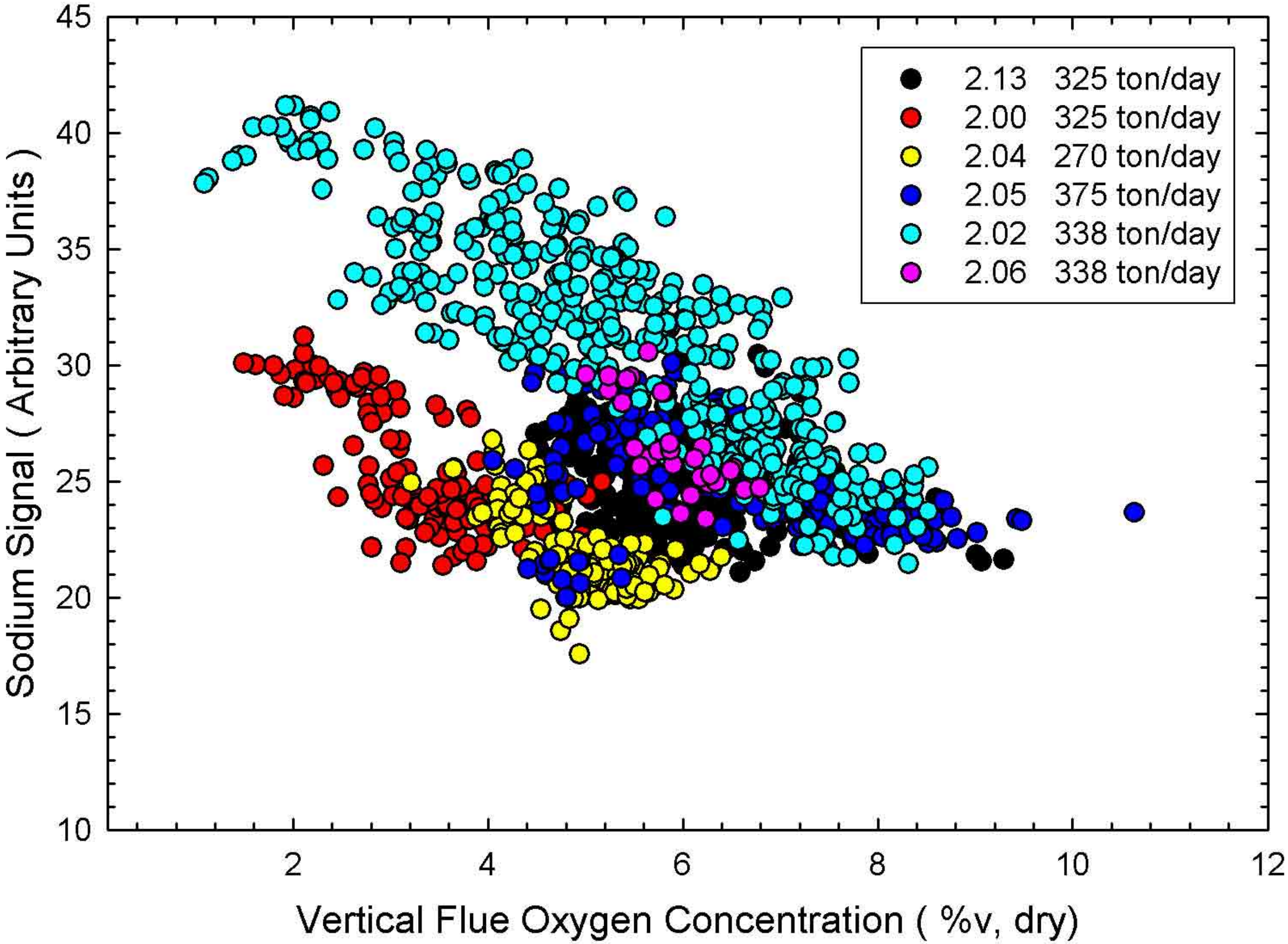


Upstairs location diluted

- Cooling water nozzles
  - 7-9 gal/min
  - 70 scfm atomizing air
  - Water contains metals
- Furnace air inleakage
  - Measured in vertical flue using GC
  - Dilution factor 1.7-2.0 including water nozzles
- Duct air inleakage
  - Deduced from gas analyzer O2 down- and up-stairs
  - Overall dilution ~2.5



Sodium varies inversely with excess O_2



- **Appears to be dilution related**
- **Samples extracted from furnace show little effect of stoichiometry ~120 ppmv Na ~20 ppmv K**

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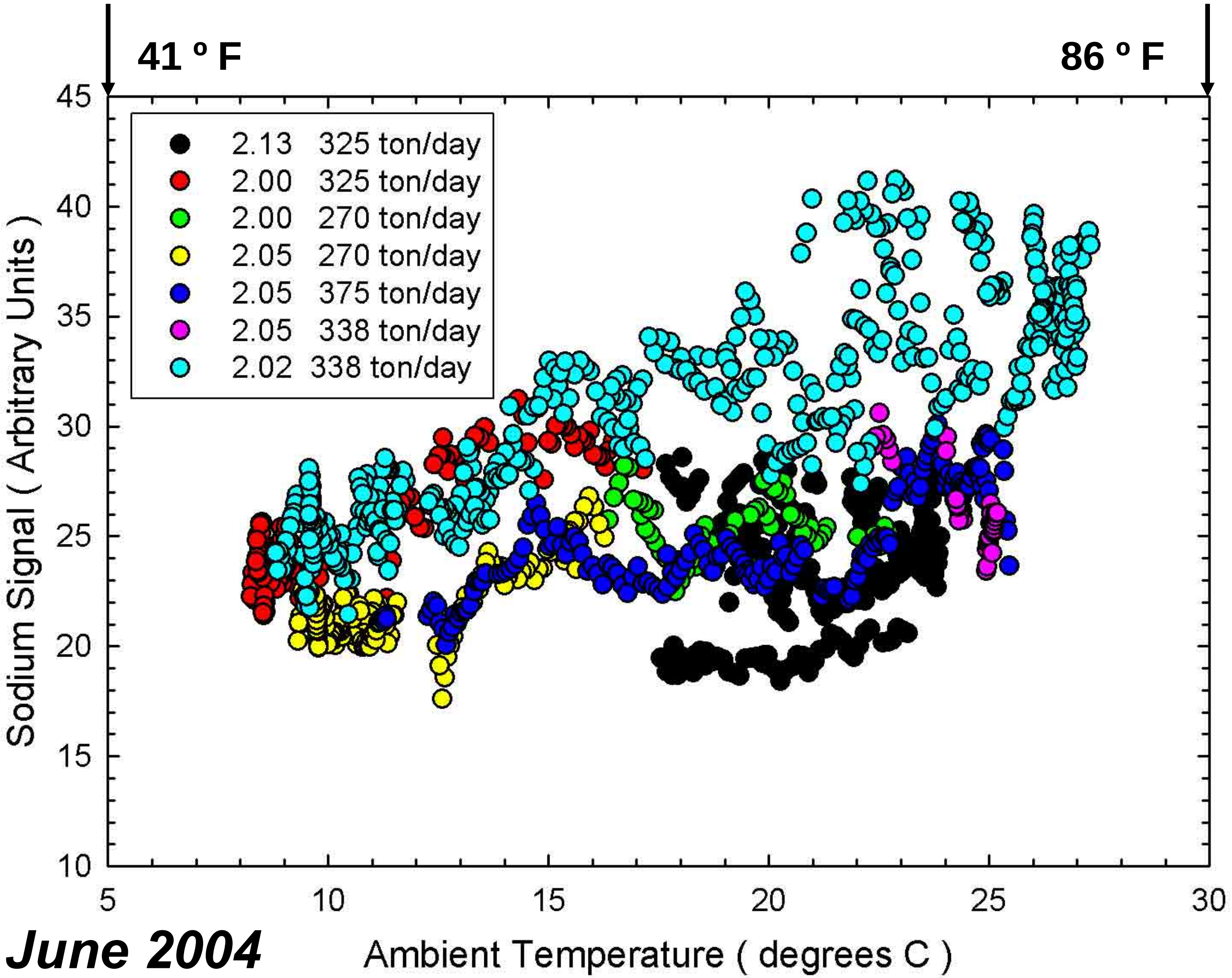
Sodium correlates with ambient T



- **Must be inleakage**

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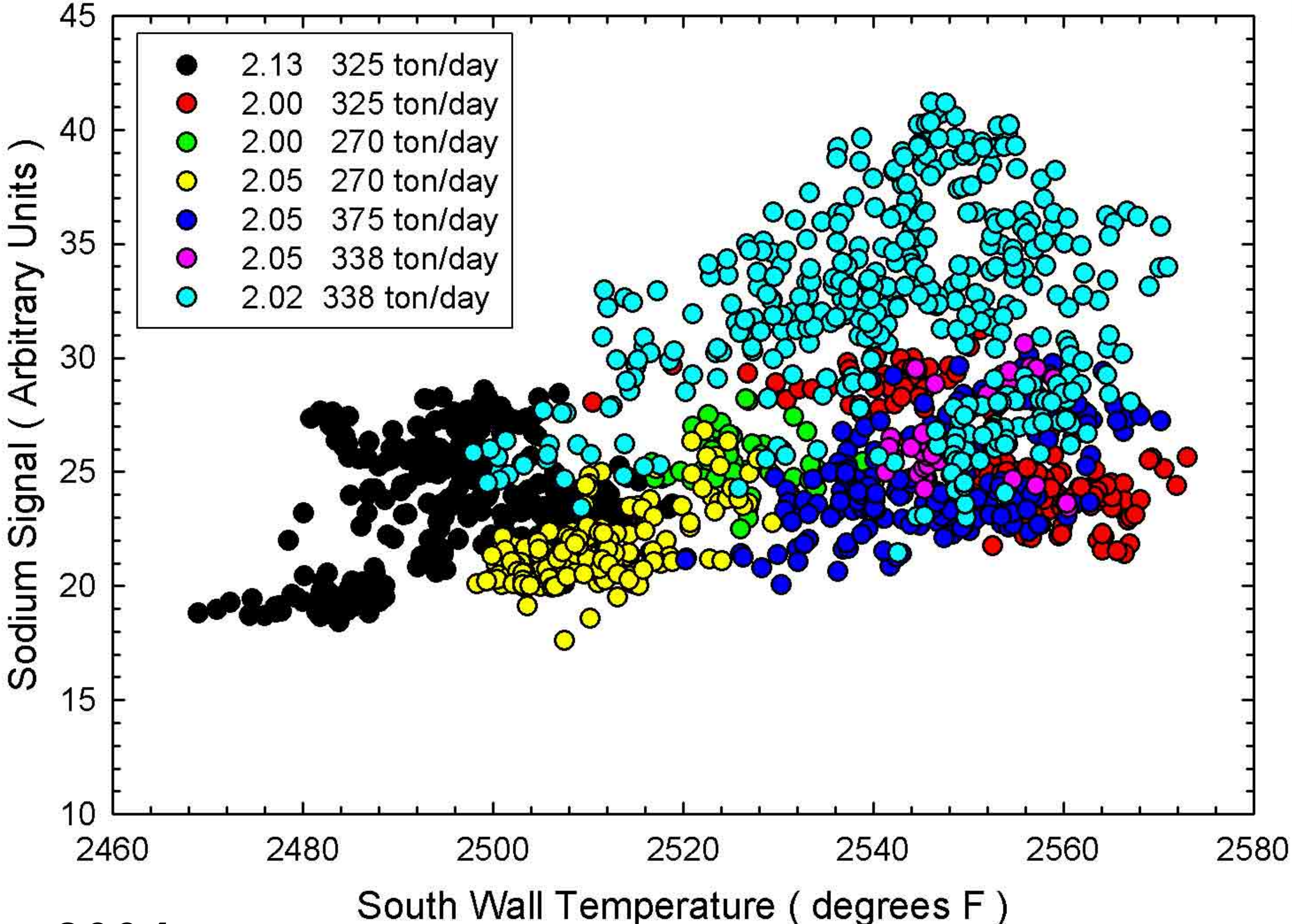
Sodium vaporization depends on furnace T



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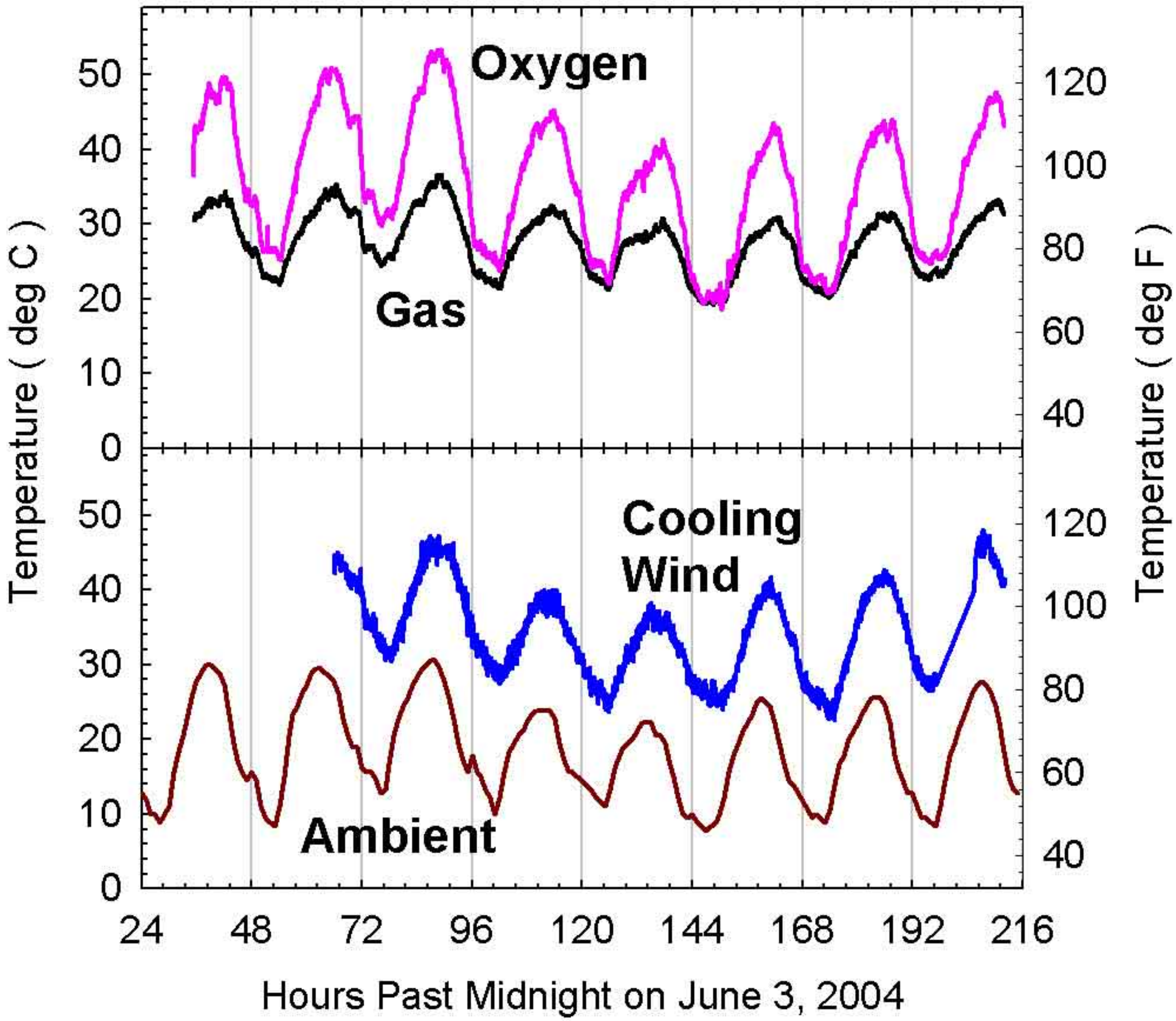
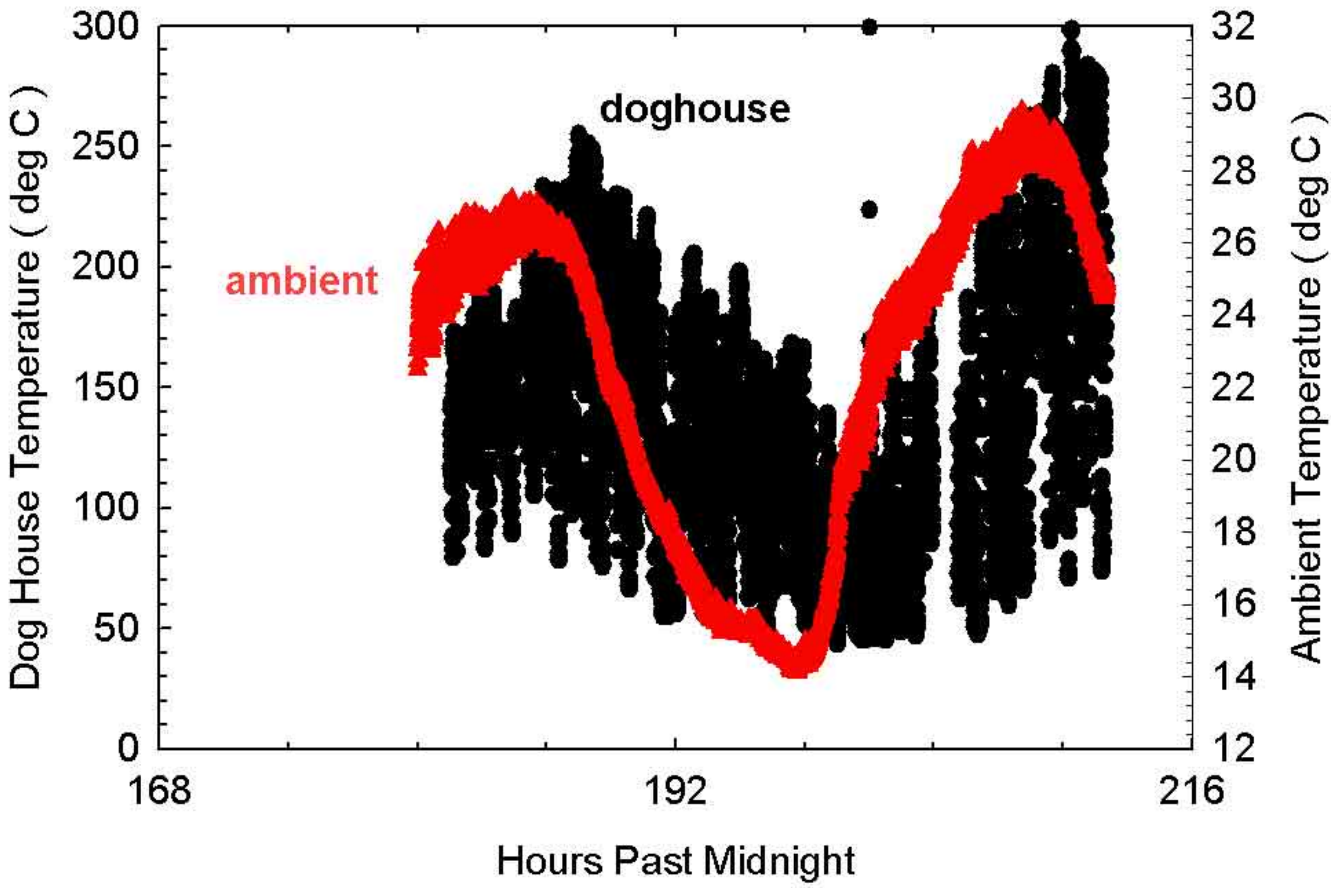
2. Quantify and determine source of air inleakage

Temperatures can affect inleakage

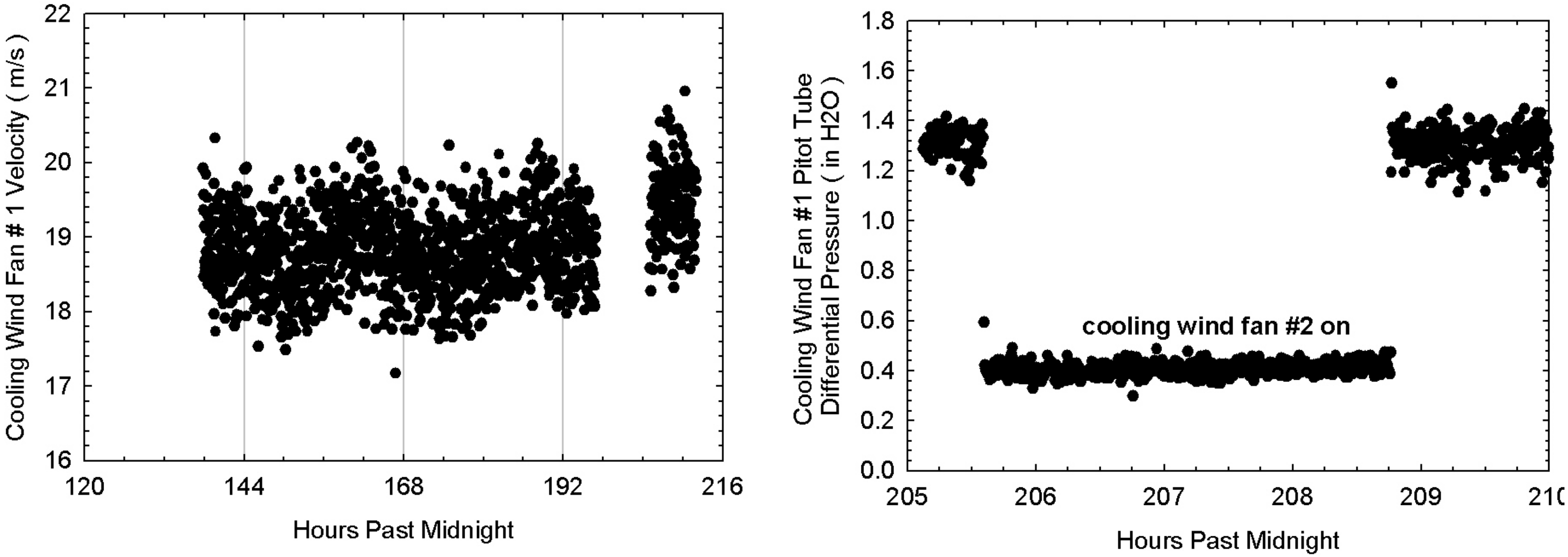


- **Single flow meter T compensation may not apply for every point**
- **Cooling wind temperature varies with ambient**

Air can enter through the doghouse, too



Cooling wind fan(s) moves constant volume



So rate of mass flow varies with ambient

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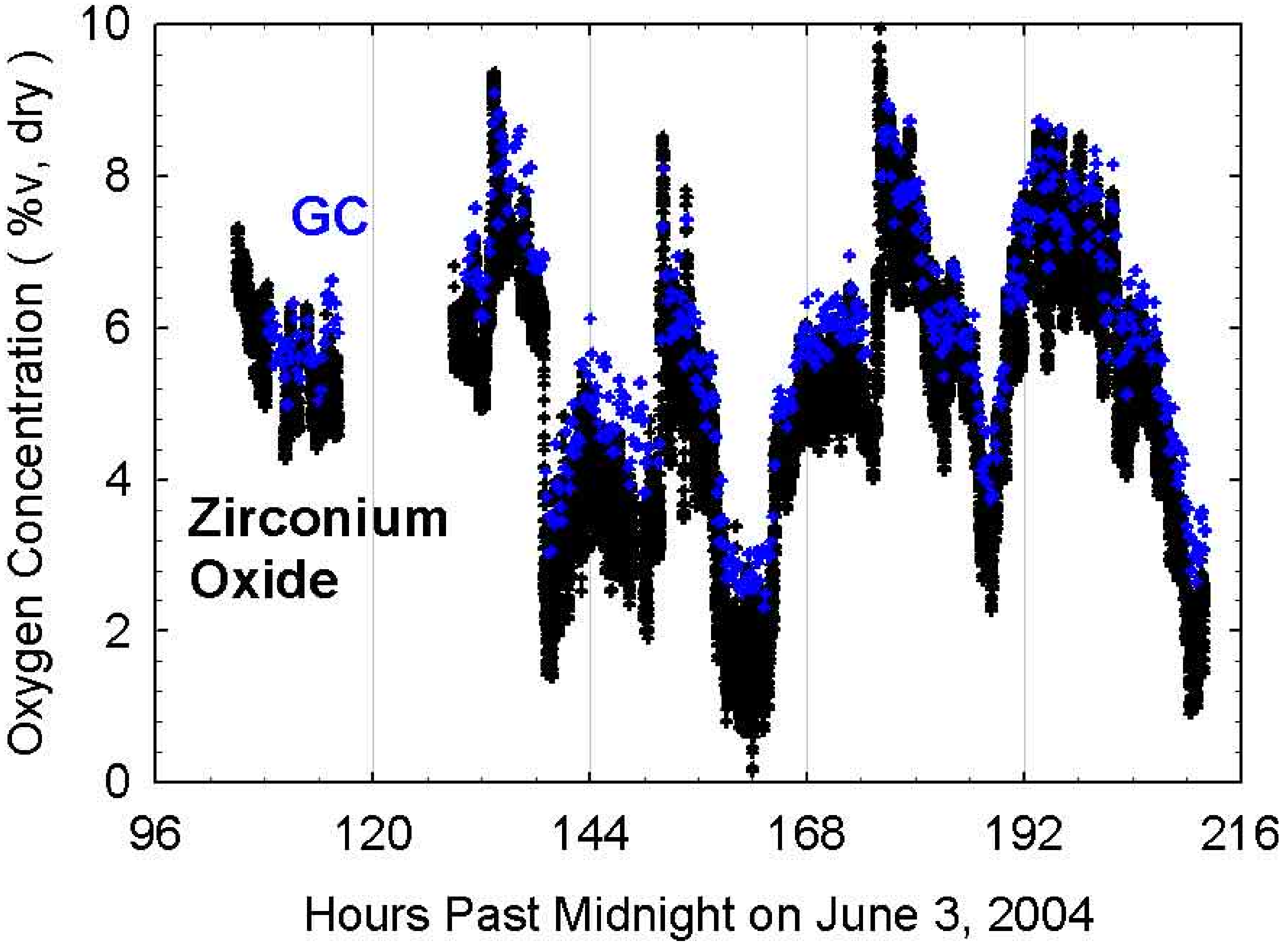
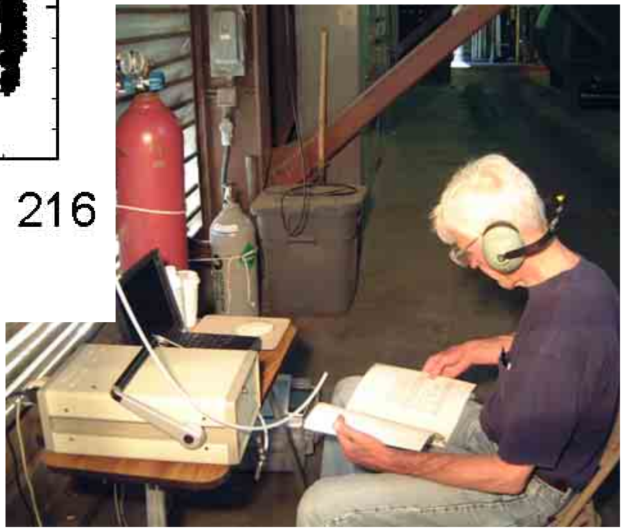
GC and gas analyzer agree for O2





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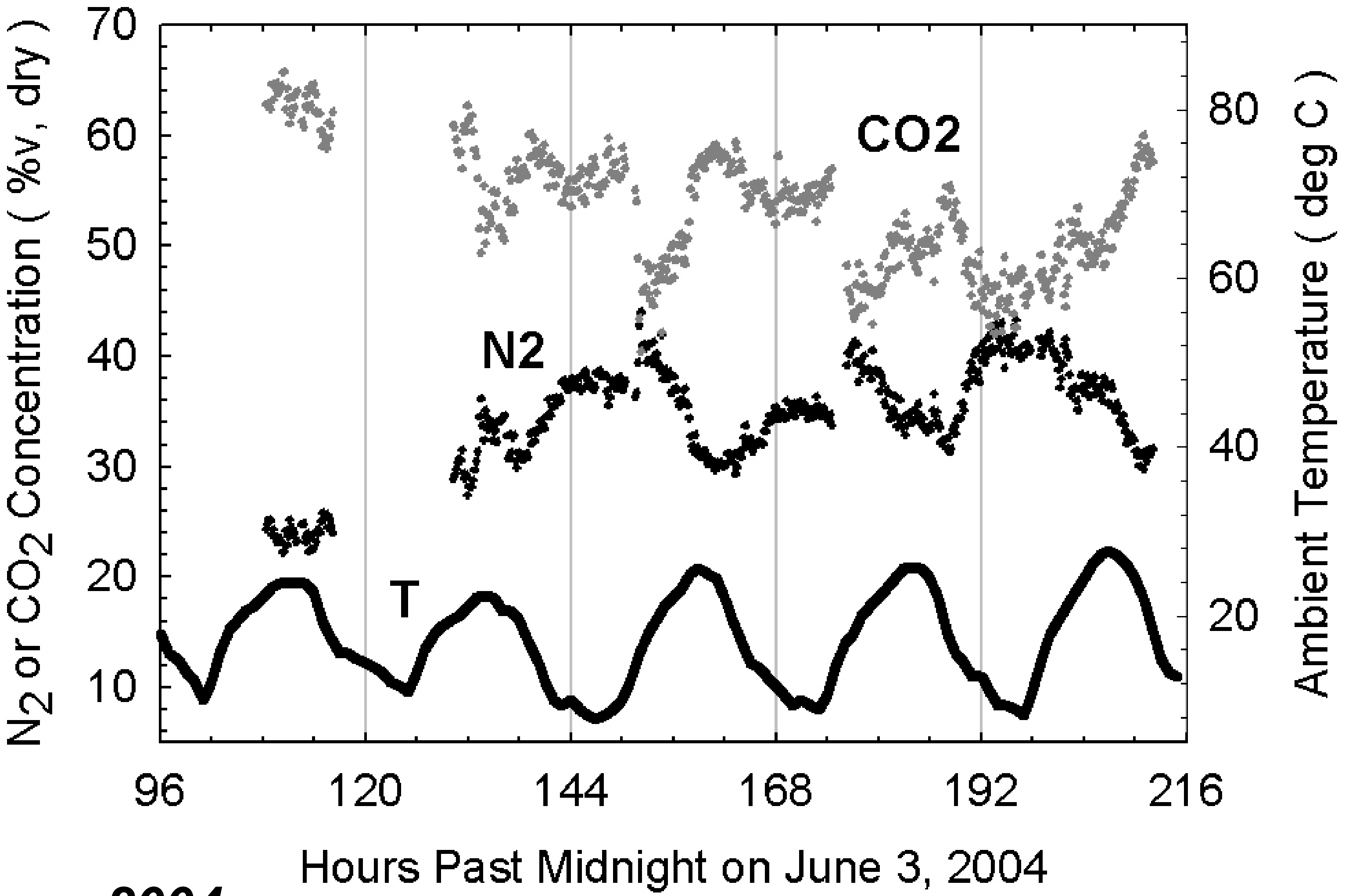
N_2 and CO_2 track ambient T



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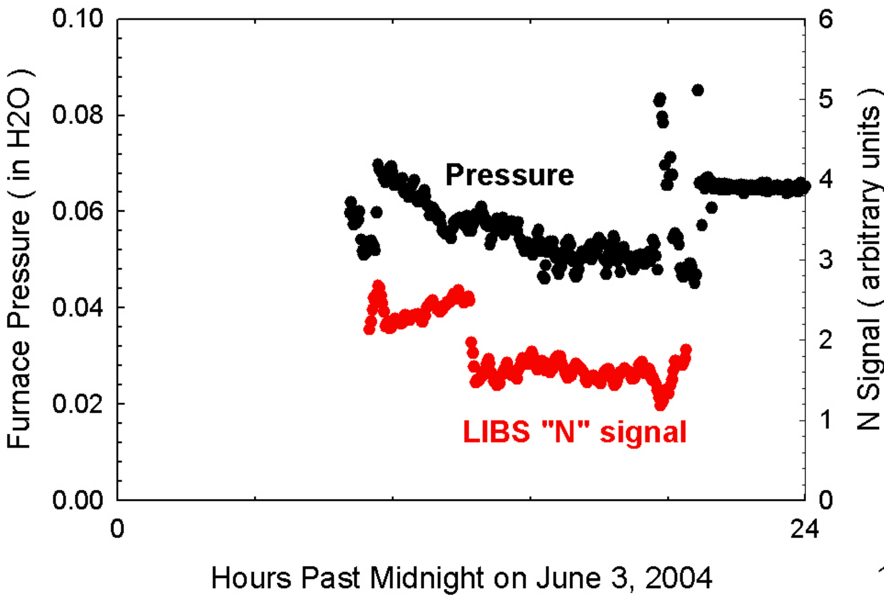
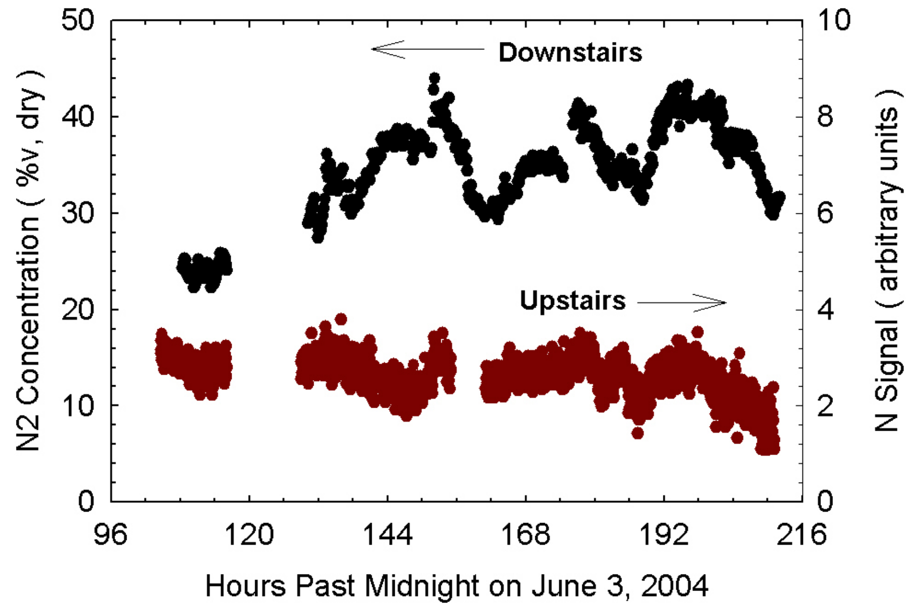
Estimated* contributions to inleakage

Exhaust flow	~140,000 scfh	
Inleakage measured with GC	~40,000 scfh	25 % of total flow
Flow into doghouse	~5,000 scfh (80% in, 20% out)	2 % of total flow

LIBS may be useful for inleakage, too





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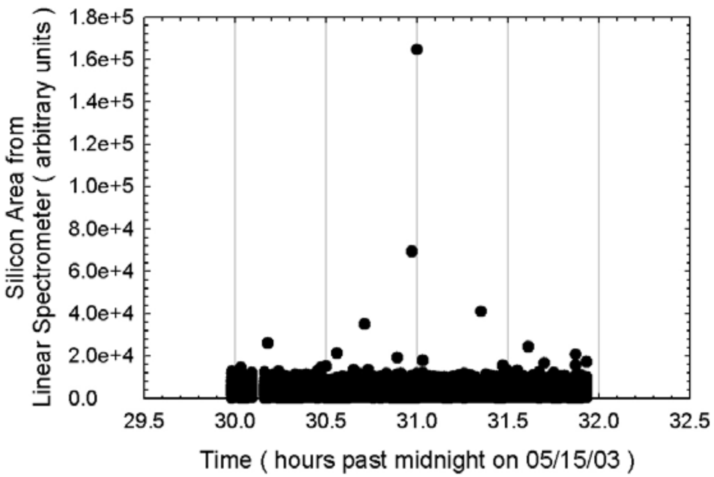
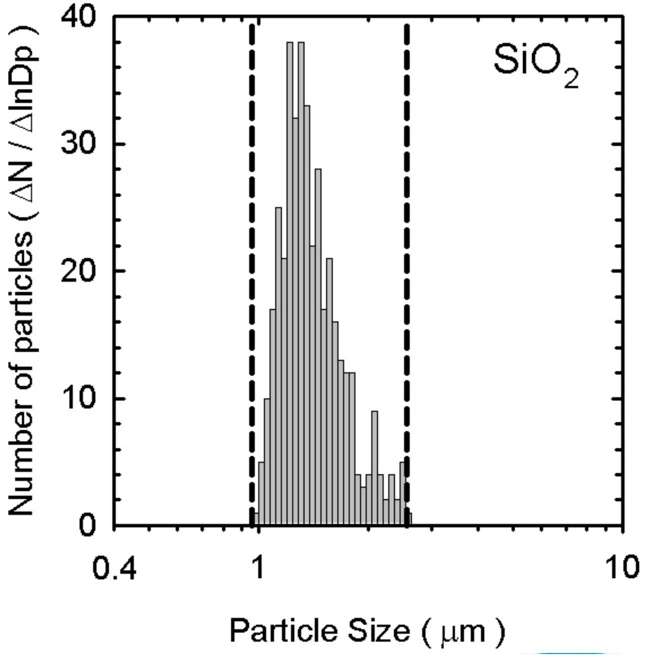
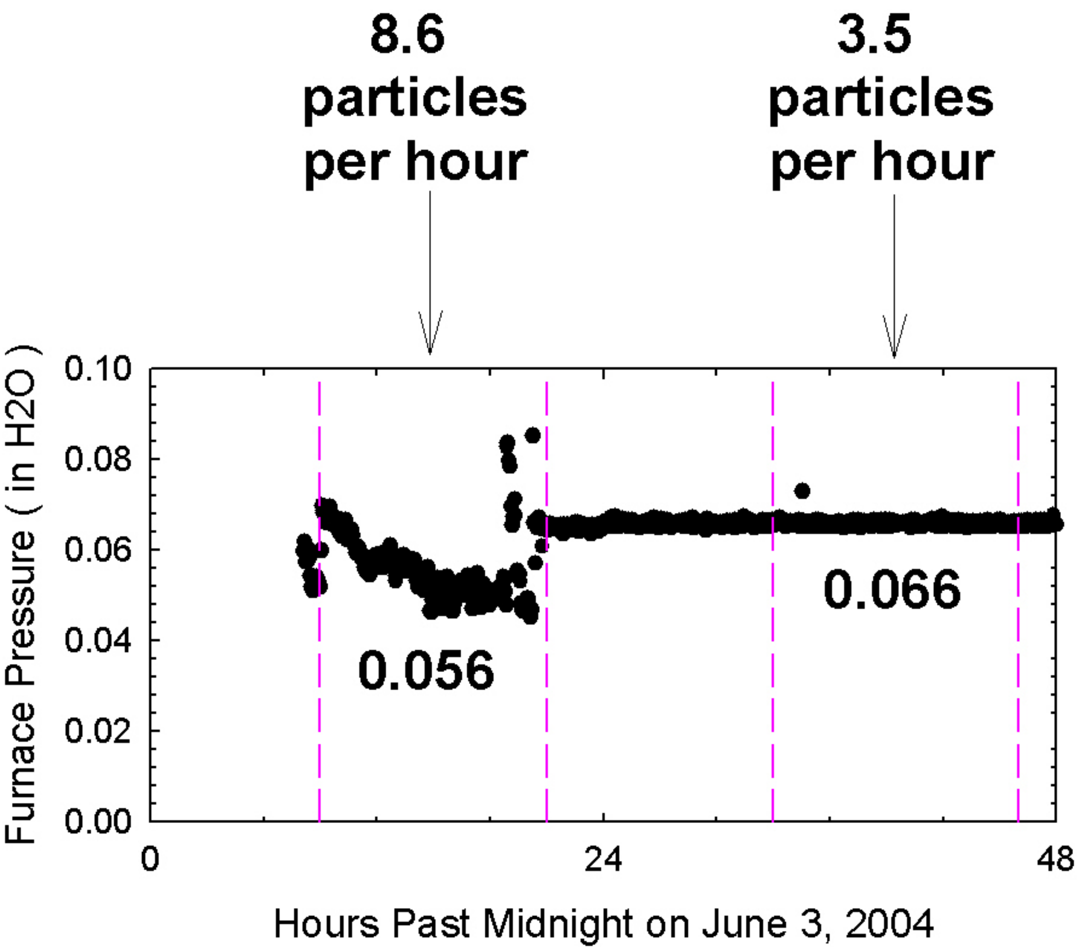


3. Examine effect of furnace pressure on batch particles

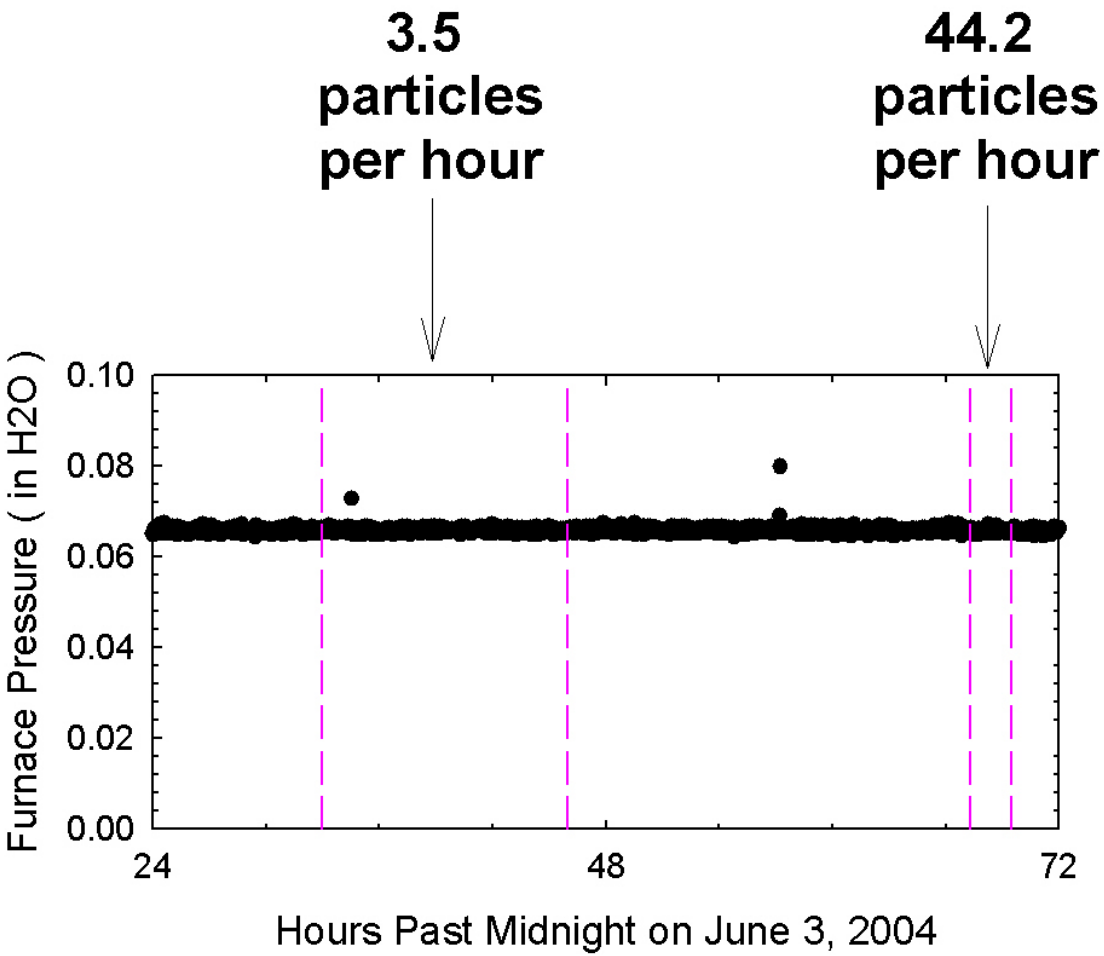


Batch particles high under manual control



- **Furnace pressure under manual control for a few hours**
- **More than twice as many batch particles counted**
- **About half of hits are Mg & half are Si**

Improved LIBS detection parameters found



- **Delay time shortened from 10 us to 1 us**
- **Gate width shortened from 150 us to 50 us**
- **Particle detection frequency improved 10X**

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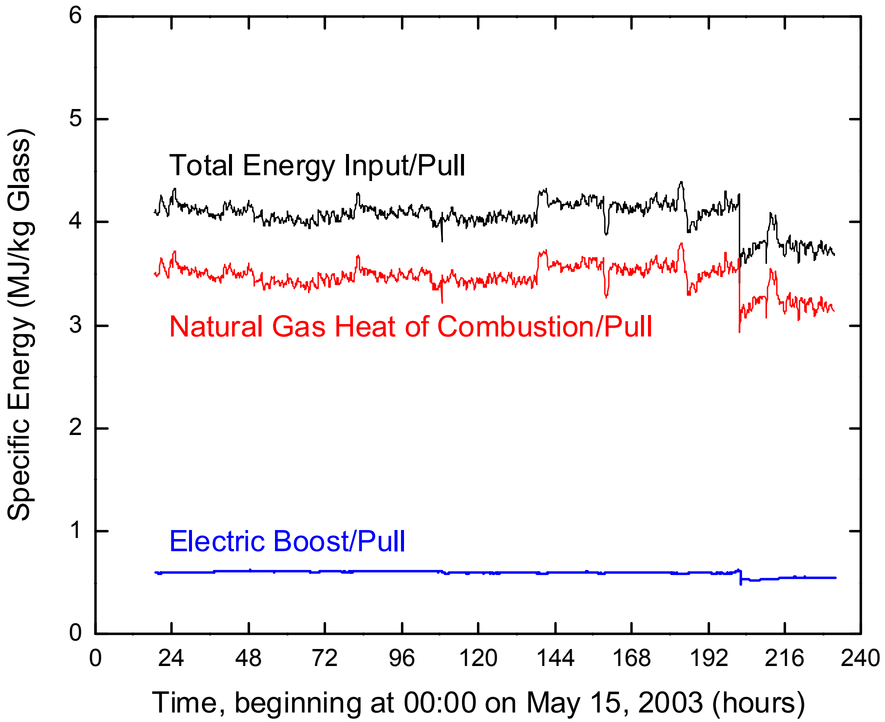
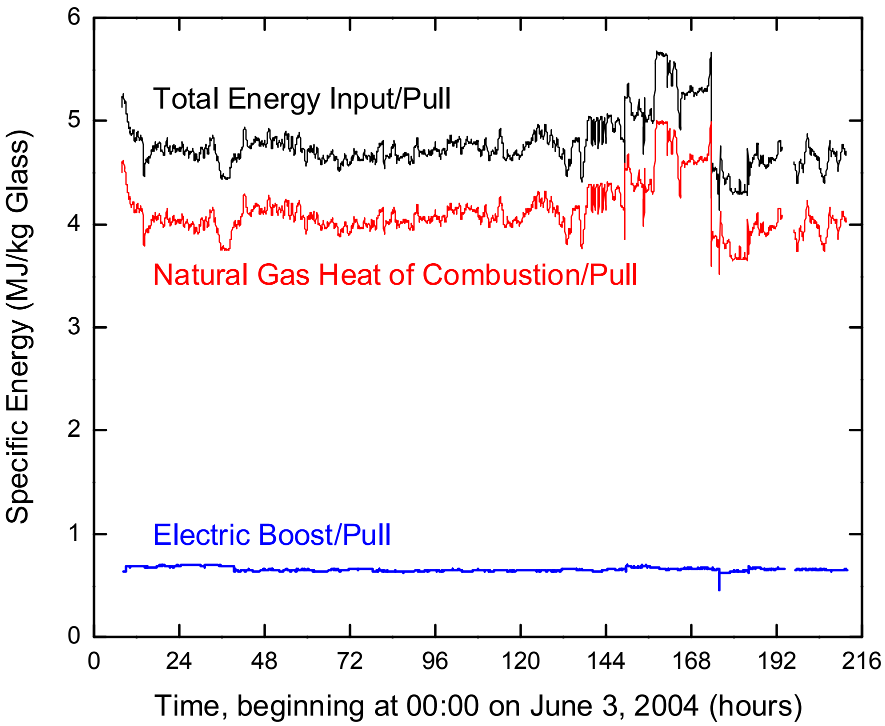
4. Expand energy analysis to include inleakage

Specific energy inputs

May 2003

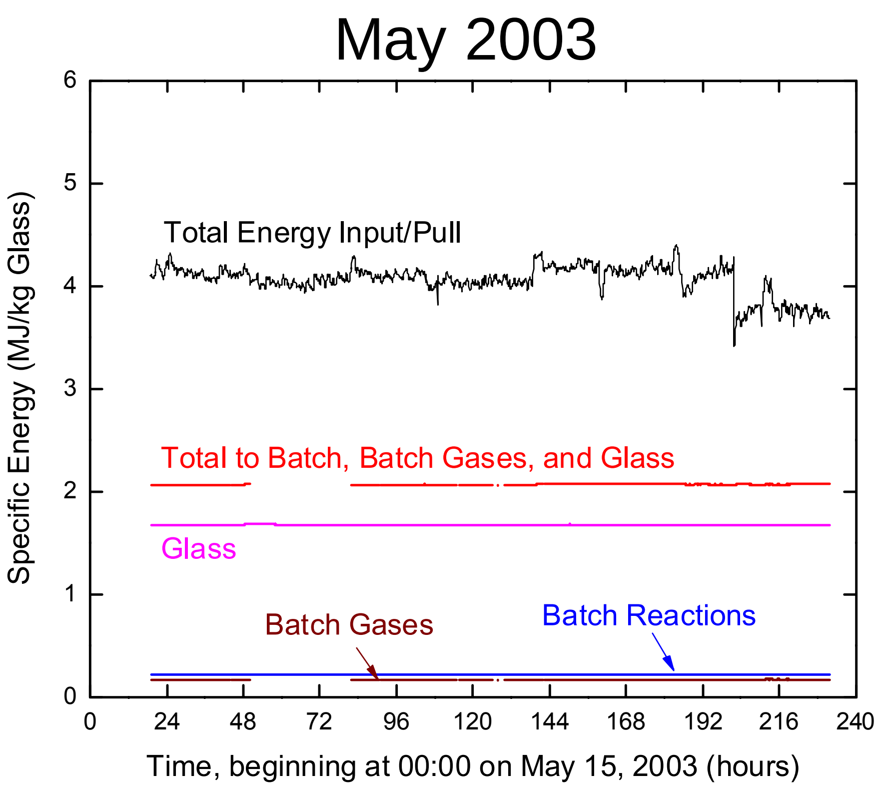


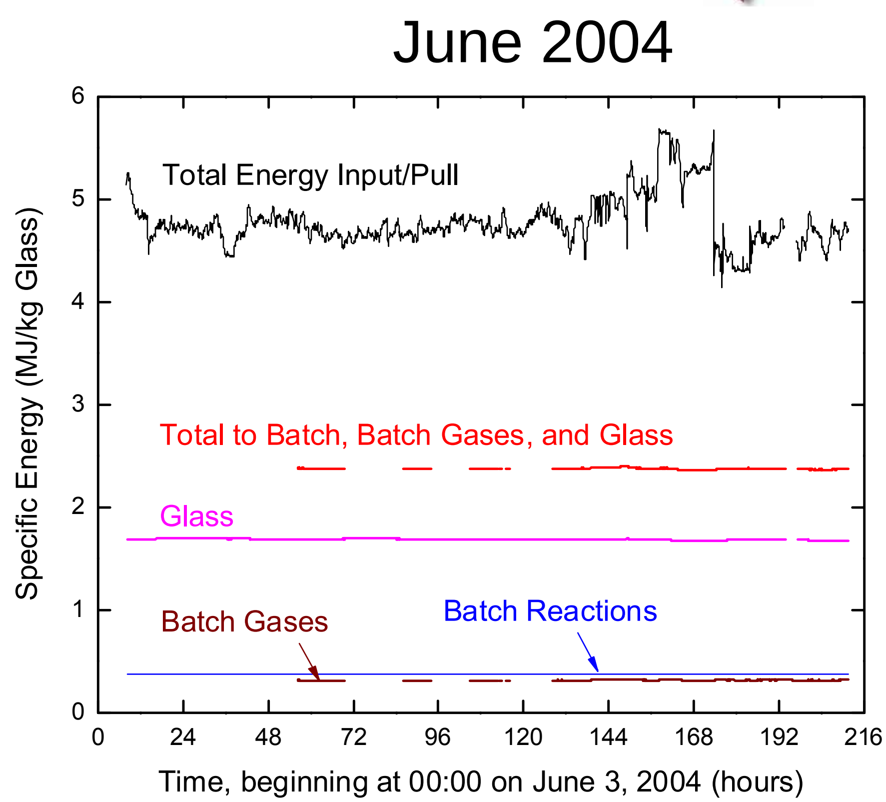
June 2004



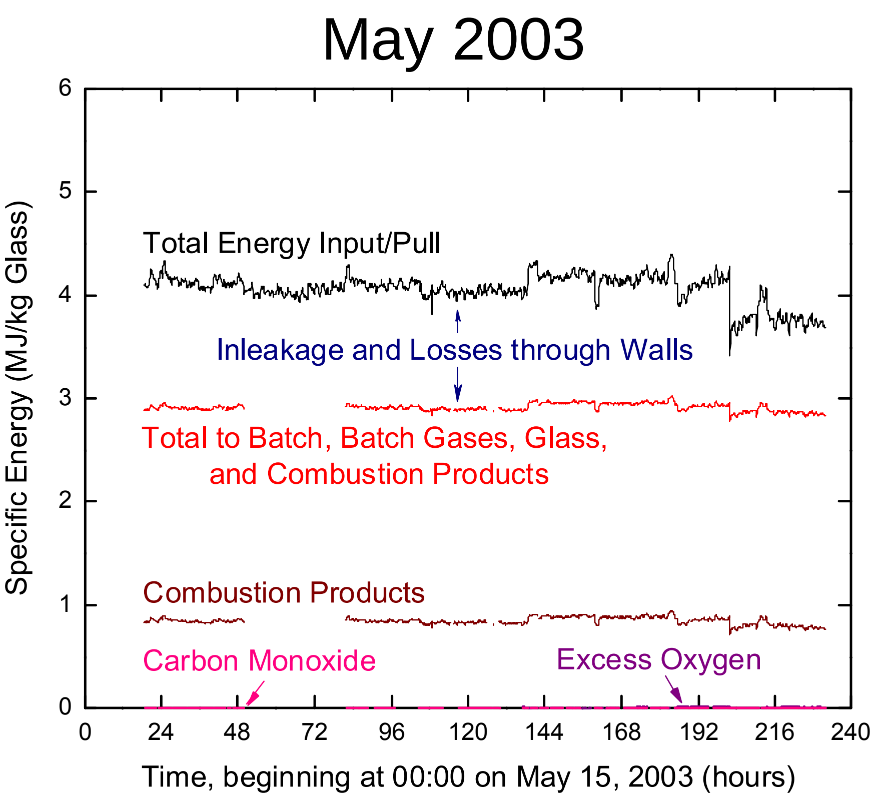
(6 MJ/kg = ~2580 BTU/lb = 5.2MMBTU/ton)

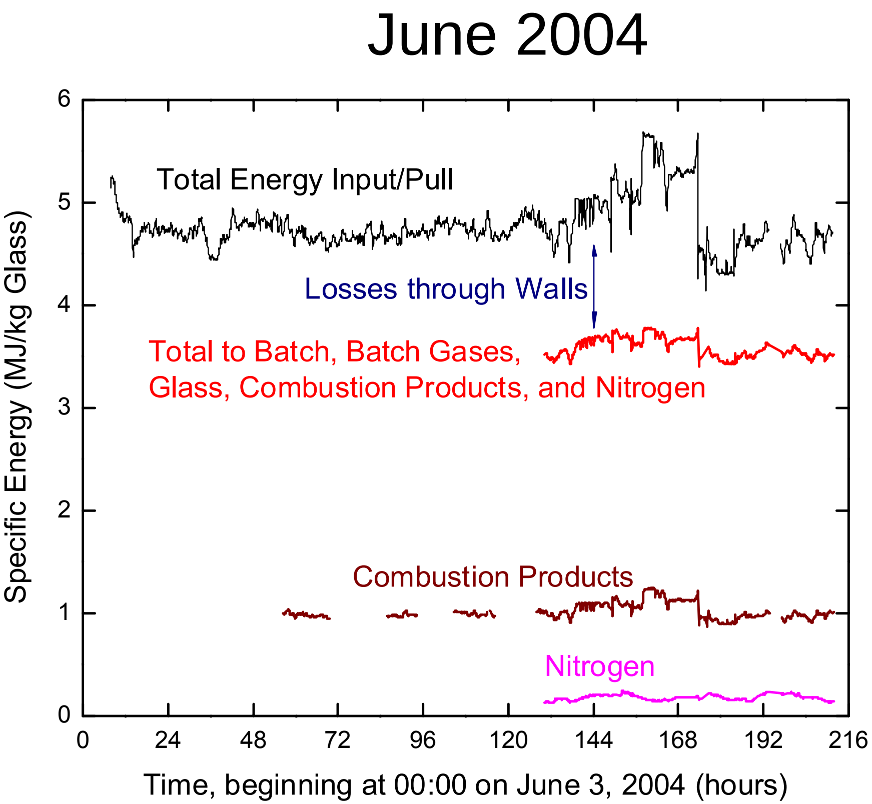
Specific energy uses





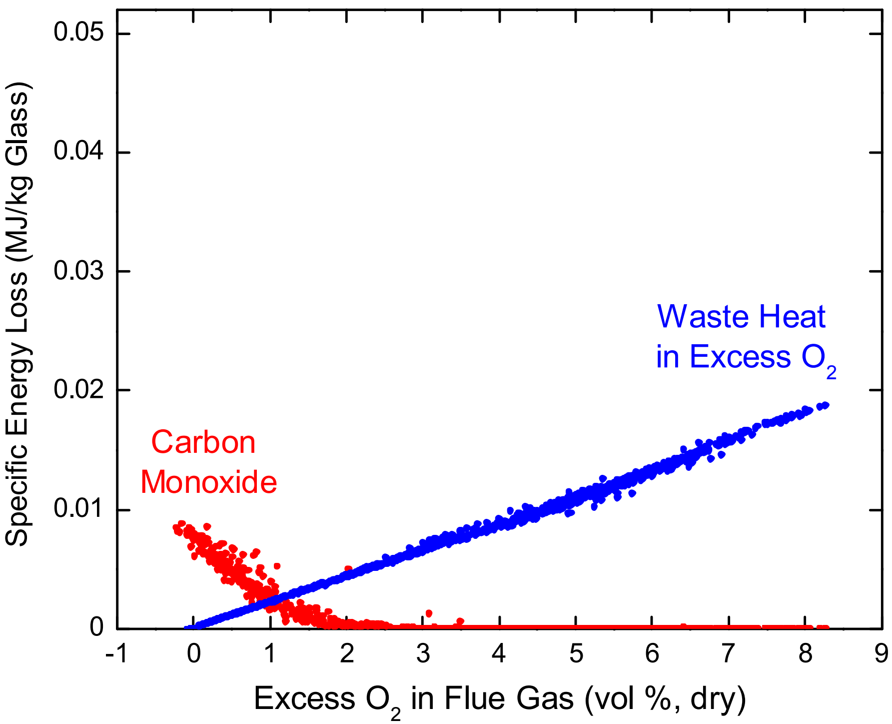
Specific energy losses





Losses to excess O_2 and CO

May 2003



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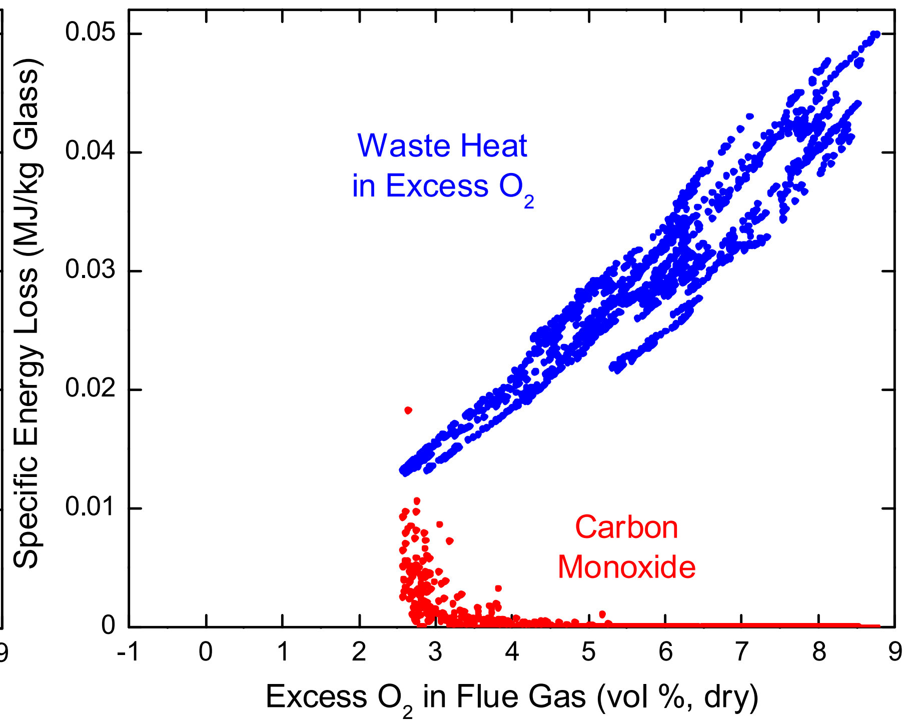
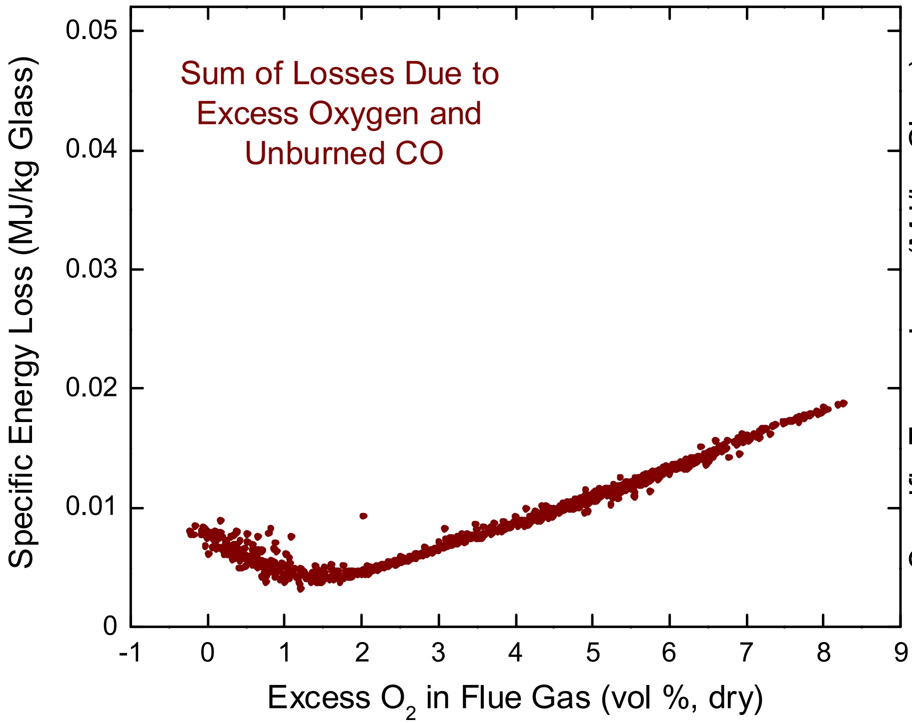


Optimum excess oxygen

May 2003



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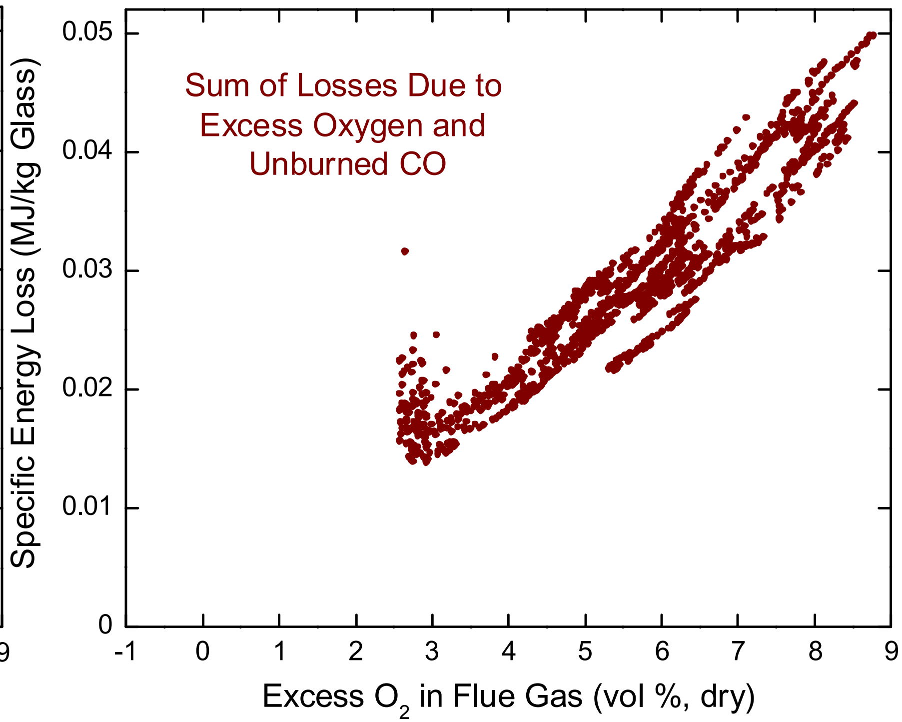


Improvements to LIBS diagnostic

- New method for baseline normalization
- Power meter pick-off installed
- Improved settings for batch particle detection
- Elimination of first-shot artifact for batch detection
- Single-shot broadband spectra detected multi-element batch particles for the first time
- Calibration issues for Na and K being examined
  - Using controlled burner and high temperature cell
- May be able to use LIBS to determine inleakage

Tasks/Milestones

No.	Task / Milestone Description	Planned Completion	Actual Completion
1	Data acquisition system	7/31/01	6/20/02
2	CO and O_2 monitors	9/30/01	12/14/01
3	Furnace exit gas temperature	10/31/01	6/20/02
4	Flame and refractory radiation	11/30/01	6/20/02
5	Synchronized records	12/31/01	6/20/02
6	Measurements of sodium	2/28/02	12/14/01
7	Sources of sodium	3/31/02	8/31/02
8	Conditions influencing sodium	4/30/02	8/31/02
9	Maximum furnace efficiency	5/31/02	6/30/04

Tasks/Milestones

No.	Task / Milestone Description	Planned Completion	Actual Completion
10	Measurements of silicon	7/31/02	12/14/01
11	Measurements of calcium	9/30/02	12/14/01
12	Correlations for metals	11/30/02	6/20/04
13	Broad-band LIBS instrument	3/31/03	10/31/01
14	Software for LIBS instrument	5/31/03	10/31/01
15	Simultaneous measurements of Na, K, Ca, and Si	7/31/03	12/14/01
16	Relationship between Na and K	8/31/03	06/01/03
17	Optimum stoichiometry	9/30/03	06/01/03
18	Sodium and calcium monitor	1/31/04	
19	Control strategy	3/31/04	
20	Demo in melting research facility	4/30/04	
21	Method for monitoring and control of volatilization and carryover	5/31/04	

Plan for the rest of FY04

- Examine temperature effects on calibration
- Further analyze furnace data
- Recommend data-based control strategy to improve efficiency and minimize alkali release
- Compile “best practices” for using LIBS to monitor particulates and corrosion in container glass furnaces
- Write final report

Budget

Estimated Budget Data as of June 2004:

			Approved Spending Plan ($000)			Actual Spent to Date ($000)		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	6/01	5/02	350	350	700	350	350	700
Year 2	6/02	5/03	350	350	700	350	350	700
Year 3	6/03	5/04	350	350	700	275	275	550
Totals			1,050	1,050	2,100	975	975	1,950

Publications and Presentations

- Seven papers and presentations
  - List available on request
- Further dissemination of information planned
  - Air in-leakage causes and effects
  - Alkali devolatilization and batch carryover
  - Furnace energy balance
- Best practices recommendation to be written
- Final report to be written

Findings

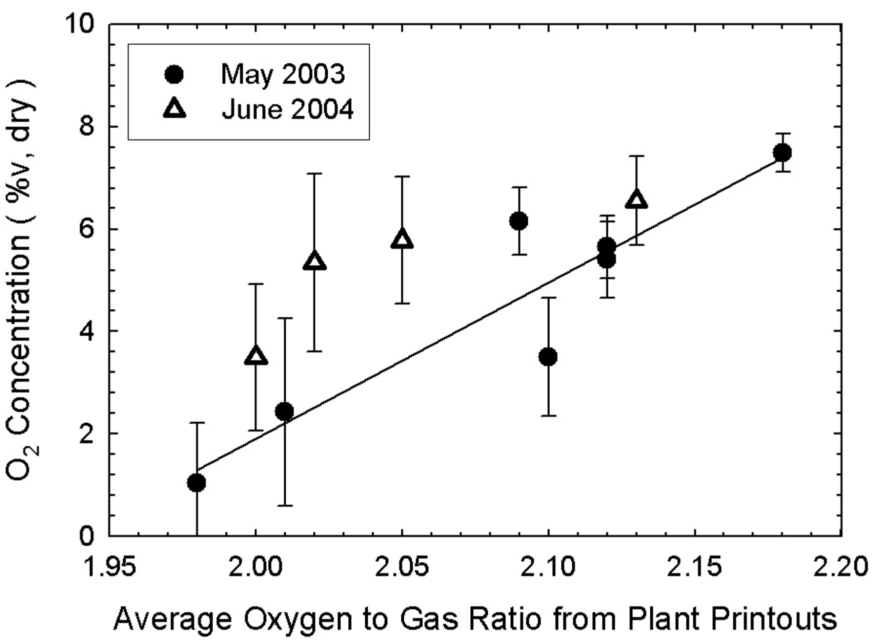
- As O_2/NG increases, O_2 and NO increase, SO_2 decreases
- Ambient temperature affects actual oxygen to gas ratio
- Na and K correlate with each other; Al, Ca, and Mg correlate with each other; no inter-correlation
  - Suggests different release mechanism for these metals
- Alkali release depends on furnace temperature
- Alkali release seems insensitive to furnace stoichiometry
- Decreasing furnace pressure encourages batch carryover
- Optimum excess oxygen for best efficiency

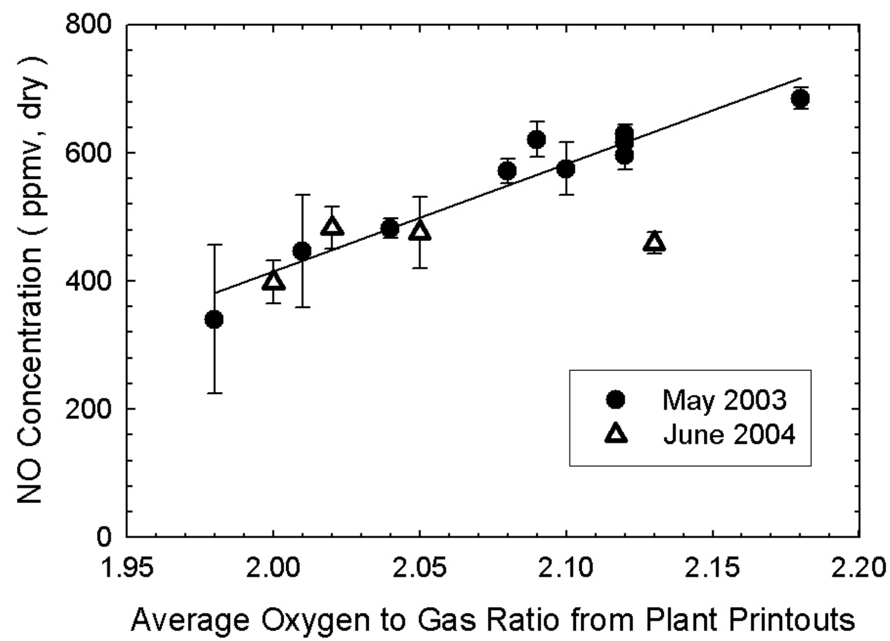
Acknowledgments

- Department of Energy
  - Elliot Levine
- Gallo Glass Company
  - Doug Moore, Plant Technical Staff
- Sandia National Laboratories
  - Jay Keller, Bob Gallagher, Jim Wang, Mark Allendorf, Steve Rice, Gary Hubbard, Howard Johnsen, Bob Steinhaus, Chris Shaddix

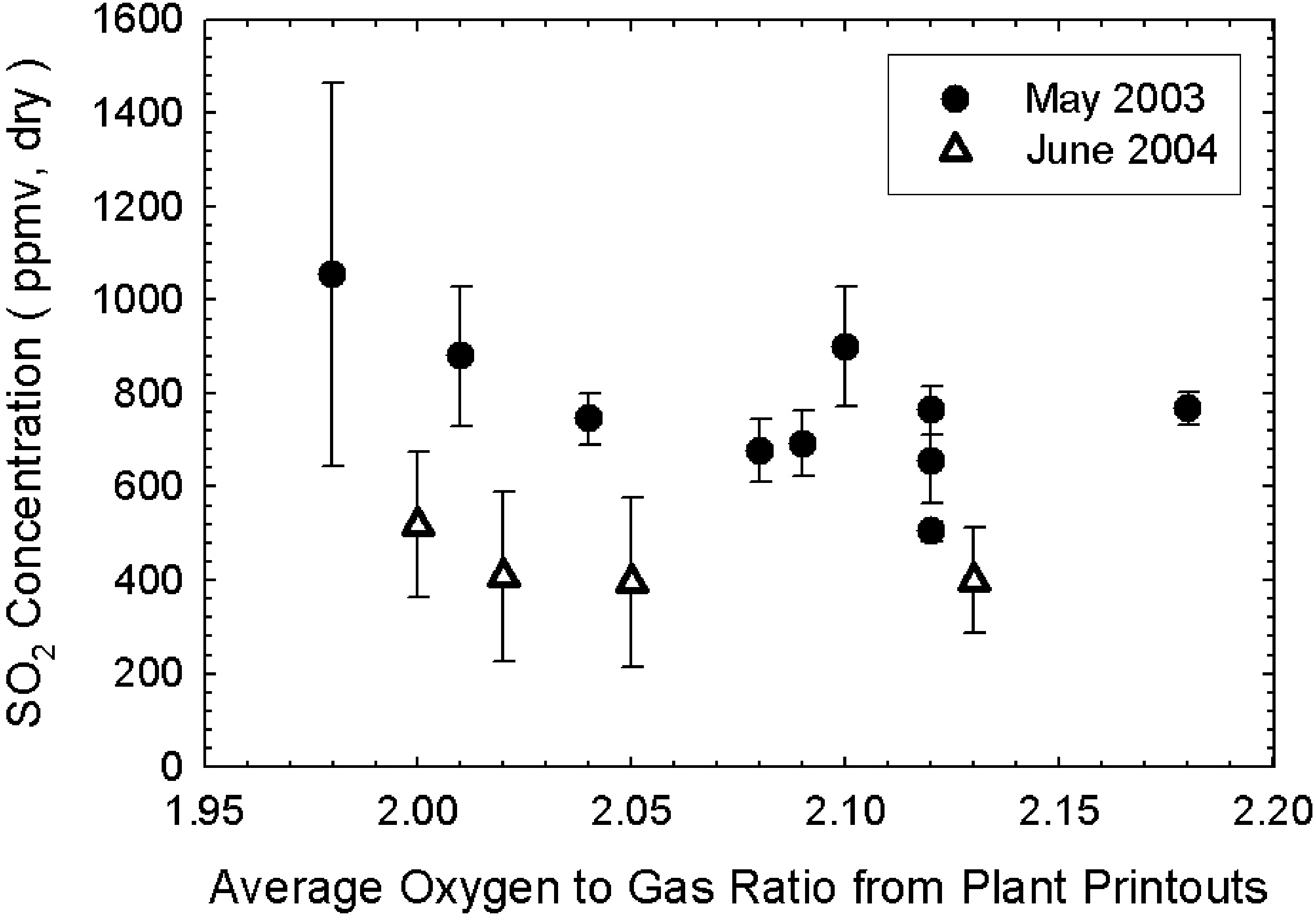
Extras

2004 compares with 2003



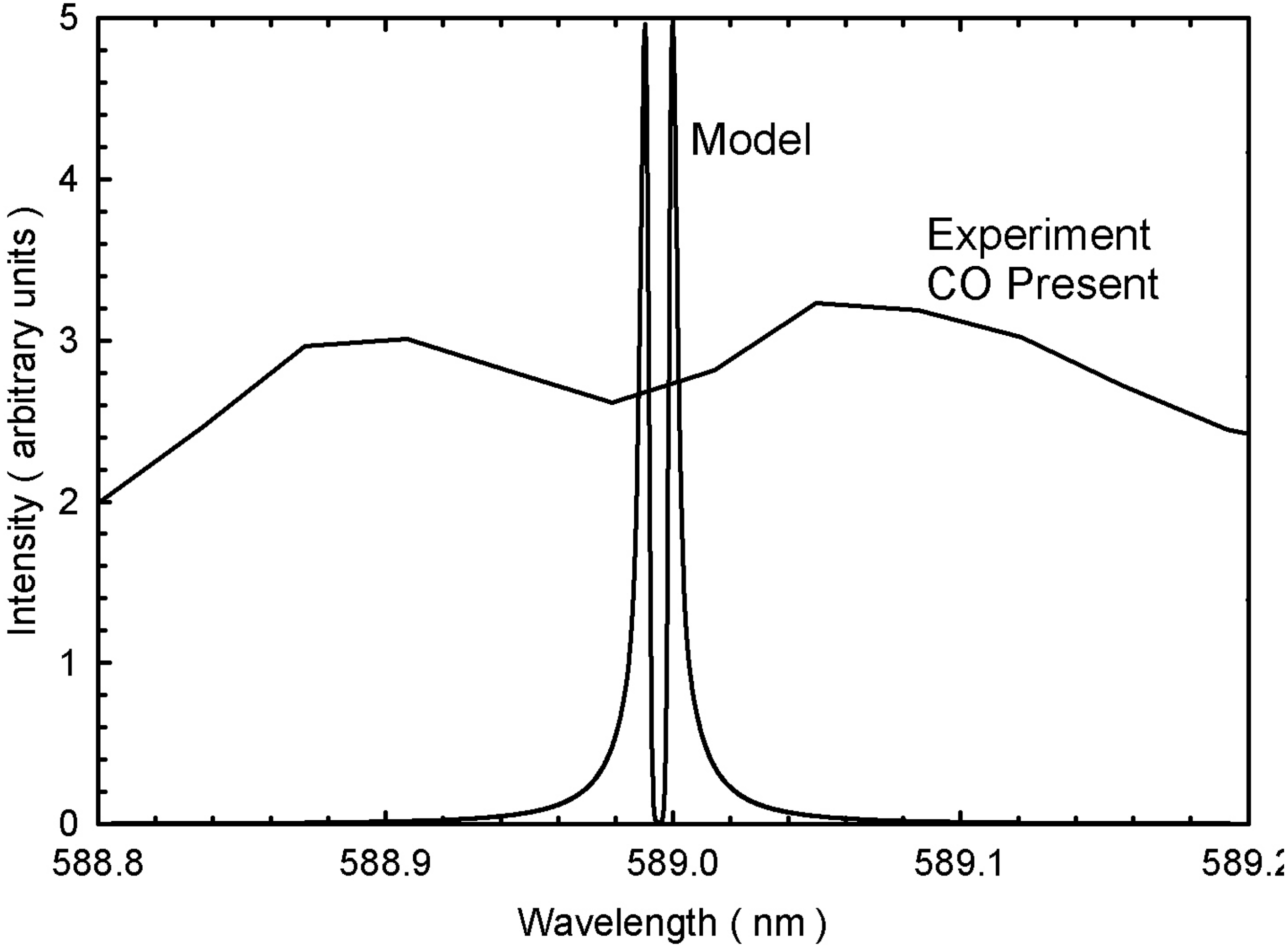


SO_2 concentrations repeat trend



June 2004

Self-reversal can be modeled



More work to do on calculating broadening