

Reinhold Environmental Ltd.



2008 NOx-Combustion Round
Table & Expo Presentation

February 4-5, 2008 in Richmond, VA



SO₃ Measurement and Detection: What we know and need to know for Fossil-Fired Measurement

*Presented at the Reinhold NO_x Combustion Roundtable
Richmond, VA
February 5, 2008*

by

~~Scott Evans~~

Caleb Wiza



Why We LOVE PowerPoint



SO₃ in a NO_x Conference !?!?

- Obviously SO₂ Oxidation through SCR
- Traditional Issues of APH Plugging and “Blue Plume”
- SO₃/Hg Codependence
- Ultra-Low SO₃ Limits in New FGDs
- Whole Idea of System-Wide Approach

Overview

- Address the problem(s)
- Method 8
- Controlled Condensation (CCS)
- Moving Forward



Definition of SO₃ (for Sampling Purposes)

1. True Chemical Definition

- SO₃ (g), H₂SO₄ (v), H₂SO₄ · H₂O (aerosol)

2. Definition by Sampling Method

- SO₃ is Sulfate caught in particular portion of Sampling Train



VS



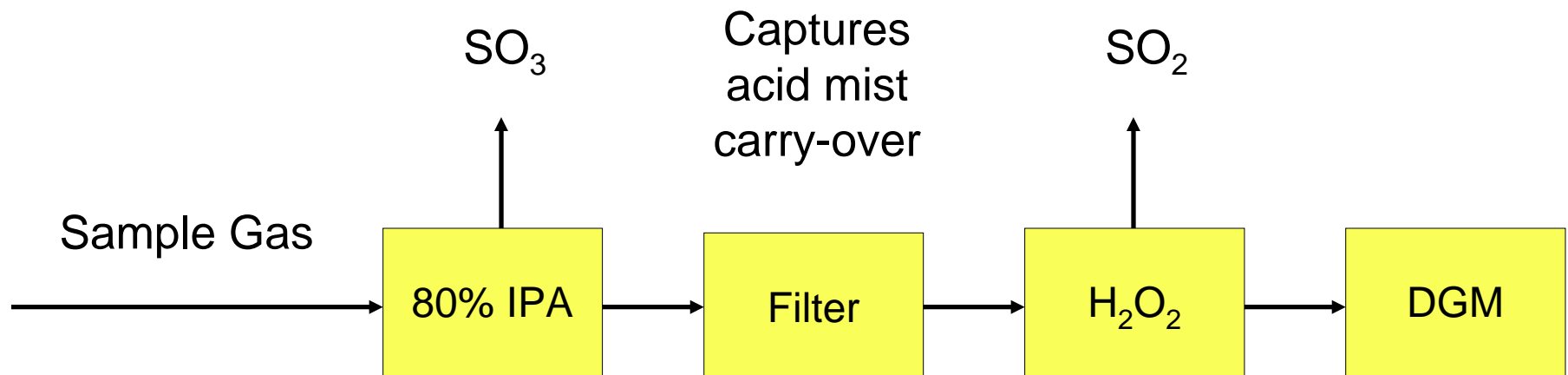
Problems

- High Precision / High Temp / High Dust
- Low Detection / High Moisture – Wet Stacks
- Method 8 Limitations
- CCS not a Method



USEPA Method 8 – Theory of Operation

- a.k.a. “Differential Absorption” Technique





In a Nutshell...

EPA Method 8 has a title that implies broad applicability for the method.

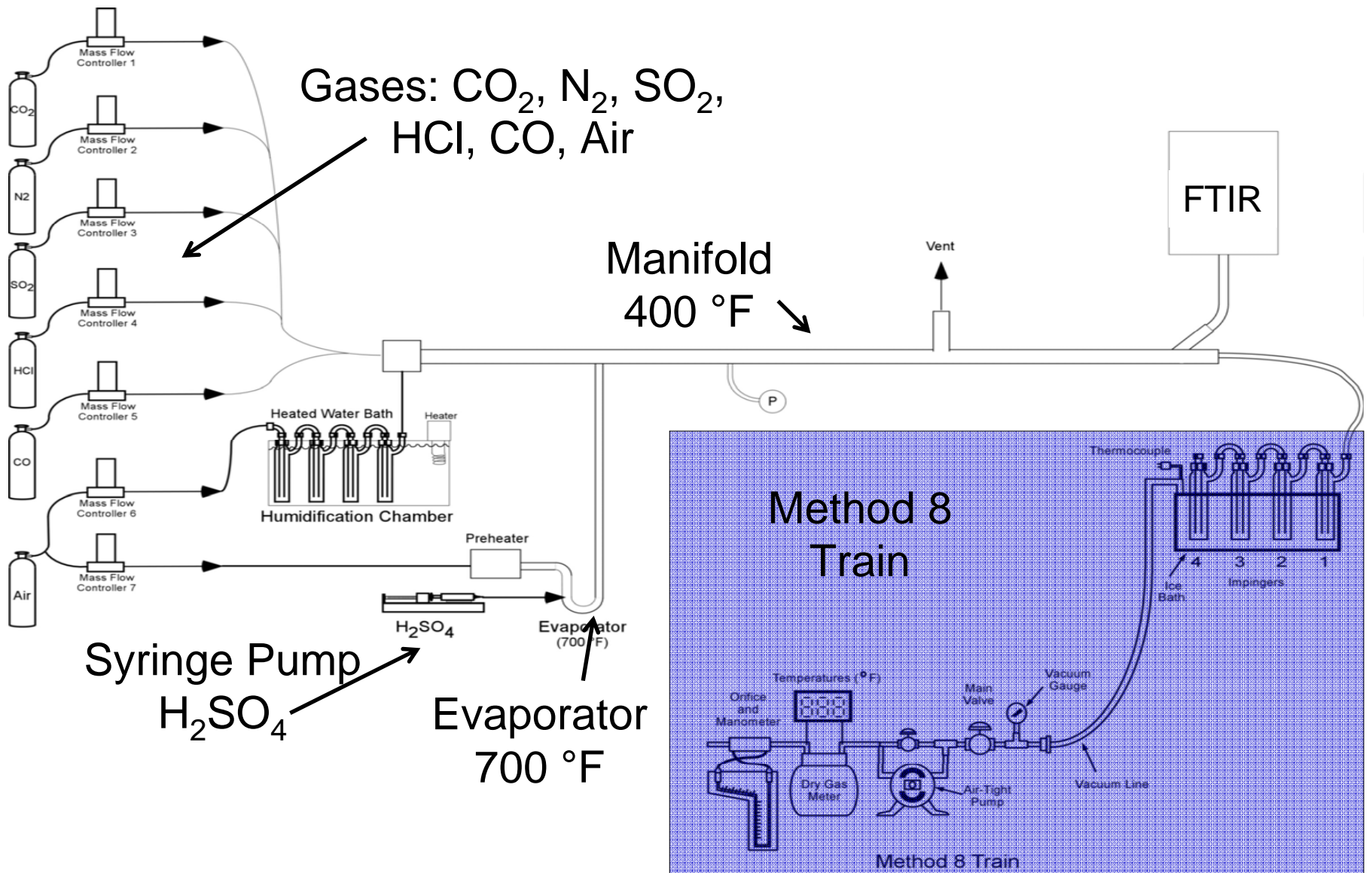
However...

It was not intended for nor validated on sources other than sulfuric acid plants

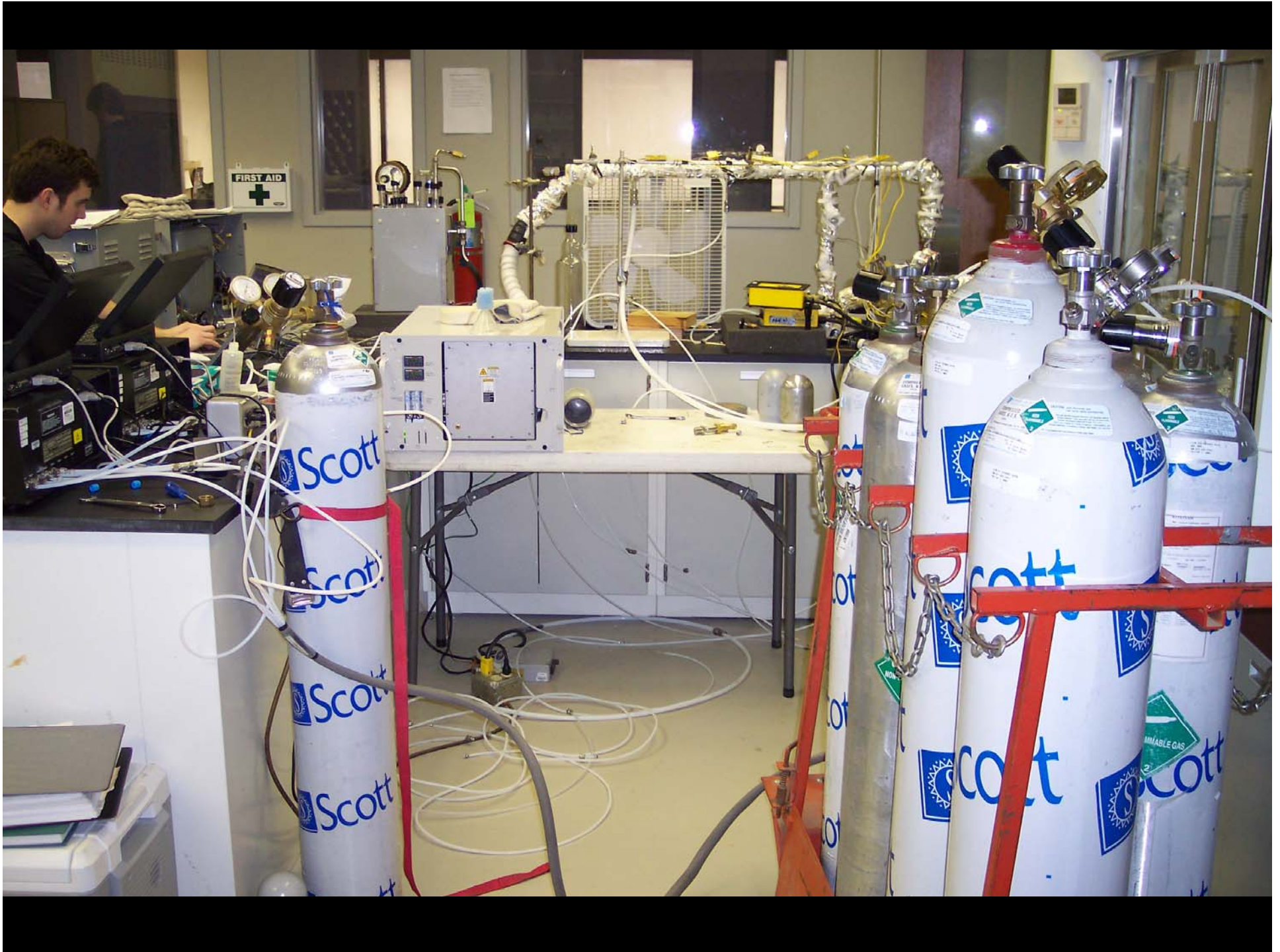
Nevertheless...

It is turning up in permits and requests for measuring SO_3 in power plants in the sub-ppm range.

Experimental Setup







Test Variables

Constituent	Fixed/Var	- value	+ value
O ₂	Var	5%	10%
H ₂ O	Var	5%	10%
CO ₂	Fixed @10%		
CO	Fixed @46 ppm		
NO _x	Fixed @9 ppm		
SO ₂	Var	10 ppm	100 ppm
SO ₃	Var	MDL	3 x MDL
NH ₃	Var	0	5 ppm

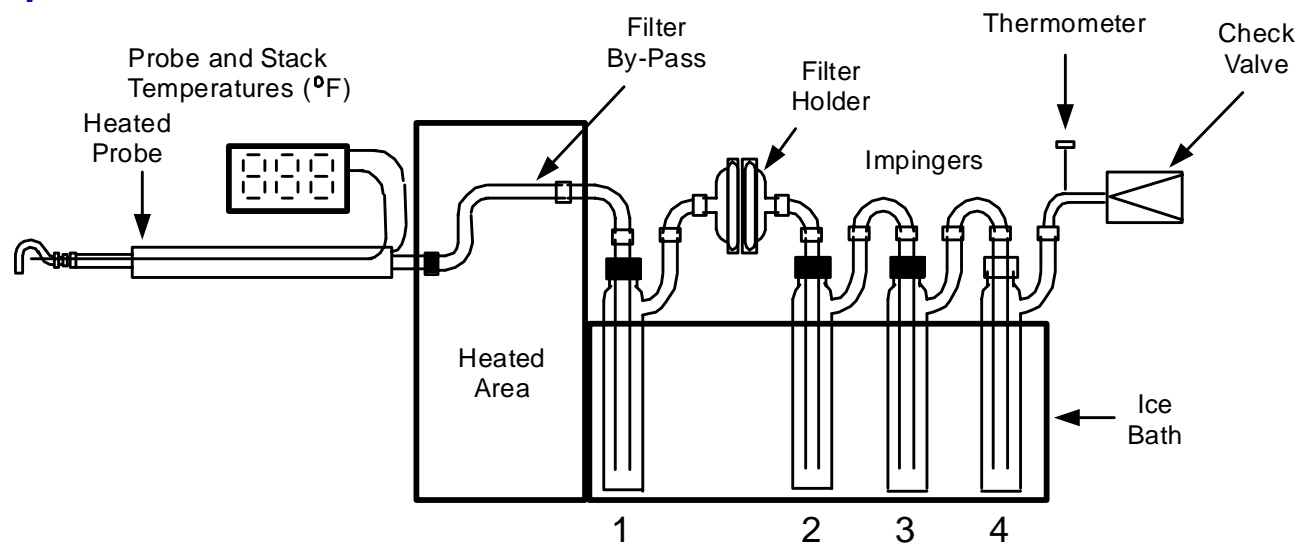
Test Matrix

2³ Factorial
Test Matrix

Run	SO ₃	H ₂ O	O ₂	SO ₂
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	+	-
6	+	-	+	-
7	-	+	+	-
8	+	+	+	-
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+

USEPA Method 8 Known Weaknesses

1. Reagents Change Over Time
2. Poor Particulate Filtration
3. Sulfite Oxidation to Sulfate
4. Highly Susceptible to Interference



USEPA Method 8 Accuracy Measurements

Recovery (%)	Source	SO ₃ (ppm)	H ₂ O (%)
312	Simulated Gas	0.1	10
104 [‡]	Coal	10	7
50.5 [‡]	Coal	7.5	11

[‡] Mitchell and Bruffey, Env. Sci. Tech., v18, 1984.

USEPA Method 8 – Precision Measurements

CV (%)	Source	SO ₃ (ppm)	H ₂ O (%)
66.1*	H ₂ SO ₄ Plant	12	0
74.3**	Coal	4.2	10
10.1	Clean Air Simulated Flue Gas	0.5	10

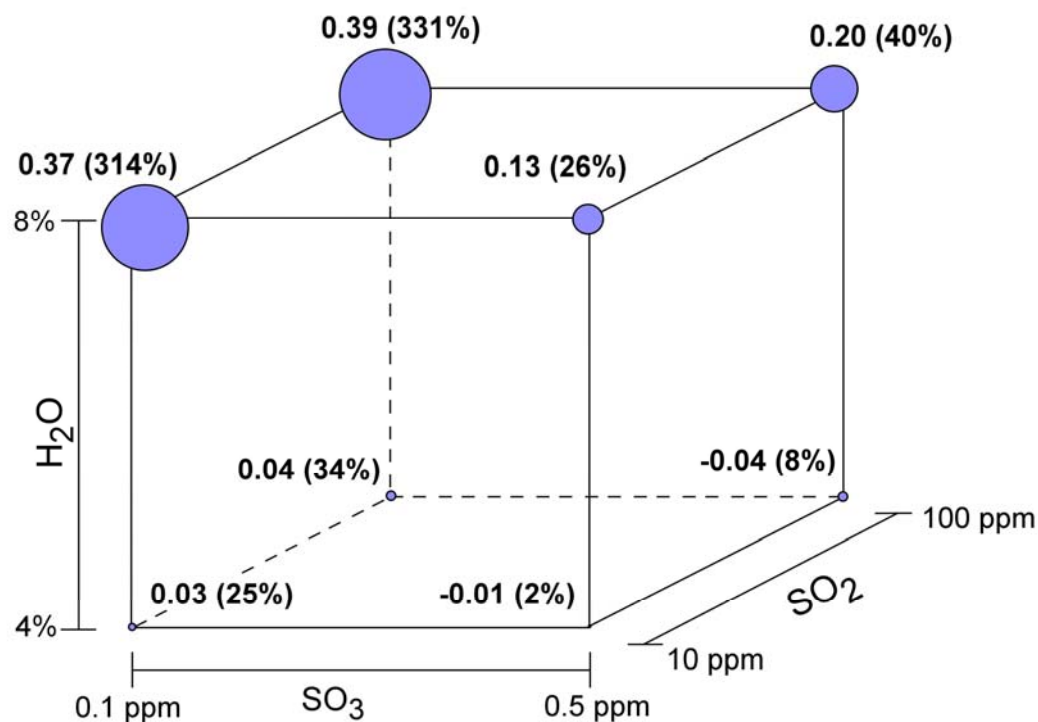
* Hamil et al., EPA 650/4-75-003, 1974

** Mitchell and Bruffey, Env. Sci. Tech. 18, 1984.

USEPA Method 8 – Established Bias

- Design of Experiment changing 4 factors to inspect bias

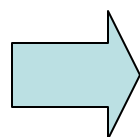
Substance	Low	High
H ₂ O	4%	8%
H ₂ SO ₄ /SO ₃	0.1 ppm	0.5 ppm
O ₂	5%	10%
SO ₂	10 ppm	100 ppm
CO	Fixed 45 ppm	
CO ₂	Fixed 10%	
HCl	Fixed 1 ppm	
NOx	Fixed 9 ppm	



USEPA Method 8 – Detection Limit

Ideal

Conditions

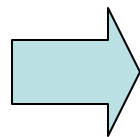


- Clean Air Laboratory-Based Experiments

- MDL of 0.16 ppm
- PQL of 0.48 ppm

Real World

Conditions

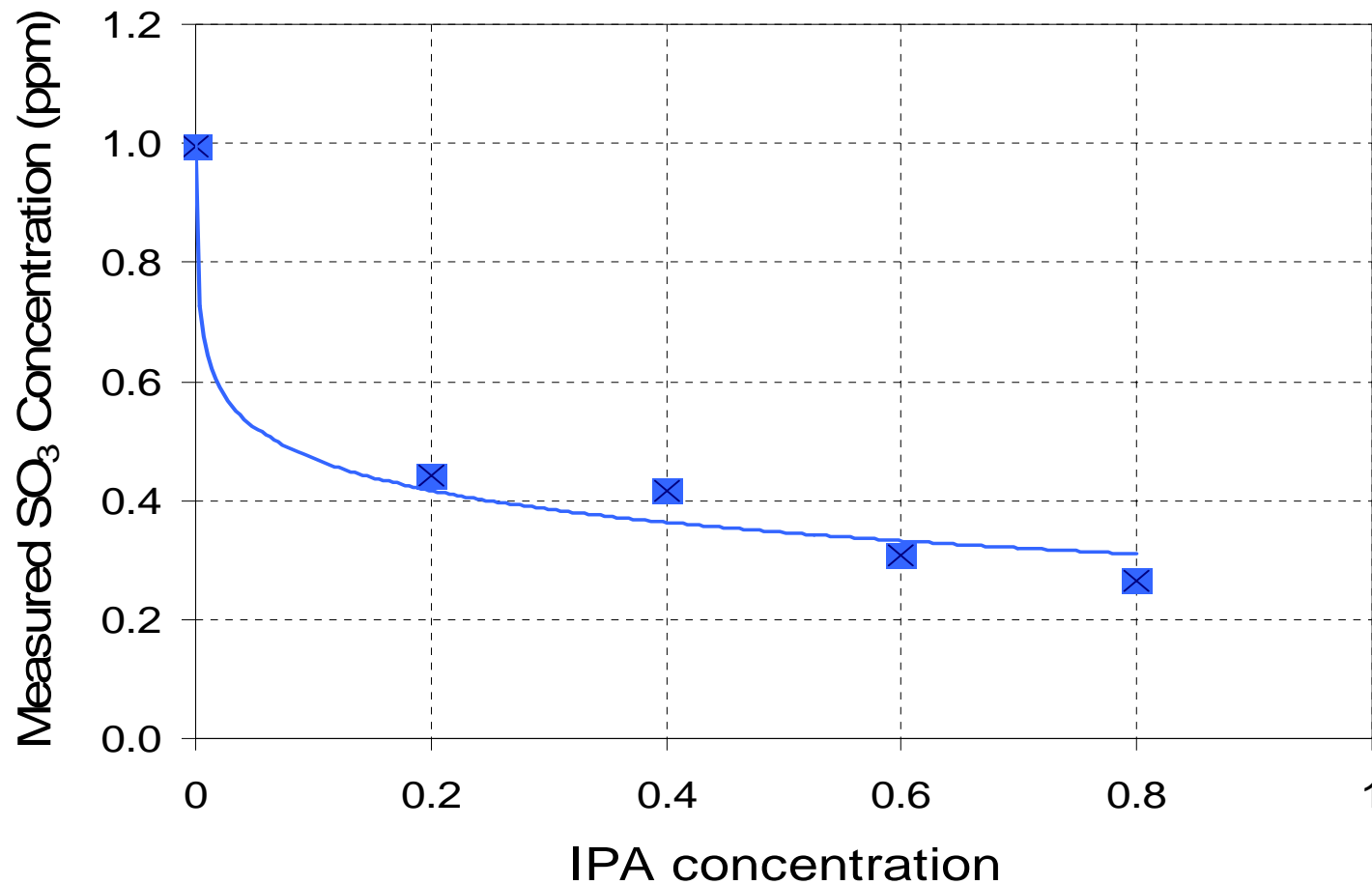


- Field Evaluation from Berger et. al.

- MDL of 6.2 ppm
- PQL of 25.2 ppm

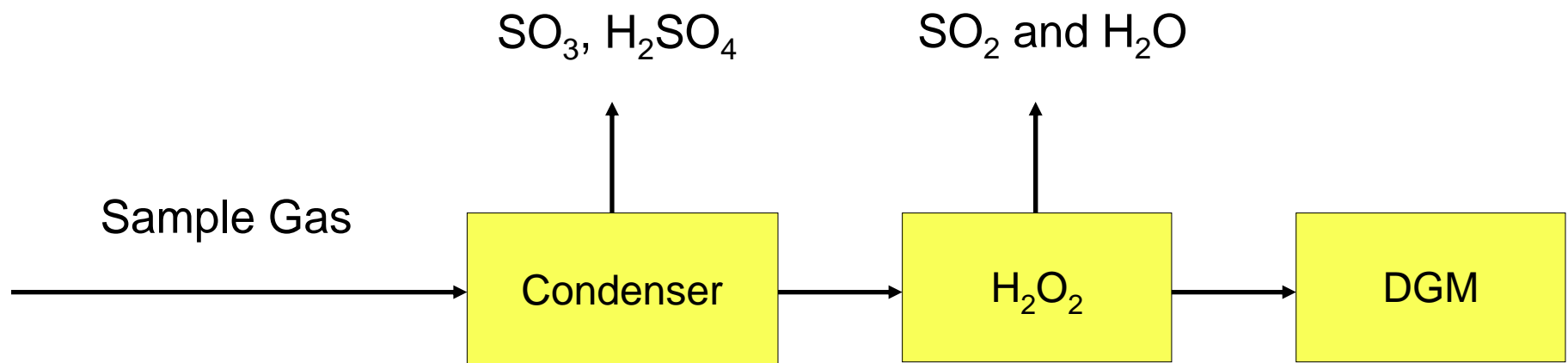
*Follows MDL Process in 40 CFR 136 App. B using standard deviation of 7 replicate runs times 3.143 (99% Student's t-statistic, n-1 df)

USEPA Method 8/Method 202 – SO₂ Bias



CCS – Theory of Operation

- Controlled Condensation Technique



CCS – Accuracy Estimates

SO ₃ Recovery (%)	Source	SO ₃ (ppm)	H ₂ O (%)
78.9 [§]	Alkaline Coal	11.5	4.9
92.2 [†]	Alkaline Coal	0.9	7
97.4 [†]	Fuel Oil	14.2	2

§ Maddalone et al., 70th Annual Air Pollution Control Association, 1977

† Blythe et al., Megasyposium, 1999. Percent recovery is on a relative basis.

CCS – Precision Estimates

CV (%)	Source	SO ₃ (ppm)	H ₂ O (%)
11*	Simulated Coal	13.3	5.5
5**	Coal	9	7-10?
32.2†	Coal (10 hour duration)	-	-

* Maddalone

** Berger et al., Am. Ind. Hyg. Assoc. Journal, 1972.

† Maddalone TRW

CCS – Estimated Detection Limits

- Maddalone et. al. Lab Experiments*
 - MDL of 6.0 ppm
 - PQL of 18.0 ppm
- Berger et. al. Field Measurements
 - MDL of 1.5 ppm
 - PQL of 4.8 ppm
- Reported MDLs
 - ASTM said 10 ppm in D3226-73T
 - NCASI said 0.15 ppm on Portland Cement Kilns

* Calculation does not meet quality standards of 40CFR136 App B, used for comparison only.

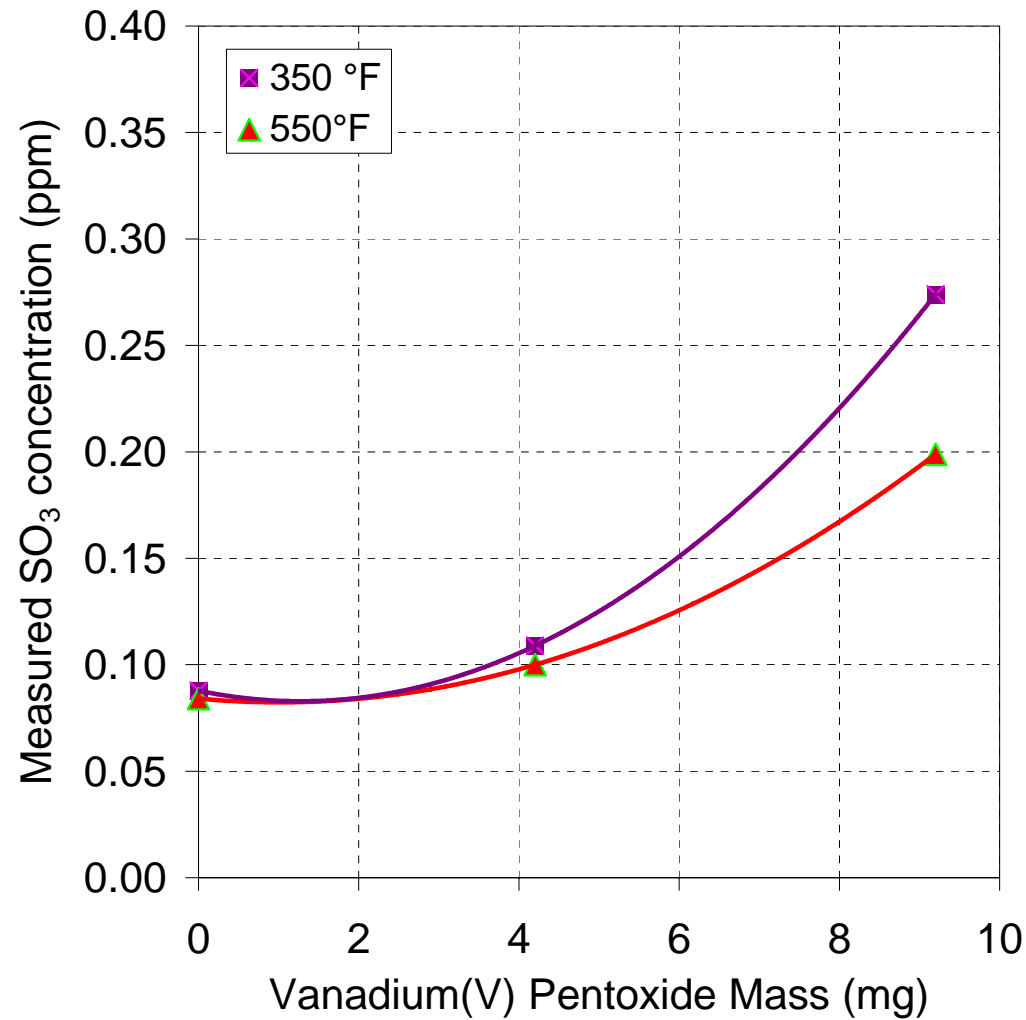
CCS – “Nobody’s Perfect”



Ruh Roh
Raggy

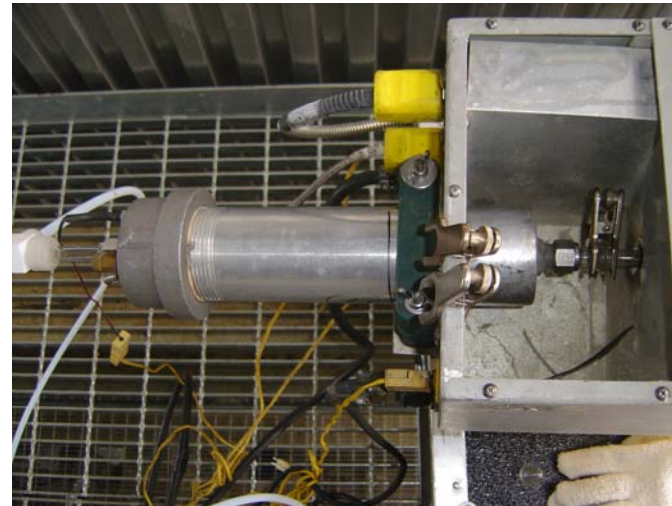
CCM – Vanadium Bias

**VERY
LITTLE
IMPACT !!!**

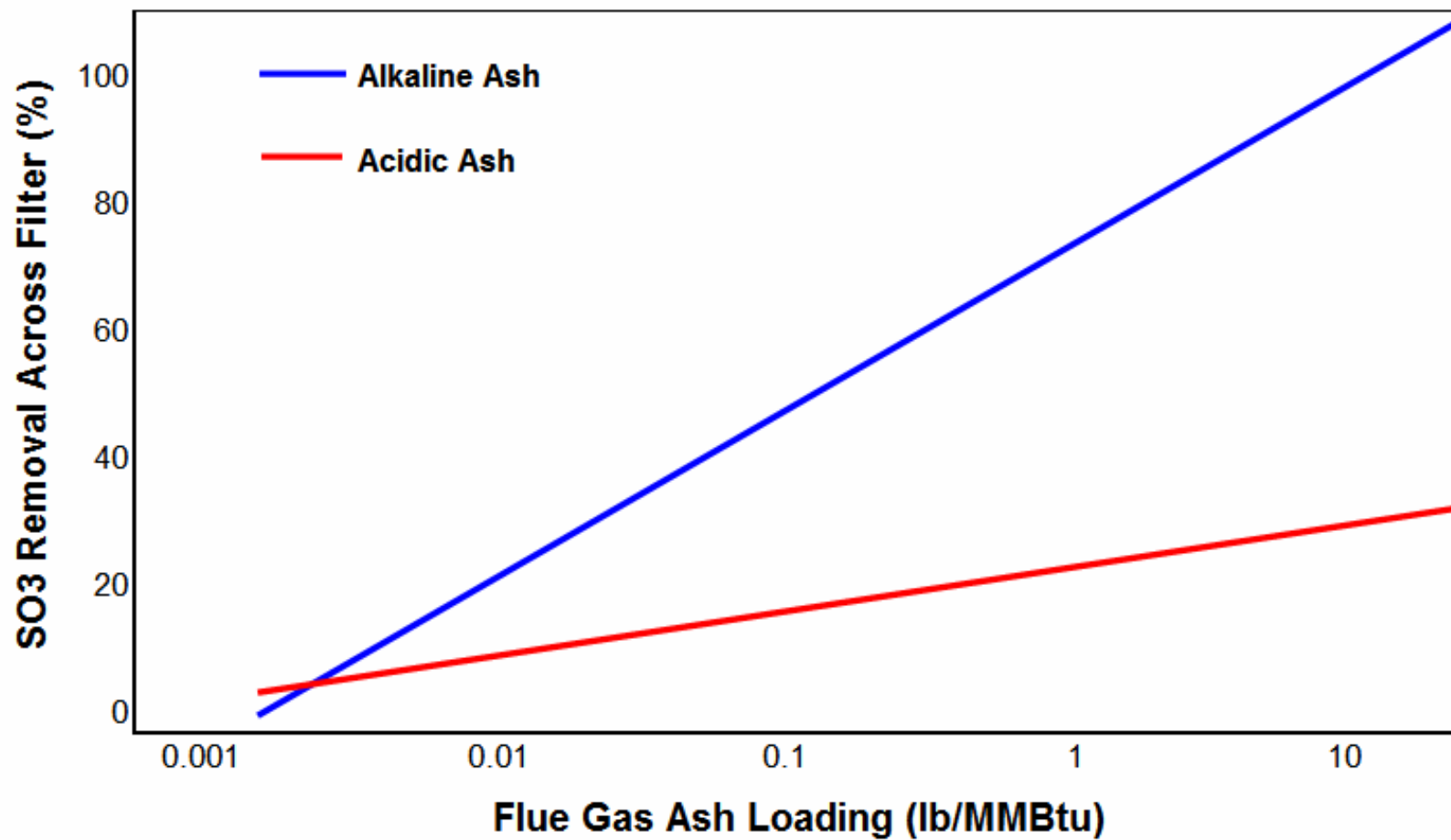


CCS – Sulfate Speciation/Collection

- High Temps may change phase of SO_3
- Sulfate Containing Compounds – ABS
- Collection of Aerosols – non-Isokinetic
- All Quartz Extraction System

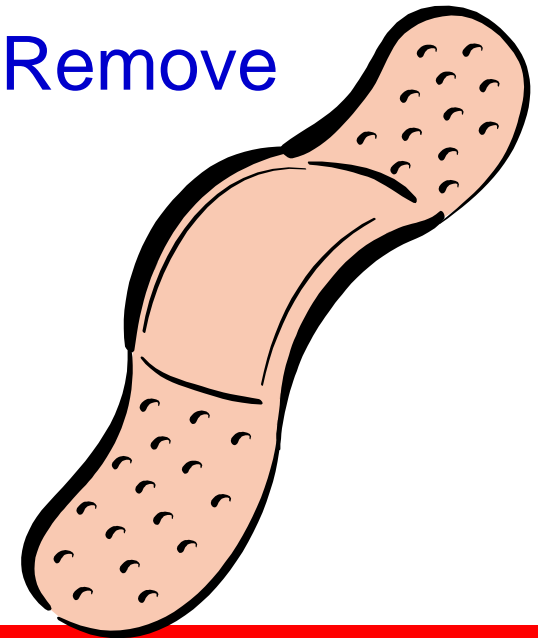


CCS Bias – Ash Filter Cake Effects



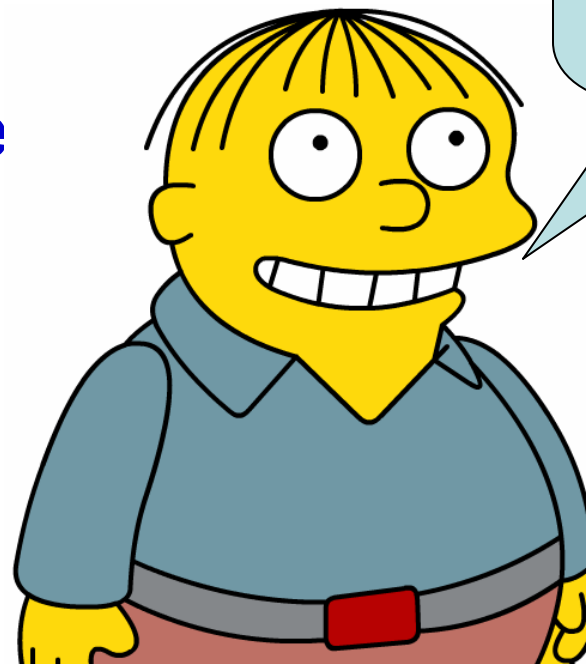
Quick Fixes

- Adjust Sampling Temps to avoid Phase Shift
- Alter Extraction Mechanisms to Remove Particulate without Filter Cake
 - Inertial Separators
 - Mini-ESPs????



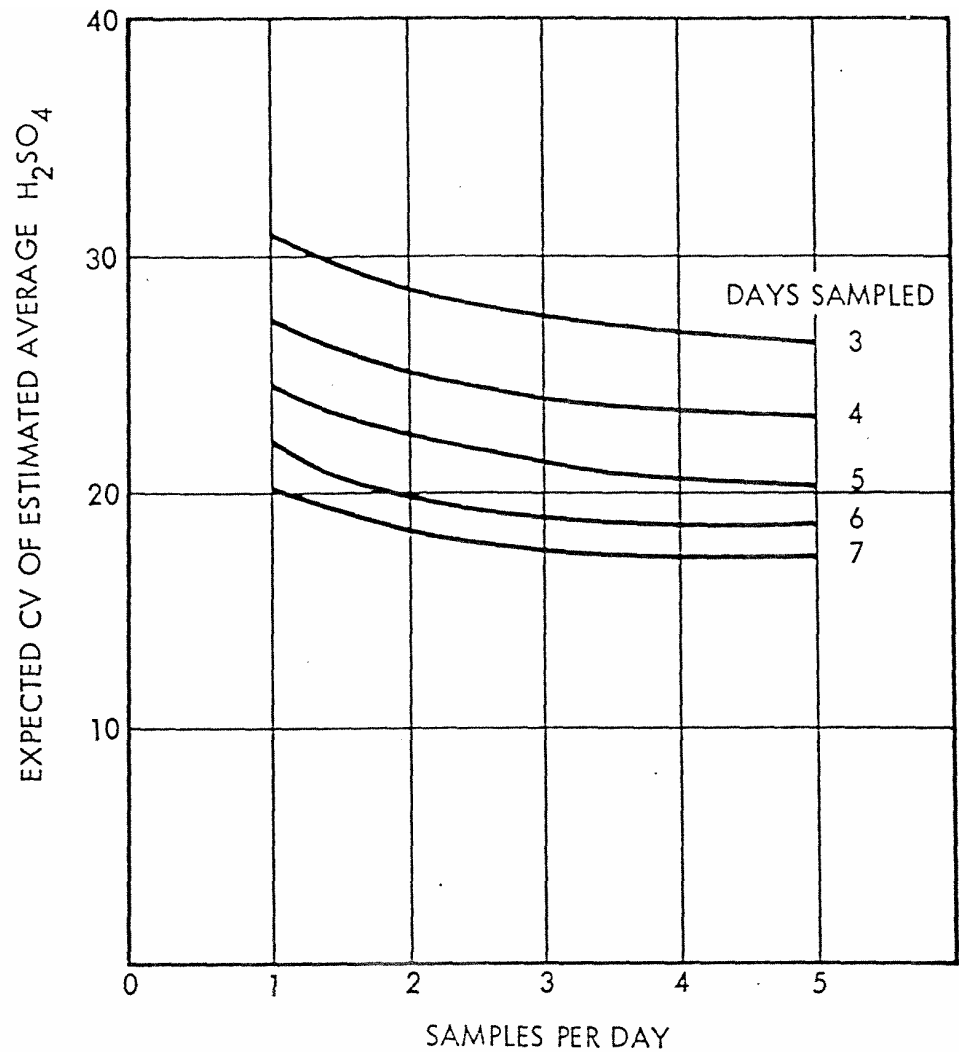
Best Method May Be No Method

- No constraints imposed
- Pick and Choose
- Think Performance-Based Approach



I ch- ch-
choose you
CCS !!!

Maddalone Knew – “More Samples”



† Maddalone TRW

Science Project

- Custom Test Program based on Needs



Paired Trains

- “Instant Validation” and Feedback



Improve QA

- Vary Sample Times – Ash Effects
- Convert to Isokinetic – Aerosols
- Fuel Analysis and Boiler Operation
- Collected Ash Analysis
- Control Train versus Variable Train
- Dynamic Spike Recovery

How important is confidence in your data?!?



Method Diagnostic Summary

Paired Train Agreement (using ppmdv @ 3% O₂)

	Run No.	1	2	3	Average
Location A					
ABS	Absolute Difference (<1.0 ppm) ¹	0.26	1.27	0.25	0.59
%RD	% Relative Deviation (<10%) ¹	1.8	8.7	2.1	4.2
Location B					
ABS	Absolute Difference (<1.0 ppm)	0.40	0.17	0.18	0.25
%RD	% Relative Deviation (<10%)	10.5	7.3	4.9	7.6

Sampling System Bias Test (using ppmdv @ 3% O₂)

	Run No.	4	7	Average
Location A				
ABS	Absolute Difference (<1.0 ppm)	0.14	0.53	0.34
%RD	% Relative Deviation (<10%)	1.1	3.6	2.4
Location B				
ABS	Absolute Difference (<1.0 ppm)	0.20	0.91	0.56
%RD	% Relative Deviation (<10%)	7.7	25.4	16.6

¹ Either the Absolute Difference or Relative Deviation may be used to verify performance.

Future Work

- MDL study on CCS
 - High Moisture / Low Concentration
- “Filter-less” Probe
- Portable Spiking System
- Performance-Based Methodology
- Validation and Study of Matrix Effects
- Evaluate Other Approaches
- Less Words on Slides

Conclusions

- Method 8
 - MDL: 0.16 to 6.2 ppm
 - Recovery: 50% to 312%
 - CV: 10% to 74%
- CCS
 - MDL: 0.15 to 6.0 ppm
 - Recovery: 79% to 97%
 - CV: 5% to 32%

Conclusions

- Just Say NO to Method 8 on Fossil-Fired Plants



Questions ????

Is something
burning
again?





Workshop

- What do you see as greatest needs in terms of SCR Measurement?
- Any personal experiences?
- What would you like to see happen to ensure your needs are met?